Precursor design of vapour deposited cubic boron nitride versus diamond

Karin Larsson

Department of Materials Chemistry, Angstrom Laboratory, Box 538, 751 21 Uppsala, Sweden;
Karin.larsson@mkem.uu.se

Abstract. The similarities and dissimilarities in the growth of diamond vs. cubic boron nitride (c-BN) were studied using quantum mechanical calculations. Great similarities were observed when considering the surface stabilization by H atoms. Very great similarities were recorded when considering the adsorption of various growth species to these materials. It was found necessary to avoid mixtures of B- and N-containing species in the gas phase during c-BN growth, since they should most probably result in a mixture of these species also on the surfaces. Greater dissimilarities were observed when studying the surface migrations on the diamond and c-BN surfaces and nucleation of the cubic phases on the corresponding hexagonal ones. Nucleation of diamond/c-BN on graphite/h-BN was found to be energetically feasible. This was calculated to be especially the situation for the armchair edge of the basal plane of h-BN and of the zigzag edge of the basal plane of graphite. These theoretical results can be used as guidelines in the strive towards thin film deposition of c-BN using gentle chemical vapour deposition methods like atomic layer deposition.

Key words: atomic layer deposition, theoretical, quantum chemistry, growth, surface processes, diamond, boron nitride.

1. INTRODUCTION

Diamond and cubic boron nitride (c-BN) are two compounds with great similarities. They are both primarily covalent compounds with electronegativities (according to Pauli) of 2.04(B), 2.55(C), and 3.04(N), respectively. They are iso-electronic regarding the valence electrons and possess very similar thermal and physical properties (e.g. extreme hardness, extreme band gap, high thermal conductivity, transparency) [1,2], but also very great dissimilarities. For instance, c-BN shows a very high thermal stability in contact with Fe, Co, and Ni [2] and is, hence, useful as protecting coating of iron-containing materials. Cubic boron nitride can also be made as both n- and p-type semiconductor material [1], in contrast to diamond, for which it is very difficult to n-type dope with other species

than N [3]. The most striking difference between diamond and c-BN is, however, the severe difficulties in depositing c-BN with gentle chemical vapour deposition (CVD) methods, whilst reproducible thin films of diamond are easily obtained.

Chemical vapour deposition growth of thin films includes very complex and dynamic gas phase/solid surface reactions: adsorption of gaseous species to the growing surface, abstraction of adsorbed species by gas phase ones, surface migration, and the final incorporation into a lattice site. Also, a great degree of competition exists between growth species and surface terminating ones. Hence, it is of major importance to achieve a deeper understanding of the governing factors for gas phase and growth relationships in order to be able to control the surface reaction pathways towards the production of a material with a specific phase composition.

There are some generally assumed conditions that have to be achieved in order to be successful in the growth of the cubic phases of C and BN: (i) stabilization of the cubic surfaces during growth, (ii) a sufficiently strong adsorption of growth species, (iii) a sufficiently high surface mobility of the growth species, (iv) nucleation and growth of the cubic phases on the hexagonal counterparts, (v) preferential etching of the hexagonal phases, and (vi) prevention of secondary nucleation of hexagonal phases. The present investigation concentrates on factors (i)–(iv). However, the main goal is not only to outline the similarities and dissimilarities in the growth processes of diamond and c-BN but to present an example (and give some ideas) of what can be done with theory in, e.g., the prediction of reaction pathways in the CVD/atomic layer deposition (ALD) growth of materials with tailor-made material properties.

2. METHODS

Calculations based on the Hartree–Fock (HF) and density functional theory (DFT) methods are used in the present study. These methods are the most accurate ones, where all electrons are taken into consideration. This is especially important when studying surface reactions where bond formations and disruptions have taken place. Reaction mechanisms and material properties like atomic structures, bonding and vibrational properties, as well as magnetic properties, can then be carefully investigated. Unfortunately, this can only be done on smaller systems (up to about 100 atoms). If larger systems are demanded, a lower level of accuracy in the calculations has to be used. Parameterization of various levels has to be introduced in the Schrödinger equations. Hence, the possibility of most accurate monitoring of, e.g., the surface growth processes has been most severely diminished, but material properties like bulk diffusion, segregation, and mechanical properties can still be studied most carefully. Examples of theoretical methods with their inherent possibilities are demonstrated in Fig. 1.

The Schrödinger equations were solved using the *ab initio* molecular orbital method at the HF level of theory and the first principle DFT method. Due to
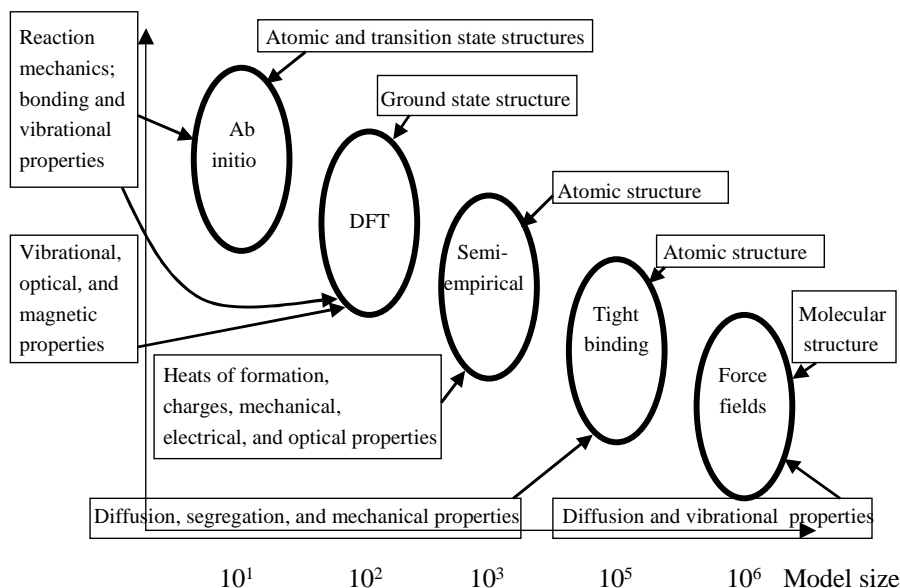
Fig. 1. Overview of theoretical methods to be used in the investigation of material properties.

inadequate treatment of the instantaneous correlation between motions of electrons in the HF theory, electron correlation treatments were performed by using a second-order Möller–Plesset perturbation theory (MP2). The split-valence basis set with polarization functions (6–31g**) was employed in an all-electron approach using the program Gaussian (from Gaussian Inc.) and a cluster approach. In addition to adsorption energies, structural geometries were obtained by performing geometry optimizations. The adsorbate and closest neighbours in the surface were then relaxed, while the others were kept fixed in order to hold the characteristics of the bulk. The DFT calculations were based on periodic boundary conditions (using a supercell in modelling the surfaces) and gradient corrections to the exchange and electron correlations (GGA-PW91), in combination with ultrasoft pseudopotentials and k-points generated by the Monkhorst–Pack scheme (using the program CASTEP from Accelrys, Inc.). Structural geometries were also here obtained by performing geometry optimizations.

3. RESULTS AND DISCUSSION

3.1. Growth of cubic phases on cubic ones

3.1.1. Surface stabilization

An important role of H during CVD of diamond is to maintain the sp^3 configuration of surface carbons [4]. The question is if X (X = H, F, Cl, Br) has a similar effect on the c-BN surface (Fig. 2). It has earlier been observed

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theoretically that both H and F are very effective in stabilizing the diamond (1 1 1) surface, whilst Cl is not. As can be seen in Table 1, the adsorption energies are almost identical for adsorption of H and F (431 vs. 430 kJ/mol). The angle ν_{N-B-N} (111.3 vs. 111.2) also shows an effective sp^3-hybridization effect on the surface C atoms. On the other hand, Cl does not adsorb that strongly to the surface (200 kJ/mol), and Br does not have any tendency to adsorption at all.

The (1 1 1) surface of c-BN consists of alternate layers of B and N (see Fig. 2). If we now compare with adsorption studies on the B-rich plane on the c-BN (1 1 1) surface, we can see that H has a surface stabilizing effect almost identical to diamond (1 1 1) [5–7]. However, F does have a tendency to bind much more strongly to this type of c-BN surface (653(c-BN) vs. 430(diamond) kJ/mol). It is interesting to notice that the N-rich c-BN (1 1 1) surface will give a comparable adsorption strength for H (465 kJ/mol) and a much lower one for F (251 kJ/mol). For comparison, a similar stabilization study of H-termination to the (1 1 0) surface has also been performed [8]. This type of surface consists of both B and N sites. It was then found that H will bind almost identically strongly to both B and N surface sites, 418 vs. 416 kJ/mol, which is somewhat lower than the adsorption of H to c-BN (1 1 1). Both H and F have hence proved to be effective in stabilizing the c-BN and diamond surfaces investigated in the present study. But the question is: is F too strongly bonded to c-BN?

3.1.2. Gas phase abstraction with gaseous species

As can be seen in Fig. 3, gas phase abstraction of terminating H species with gaseous H or F species has been found to be exothermic (or weakly endothermic) for diamond (1 1 1) and c-BN (1 1 1) [6]. It is generally assumed that weak endothermic surface processes are possible in supersaturation environments within ordinary CVD setups. The situation is much more severe for F-terminating surfaces. The only exothermic reaction is here the abstraction of F from diamond (1 1 1), using gaseous H. Abstraction of surface terminating F with gaseous F is endothermic for all surfaces included in this paper. This is especially the situation for the B-rich c-BN (1 1 1) surface (an abstraction energy of +512 kJ/mol). It is hence possible to conclude that F is not a good surface stabilizing agent for a gentle (not including bombardments) CVD growth of c-BN (1 1 1).

Table 1. Energies and geometries for adsorption of surface terminating species to (1 1 1) surfaces of diamond and c-BN

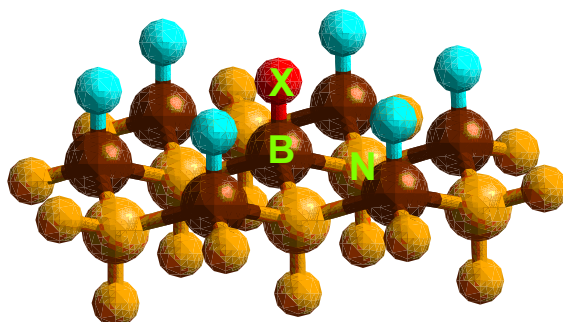|	ν_{N-B-N}		$\Delta E_{adsorption}$, kJ/mol	
	diamond	c-BN	diamond	c-BN
H	111.3	110.0(B)	431	442(B)
				465(N)
F	111.2	111.7(B)	430	653(B)
				251(N)
Cl	111.9	–	200	–
Br	112.9	–	–	–

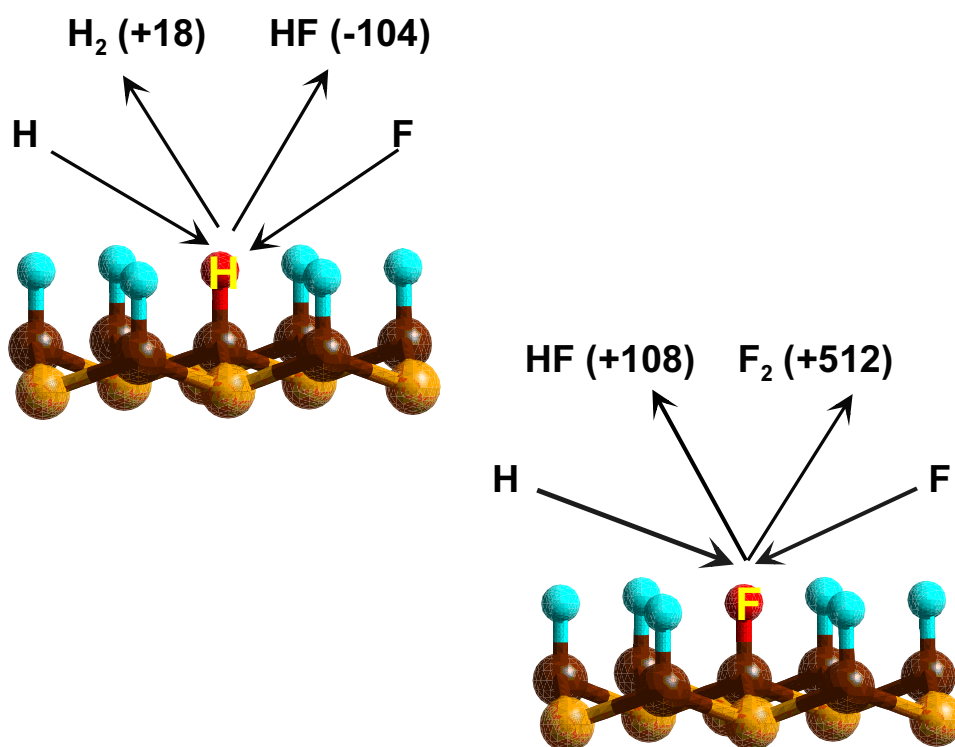**Fig. 2.** The X-terminated B-rich c-BN (1 1 1) surface (X = H, F, Cl, Br).

Fig. 3. Abstraction reactions of H (or F) from the B-rich c-BN (1 1 1) surface (in kJ/mol).
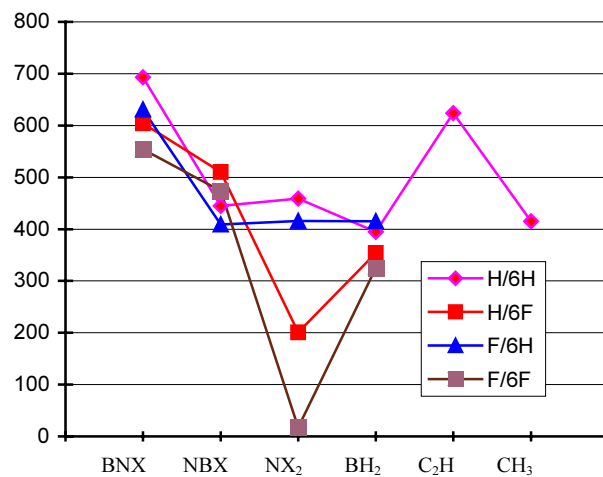
Fig. 4. Adsorption of various growth species to diamond (1 1 1) and B-rich c-BN (1 1 1) surfaces. X/6Y means that an X-terminated adsorbate is adsorbed to a Y-terminated surface (X,Y = H or F). Units: kJ/mol.
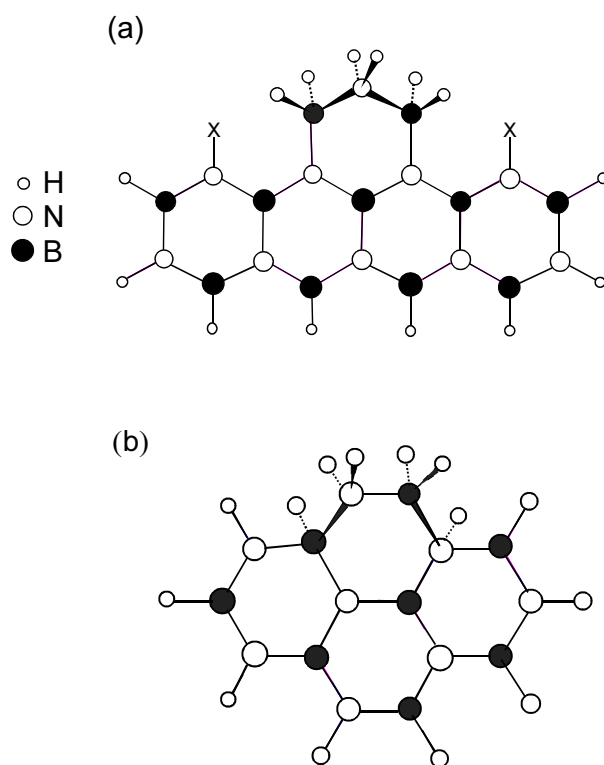

Fig. 5. Models of the cubic outgrowth from the (a) zigzag (1 0 0) and (b) armchair (1 1 0) edge of the basal (0 0 1) plane of hexagonal BN.

3.1.3. Adsorption of growth species on the cubic phases

The adsorption of H- or F-terminated growth species on H- or F-terminated (1 1 1) surfaces of diamond and c-BN, respectively, have been studied by the present author in a series of investigations [6,9–12]. It has also experimentally been assumed that CH_3 and the C_2H fragment of acetylene are the major contributing precursors in the growth of diamond [3]. It was hence of great interest to study the effect of the corresponding B- and N-containing species on the growth of c-BN. In addition, all of these species are monoradical and expected to be found during CVD of these materials.

The strongest adsorption occurs on the H-terminated surfaces. Figure 4 shows the adsorption of species to the B-rich surface of c-BN (1 1 1). It is understood that one has to look for a preferential adsorption of N-containing adsorbates to this specific surface. As can be seen in Fig. 4, there is an almost identical difference in adsorption energy between C_2H (or NBX) and CH_3 (or NX_2) (X = H or F), in favour of the latter species (a difference of about 200 kJ/mol). Unfortunately, if there is a mixture of NX_2 and BX_2 in the gas phase, most probably a mixture of adsorbed NX_2 and BX_2 species will also be on the growing H-terminated B-rich c-BN (1 1 1) surface. What is most interesting is the observation that there is a large energetical preference for adsorption of NBX to the c-BN surface (of about 220 kJ/mol compared to BNX). The possibilities of co-adsorption (including unwanted species) to the c-BN surface can be diminished by using the ALD technique instead of ordinary CVD, where gases are mixed in the reaction chambers. Another alternative is to look for growth precursors like XNBX (including both B and N).

Adsorption of NH_2 and BH_2 to B and N surface sites on H-terminated (1 0 0) and (1 1 0) surfaces of c-BN is also included in this study (see Table 2) [8,13]. It is observed that the calculated adsorption energies are numerically very similar for NH_2 adsorbed to various surface sites. This is also, to a somewhat lesser extent, the situation for BH_2.

3.1.4. Surface migration of growth species on the cubic phases

Surface migration is a very important elementary surface reaction step for an ideal growth of Frank–Van Der Merwe type. A single jump between two neighbouring surface atoms was assumed in the calculations of energy barriers of migration. The energy maximum (and transition state) on the potential energy surface was then localized using a MP2/6–31g** level of accuracy. *Ab initio*

Table 2. Adsorption energies of growth species to various c-BN planes (in kJ/mol)

Adsorption energies	(1 1 1)-plane	(1 1 0)-plane	(1 0 0)-plane
NH_2 (N-site)	–	160	–
NH_2 (B-site)	460	463	393
BH_2 (N-site)	–	420	–
BH_2 (B-site)	395	306	–

molecular dynamics was also performed using DFT-based calculations (e.g. GGA), aimed at ascertaining (at experimental temperatures) the jumping model used. The calculations showed that one of the H atoms in an adsorbed CH_3 species on an H-terminated diamond (1 1 1) surface would very quickly migrate down to a neighbouring non-terminated surface site [14]. These events resulted in an adsorbed CH_2 species, which in turn was shown to migrate very quickly over the surfaces ($\Delta E_{barrier} = 52$ kJ/mol). Hence, an adsorbed CH_3 species will quickly go over to an adsorbed CH_2 species, and further on be able to incorporate effectively in an ideal way at a monolayer surface step. However, if one still assumes a single jump of one CH_3 species, the estimated barrier of energy would become as large as 352 kJ/mol (see Table 3) [15]. For comparison, the corresponding $\Delta E_{barrier}$ for NH_2 on the B-rich surface of c-BN (1 1 1) is numerically rather similar and high (276 kJ/mol). The discrepancy is much larger, 300 kJ/mol (50 vs. 350 kJ/mol), when we compare the migration of NBH (on c-BN) with the migration of C_2H (on diamond). Molecular dynamic simulations at experimental temperatures are at present performed also for the c-BN system in order to outline the surface migration processes in more detail (similar to the situation with diamond).

3.2. Growth of cubic phases on hexagonal ones

Graphitic basal plane edges have been shown to provide nucleation sites for diamond growth [15]. The question is now if this also is the situation for the growth of c-BN on hexagonal boron nitride (h-BN). It would then be possible to use precursor design in preventing a continued growth of h-BN and instead go towards a growth of the most highly desirable cubic form of the phase. A comparable study has been performed, using graphite and h-BN, in studying the possible nucleation sites for a continued growth of the corresponding cubic phases [16,17]. The model of the hexagonal basal planes, including the various edge sites, is demonstrated in Fig. 5. As can be seen in Fig. 5a,b, X-terminated (X = F, Cl, or H) buckled (sp^3-hybridized) outgrowths or planar (sp^2-hybridized) ones were considered and modelled as nuclei on the zigzag (1 0 0) and (–1 0 0) edges, and on the armchair (1 1 0) edge, respectively. The relative energy (ΔE) for c-BN nucleation was then calculated using the equation

$$\Delta E = E_{planar} - E_{buckled} + nE_X , \qquad (1)$$

Table 3. Adsorption energies and barriers of migration, calculated (in kJ/mol) for various growth species on diamond and B-rich c-BN (1 1 1) surfaces, respectively

Migrating species	$\Delta E_{barrier}$	$\Delta E_{adsorption}$
NBH	50	693
C_2H	350	628
NH_2	276	445
CH_3	352	388
CH_2	52	416

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where the different numbers of outgrowth-terminating X atoms have been taken into consideration (X = H, F or Cl). As can be seen in Figs. 6 and 7, the energetically most stable phase of the outgrowth from the edge atoms of h-BN is the cubic one. And this is especially the situation for F-terminated outgrowths. Minor differences exist between the corresponding H- and Cl-terminated ones. In addition, the armchair edge of h-BN seems to be preferable for a cubic phase nucleation.

A similar study has been performed for H-terminated outgrowths from the zigzag and armchair edges of the basal plane of graphite [18]. It was shown there that the nucleation of the cubic phase of C is energetically more stable than that of the hexagonal phase (identical to the situation with BN). However, the main difference between the carbon and boron nitride systems is that this cubic preference is especially true for the zigzag edge of graphite. The relative energy (ΔE) in favour of diamond nucleation is then numerically 250 kJ/mol per outgrown C atom from the (1 0 0) edge, and 175 kJ/mol per outgrown C atom from the (1 1 0) edge of the basal plane of graphite.
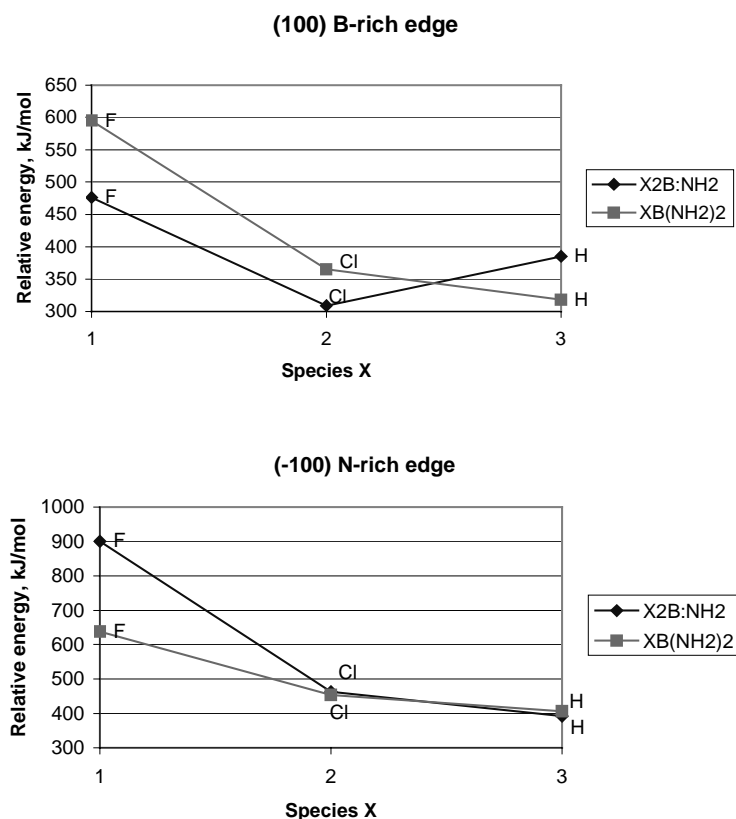

Fig. 6. Relative energies for the cubic F-, Cl- or H-terminated outgrowths from two different zigzag edges (B- or N-rich). The results, obtained from two different types of growth precursors, are presented in kJ/mol.
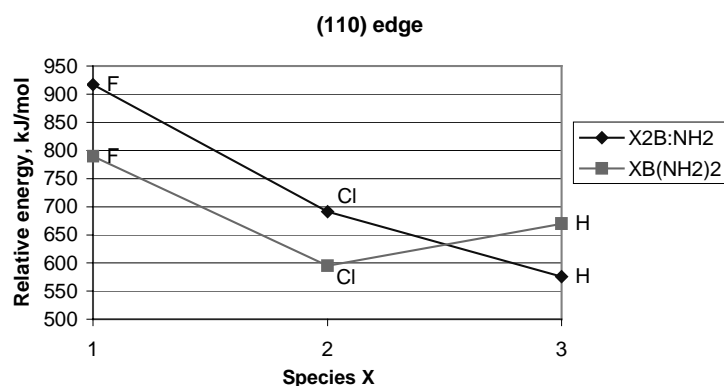
(110) edge

Fig. 7. Relative energies for the cubic X-terminated outgrowths from the armchair edge of the basal plane (X = F, Cl or H). The results, obtained from two different types of growth precursors, are presented in kJ/mol.

4. SUMMARY

Pronounced similarities and dissimilarities have been observed for the growth of diamond vs. c-BN using quantum mechanical calculations. These results are planned to be used as guidelines in the strive towards thin film deposition of cubic boron nitride using gentle CVD methods.

H has been shown effective in stabilizing both diamond and c-BN surfaces. However, termination of the c-BN surfaces with F species should be avoided, since these species are too strongly bonded to the surfaces and will also lead to unsatisfied adsorption processes including growth species. Very great similarities have also been observed when considering the adsorption of various growth species to these materials. It was found necessary to avoid mixtures of B- and N-containing species in the gas phase during c-BN growth, since they should most probably result in a mixture of these species also on the surfaces. It would then be preferable to use a CVD method where the gaseous precursors will be separately introduced into the chamber (e.g. using ALD), or use a growth precursor which inherently contains both B and N (e.g. HBNH).

Greater dissimilarities were registered in case of the surface migrations on the diamond and c-BN surfaces and nucleation of the cubic phases on the corresponding hexagonal ones. C_2H was found to have a very high barrier of energy for migration on diamond, whilst the opposite was observed for the corresponding growth species on c-BN. The opposite was recorded for CH_3 (on diamond) and NH_2 (on c-BN). Further molecular dynamic studies at experimental temperatures are under way. Nucleation of diamond/c-BN on graphite/h-BN was found to be energetically feasible. However, this was calculated to be especially the situation for the armchair edge of the basal plane of h-BN and of the zigzag edge of the basal plane of graphite.

ACKNOWLEDGEMENTS

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Kuubilise boornitriidi ja teemandi aurufaassadestuse lähtesüsteemide võrdlev kujundamine

Karin Larsson

Uuriti boornitriidi ja teemandi kasvu sarnasust ja erinevust, kasutades kvant-mehhaanilisi arvutusmeetodeid. Oluline sarnasus nende tahkiste kasvus ilmnes substraadi pinna stabiliseerimise korral vesiniku aatomitega. Vesinikul on tähtis osa teemandi aurufaassadestamise vaheetappides süsiniku aatomite sp^3-konfigu-ratsiooni säilitajana pinnakihis. Rohkesti ühist oli eri keemiliste ühendite adsorpt-sioonil nende materjalide pindadele. Leiti, et on vajalik vältida boori ja lämmas-tikku sisaldavate lähteühendite segunemist gaasilises faasis kuubilise boornitriidi kasvu jooksul, kuna selline segunemine annaks tulemuseks samade lähteühendite kontrollimatu segu ka kasvupindadel. Sellistel juhtudel tuleks eelistada ajas lahu-tatud lähteainevoogudega aatomkihtsadestusprotsessi keemilisele aurufaassades-tusele, milles traditsiooniliselt juhitakse reaktiivsed lähteained reaktsioonikamb-risse samaaegselt. Suuremat erinevust märgati migratsiooni puhul boornitriidi ja teemandi pindadel ning ka kuubiliste faaside nukleatsiooni korral vastavatel heksagonaalsetel faasidel. Teemandi ja kuubilise boornitriidi nukleatsioon grafii-dil ja heksagonaalsel boornitriidil osutus energeetiliselt soodustatuks.