Theoretical Investigations of Boron Related Materials Using DFT

IGOR ARVIDSSON
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Abstract

In the history of Chemistry, materials chemists have developed their ideas mainly by doing experiments in laboratories. The underlying motivation for this laboratory work has generally been pure curiosity or the ambition to find a solution to a specific problem. Minor changes in the composition or structure of a material can cause major changes in its properties. The development of powerful computers has now opened up the possibility to calculate properties of new materials using quantum mechanical methods.

The Chemistry of different boron-related materials has been evaluated in this thesis by Density Functional Theory (DFT). Cubic boron nitride (c-BN) is a most interesting material for the microelectronics and tool industry. During thin film deposition of c-BN, several problems arise which most often result in unwanted BN isomers. Chemical processes at the (110) and (111) surface of c-BN have been investigated in order to shed light upon some of these complex processes. Typically adsorption energies and surface reconstruction were found to differ significantly between the two surfaces.

Other materials investigated are layered transition-metal diborides (MeB2). Incorporation of transition-metal atoms into elemental boron in its most fundamental structure, α-boron, has also been investigated. The calculations on MeB2 focused on the stability of the planar compared to the puckered structure of MeB2. Stability was investigated by calculating Density of States (DOS) and bond populations. Deviations in the cell parameters from their ideal values were also considered.

A separate project concerned reactivity of the TiB2(001) surface. Molecular and dissociated adsorption energies and adsorption geometries were calculated for H2, H2O and O2. It was concluded that the titanium surface was more reactive than the boron surface and that the adsorption energies were comparable to or stronger than other well known surface-active compounds like TiO2.

Keywords: boron nitride, density functional theory, chemical vapour deposition, atomic layer deposition, surface reactivity, adsorption, abstraction, computational chemistry

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List of papers

This thesis is a summary of the following papers. Each article will be referred to by its Roman numeral.

I Solid solutions of 3d-metal atoms in boron icosahedra; a structural and energetic investigation
   In manuscript.

II Adsorption of H, NH₃, BHₓ and BBrₓ on a (110) surface of c-BN: A quantum-mechanical DFT study
   Diam. and Rel. Mater. 16 (2007) 131-137

III Influence of Surface Terminating H and F on Structural c-BN Collapse
   Submitted to Thin Solid Films.

IV Relative stability between planar and puckered structures of 3d-metal diborides: A quantum mechanical study
   Submitted to J. Phys. Chem.

V Surface reactivity of TiB₂(0001), adsorption studies of H₂, H₂O and O₂
   Submitted to Surf. Sci.
Comments on my own contribution to the papers in the thesis

I. All calculations and the main author of the paper.

II. All calculations and the main author of the paper.

III. Planning of the calculations and a major part of the writing of the paper.

IV. All calculations and the main author of the paper.

V. All calculations and the main author of the paper.
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### Abbreviations

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<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
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<td>AM1</td>
<td>Austin model hamiltonian of first degree</td>
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<td>CASTEP</td>
<td>Cambridge sequential total energy package</td>
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<td>c-BN</td>
<td>Cubic boron nitride</td>
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<td>CVD</td>
<td>Chemical vapour deposition</td>
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<td>DFT</td>
<td>Density functional theory</td>
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<td>DOS</td>
<td>Density of states</td>
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<td>FFT</td>
<td>Fast fourier transformation</td>
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<td>GGA</td>
<td>Generalized gradient approximation</td>
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<td>h-BN</td>
<td>Hexagonal boron nitride</td>
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<td>HTHP</td>
<td>High-temperature high-pressure</td>
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<td>LDA</td>
<td>Local density approximation</td>
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<td>LSDA</td>
<td>Local spin density approximation</td>
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<td>SCF</td>
<td>Self consistent field</td>
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Introduction

1.1 Elemental boron

Elemental boron is a light, refractory material. It is hard and has a high mechanical strength, as well as chemical inertness at room temperature. It is also efficient in absorbing neutrons [1]. Due to these qualities, boron has been used as a protective and refractory coating in *e.g.* fission reactors. One technique commonly used in depositing thin films of boron is chemical vapour deposition (CVD). Boron halides precursors, such as BCl$_3$ or BBBr$_3$, are commonly used as precursors which are then reduced by hydrogen to obtain pure boron [2,3]. This is an element with three valence electrons (*i.e.* an electron deficient element) which causes boron to adopt somewhat unusual structures. For example a predilection for cage structures with three-centre, two-electron bonds. Other boron related materials mentioned in this thesis are planar layered structures, puckered layered structures and diamond-like boron nitride (Fig 1.1).

![Figure 1.1 The structures of a boron icosahedron, planar metal diboride, puckered metal diboride and cubic boron nitride.](image)

Other cage structured materials as the fullerenes have shown to be able to encapsulate atoms. The fullerene C$_{60}$ with its diameter of 7.0 Å, is able to encapsulate several different metal atoms, *e.g.* LaC$_{60}$ and the well known superconducting trimetal compounds A$_3$C$_{60}$ (A = alkali metal) [4,5]. It is therefore interesting to investigate the possibilities for endohedral MeB$_{12}$ formation (with a B cage diameter of 3.8 Å). Earlier investigations of metal incorporation into α-B have mostly regarded solubility of alkali metals (*e.g.* Li) or alkaline earth metals (*e.g.* Ca and Mg) [6,7]. Compared to these types of metals, transition-metals, whose solubility are investigated in paper I, have more diverse oxidation numbers. When moving from left to right along
the 3d row in the periodic table, the number of valence electrons increases which will affect the ability to donate electrons. This difference in the ability to donate electrons opens up the question if the degree of electron transfer to the B cage can be correlated to the possibility to incorporate different 3d-transition-metal atoms, and/or if it affects the geometry of the resulting icosahedron. The incorporation of alkali metals into α-B has been observed to affect the work function and changing the semi-conductivity from p-type to n-type [8]. An earlier investigation regarding incorporation of H into elemental α-B also considered the ability to incorporate the H atom inside the icosahedron (apart from the outside position). This showed that an endohedral solid solution of hydrogen in α-B were possible with a substantial energy barrier between the inside to the outside position [9].

A similar investigation of the possibility for endohedral 3d-transition-metal dodecaboron (MeB₁₂) into α-B has been performed in the present thesis (paper I).

1.2 Boron nitride

1.2.1 General about boron nitride

Cubic boron nitride (c-BN) is isoelectronic to diamond, having the same crystal structure with strong sp³ hybridized bonds. It is among the hardest known material, being second only to diamond (Vickers hardness of 4500 kg mm⁻²) [10]. This makes it interesting as a protective coating for e.g. cutting tools. In addition, c-BN has interesting thermal, electrical and optical properties [11]. Compared to diamond, c-BN has some advantages such as inertness to ferrous materials and resistance to oxidative environments at high temperatures [12]. One other dissimilarity to diamond is that c-BN is a binary compound constituted by elements with different electronegativities (i.e. the bonds are polarized).

1.2.2 Growth of boron nitride

Compared to diamond which can be grown using CVD, it has been showed that c-BN is very difficult to grow with common CVD techniques. The common procedure used for thin film growth of c-BN is physical vapour deposition (PVD) which was reported as early as 1970 [13]. It had earlier been grown in bulk crystalline form using high-pressure high-temperature techniques [14]. PVD is a sputtering technique using high energy ion bombardment followed by condensation on a substrate. This crude method results in different phases of BN and the films have high compressive stress causing defects and poor adhesion [15]. Due to these negative effects, the
development of a successful route using CVD is highly interesting. An alternative to CVD is atomic layer deposition (ALD) where the gaseous precursors are sequentially inserted [16]. Both methods use hot gaseous precursors, reacting on or in the vicinity of a substrate. The chemical processes that take place in the gas phase are very complex and are affected by e.g. temperature, gaseous composition, pressure, substrate material and gas flow rate. A major advantage of ALD, compared to CVD, is the possibility to control the number of atomic layers exactly due to the separately pulsed gaseous precursor (in CVD the thickness is controlled by the deposition time). The ALD procedure also avoids non-wanted reactions between the different gaseous precursors in the gas phase, thus allowing the chemical reactions at the substrate control the process. A negative aspect is a much lower growth rate. Various B-containing precursors (such as B2H6, BF3, BCl3, BBr3 and B3N3H6Cl3) are used for deposition of BN [17]. The most common N-containing precursor is NH3 with a higher reactivity compared to N2. The plausible growth precursors NH3 and BBr3 were used as theoretical precursors in paper II, and in paper III both surface H- and F-termination were investigated assuming the F atoms to originate from e.g. BF3.
Figure 1.2 An illustration of a four step ALD process. (A) Adsorption of the first precursor. (B) Purging to remove excess precursor gas and reaction products. (C) Reactions between the first and second precursor. (D) Purging of an inert gas resulting in a thin film layer.

Fig. 1.2 is an illustration of a general ALD procedure. Fig. 1.2a shows a precursor supplied at a substrate where the precursor binds more or less strongly to the substrate. Between the first and second pulse a cleaning pulse (usually argon or nitrogen) is supplied to remove excess precursor gas (Fig. 1.2b). A second precursor is supplied reacting with the initial precursor, on or in the vicinity of the substrate (Fig. 1.2c). Finally, the ALD reactor is purged with another cleaning pulse resulting in a thin film layer (Fig. 1.2d). A CVD process is very similar, but do not have separated steps. Thus, the A and C steps are merged.

1.2.3 Adsorption to boron nitride
In paper II, adsorption reactions of the gaseous species BBr_x (x= 1-3) and NH_x (x= 1-3) onto the c-BN(110) surface have been especially illuminated as the most important elementary reactions during c-BN growth. A similar investigation have earlier been made for the (111) surface which showed the necessity for decomposition of the precursors [18]. The energies for the adsorption process are calculated according to Eq. 1.1, being valid for both CVD and ALD:

$$E_{ads} = E_{surf+species} - E_{surf} - E_{species}$$  \hspace{1cm} (1.1)$$

where $E_{surf+species}$ and $E_{surf}$ are the total energies for the surface with or without an adsorbate, respectively, and $E_{species}$ is the total energy for the gaseous adsorbate. An exothermic reaction, resulting in a more stable product than its reactants, results in a negative value of $E_{ads}$. 
Problems arising during thin-film growth of c-BN are competing reactions producing isomorphs to c-BN, like the more common hexagonal boron nitride (h-BN). Hexagonal BN is a material similar to graphite with sp²-hybridized bonds, and is therefore not as hard and abrasive as c-BN. To obtain c-BN during thin film growth it has been shown that it is very important to terminate the surface with e.g. H (or F) to keep the sp³-hybridized structure [19]. Without a terminating species, the surface tends to relax into a sp²-bonded surface structure, thus a counterproductive step towards c-BN growth. In paper III, the effect of F- and H-termination on the structural collapse of c-BN(111) and (110) surfaces has been investigated which yields important information of their ability to effectively uphold the cubic structure during growth.

Calculations were also made for adsorption to clusters of BN of two different sizes (paper II). These calculations give information of i) a BN clusters ability (compared to a planar surface) to adsorb species originating from the gaseous precursors, and ii) the size-dependency for the adsorption process. The DFT calculations were also compared to semi-empirical methods to evaluate the reliability of semi-empirical calculations applied to BN systems.

1.3. Transition-metal diborides
1.3.1 General about metal diborides
In B₁₂ structures, the electron deficiency causes three-centre, two-electron bonds. In BN, the N atoms donates electrons to the B atoms thus filling its octet, and in metal diboride (MeB₂) structures it is the metal atoms that donate electrons to the boron atoms which stabilizes the boron in planar or puckered sheets. The planar sheets consist of strong bonds with delocalized electrons creating metallic conductivity. These planar sheets also have high phonon frequencies. The bonding properties disappear if the sheets are transformed into puckered sheets.

Besides metallic conductivity within the boron sheets, planar metal diborides have several interesting properties such as high melting points, high thermal conductivities, low electrical resistance and low work functions [20,21]. The difference in bonding between the layers compared to the bonding along the layers give rise to anisotropy in its properties such as thermal expansion and lattice vibration [22,23]. Another fascinating aspect of the chemistry of planar MeB₂ is the superconductivity at 38° K for MgB₂ [24]. The explanation of this remarkably high temperature for such a simple compound is thought to be the strong phonons along the planar sheets of boron, which is also dependent of intact planar layers.
1.3.2 Energetic stabilities of planar vs. puckered structures of MeB$_2$

The most common structure of MeB$_2$ is the planar AlB$_2$ structure (space group P6/mmm) \[25,26\] consisting of planar layers where the metal atoms are “intercalating” the graphite-like sheets of boron. Each metal atom has a coordination number of 12; two honey-comb structures of boron atoms surround the metal atoms at two sides (Fig.1.3). Related structures to the planar AlB$_2$ structure are the puckered ReB$_2$ and RhB$_2$ structures with a somewhat more complicated stacking of the layers.

![Figure 1.3 The planar and puckered structure of MeB$_2$.](image)

Bonding in metal diborides (AlB$_2$ structure) is quite complex and consists of covalent bonds with some ionic contributions. There are strong bonds between the boron atoms within the boron sheets (of p$_x$- and p$_y$-type), weaker covalent bonds between the boron and metal atoms (from the metal d$_{x^2}$- and d$_{yz}$- orbitals), and anti-bonding overlaps between the metal atoms in different layers created by the d$_{z^2}$-orbital. The electrons are delocalized within the boron sheets, thus creating metallic conductivity which is an important property for the whole compound. This conductivity along the boron sheets disappears when the sheets becomes puckered. It seems that a combination of electron transfer from the metal atoms to the boron sheets, and general sterical aspects, are responsible to the transformation from a planar to a puckered structure. It has earlier been theoretically shown that the cohesion energy of the planar metal diborides is highest for the lightest 3d-metals, ScB$_2$ and TiB$_2$, whereafter the cohesion energy were shown to decrease \[27, 28\].

In paper IV, the stability of planar 3d-metal diborides relative to the puckered structure has been calculated in order to investigate the destabilizing effect of the more electron rich transition-metals of the 3d period. Besides calculating the energetic stability, the bond populations between metal-metal, boron-boron and metal-boron were investigated. The experimentally known cell-parameters for ScB$_2$, TiB$_2$, VB$_2$, and CrB$_2$, MnB$_2$ and FeB$_2$ which were compared with the parameters obtained in the calculations. MnB$_2$ and FeB$_2$ are high-temperature phases (1373° C and 2343° C respectively) and tend to reorganize at lower temperatures \[29-31\]. A similar theo-
retical investigation regarding the relative energetic stability between the planar and the puckered structure of the MeB₂ of the 4d transition-metals have been made. It was there concluded that the puckered form becomes more stable than the planar form from the fourth transition-metal, MoB₂ [32].

1.4. Surface reactivity of TiB₂

One of the most stable planar MeB₂ compound is TiB₂. The Ti atom is small and donates its valence electrons to the sheets of boron making them negatively charged. TiB₂ receives a lot of interest, due to its extreme hardness, strength and resistance to corrosive environments [33,34]. Since the structure of TiB₂ is layered, different degrees of surface reactivity for the two different surface termination types (Ti and B) are expected. The negatively charged boron layer has delocalized electrons, thus having metallic conductivity within the sheets. This behaviour is contrary to the more isolated and positively charged Ti atoms.

A theoretical investigation concerning the most stable surface termination has earlier been reported [35], and it showed that the Ti terminated surface is the most stable. Considering the relaxation of the TiB₂ surface, it was then showed that the surface slab requires geometrical relaxation of the two uppermost atomic layers. Those layers were also the only ones that showed any significant electronic effect due to relaxation, measured by changes in Mulliken atomic charges [35].

In order to investigate the surface reactivities of the (001) surfaces of TiB₂, the molecular and/or dissociative adsorption energies have in paper V been calculated for different species (H₂, H₂O and O₂), representing molecules with different number of bonds, valence electron structure and geometries. Changes in Mulliken charge at the adsorption site (indicating electron transfer) and adsorption geometries were also considered. For the situations where the adsorbed species did not dissociate spontaneously, the energy barrier for the dissociation was also calculated.
2. Methodology

2.1 Quantum mechanical calculations

In order to optimize geometries and calculate the energy of a system, several methods are available; e.g. force field methods based on classical mechanics, semi-empirical methods with parameters obtained from experimental data, and so called \textit{ab initio} methods. In the latter method the parameters are not generated from experiments. \textit{Ab initio} quantum mechanics is highly accurate in describing the electronic details of a ground state system but is also very computational demanding. In general, the main question is how to solve the time-independent Schrödinger equation, which can be written as:

\begin{equation}
\hat{H}\Psi = E\Psi
\end{equation}

where $\hat{H}$ is the Hamiltonian operator, $\Psi = \Psi_1,\Psi_2,\ldots,\Psi_n$ is the wavefunction, and $E$ is the electronic energy of the system. Solving the Schrödinger equation to the eigenfunctions ($\Psi_n$) generates the energy ($E$).

The Hamiltonian, $\hat{H}$, consists of different terms which take into account the interactions between nucleus-electron ($\hat{V}_{ne}$), electron-electron interactions ($\hat{V}_{ee}$) and the kinetic energy ($\hat{T}$) (Eq. 2.2):

\begin{equation}
\hat{H} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}
\end{equation}

To be able to solve the Schrödinger equation various approximations must be used. A fundamental approximation is the Oppenheimer approximation which states that due to the enormous difference in masses of the electrons compared to the nucleus, the motion of the nucleus can be ignored and the motion of the electrons can be treated separately. An important theorem, the variation principle, states that the energy of a trial wave function can never be more negative than the true energy of the system. This theorem let us use the iterative self-consistent-field (SCF) method to obtain accurate geometries and electronic structure of our system by inducing minor perturbations to the system. A perturbation resulting in a lowering of the energy indicates a more stable system. This method is thus a way to approach the ground state energy. The iteration is ended when a certain convergence level of accuracy has been reached.
2.1.1 DFT

The history of DFT can be traced all the way back to 1927 at the early beginning of quantum chemistry. At that time, Fermi stated that the energy of a system can be directly related to its electron density $E = f(\rho)$ [36-38]. For decades, problems with adjustment of especially the exchange term, created incorrect results like overestimation of the chemical bond. Not until 1964 the theorems of Hohenberg and Kohn helped to solve many of the problems and a major breakthrough could be made [39]. Their work was awarded with the Nobel Prize in 1998. Through the years, improvements have continuously been made in the field of DFT. Adjustments of the computational methods and development of powerful computers have in the last decades made DFT one of the most useful methods in computational chemistry.

The relation between the energy and the electron density can be written as:

$$E[\rho] = T[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$  \hspace{1cm} (2.3)

where $T[\rho]$ represents the kinetic energy, $E_{\text{ne}}[\rho]$ the nucleus-electron interaction, $J[\rho]$ the coulomb interaction energy, and $E_{\text{xc}}[\rho]$ the exchange-correlation energy. The problematic term in Eq. 2.3 is $E_{\text{xc}}[\rho]$, the exchange-correlation energy, which needs to be approximated to achieve accurate, meaningful results. This can be made in different ways.

One method of approximation is the local density approximation (LDA), which is based on the model of the uniform electron gas. Here the electron density is assumed to change slowly on an atomic scale and can therefore be treated locally. The exchange-correlation part can be written as:

$$E_{\text{xc}}[\rho] = \int \rho(r) \varepsilon_{\text{xc}}(\rho) dr$$ \hspace{1cm} (2.4)

Here $\varepsilon_{\text{xc}}$ represents the exchange and correlation energy for a specific particle. This can be further divided into two separate terms:

$$\varepsilon_{\text{xc}}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$$ \hspace{1cm} (2.5)

The exchange part ($\varepsilon_x$) is known as the Dirac exchange-energy [40] which can be written as:

$$\varepsilon_x(\rho) = -C_x \rho(r)^{1/3}$$ \hspace{1cm} (2.6)

A widely accepted formula for the correlation term ($\varepsilon_c(\rho)$) in LDA has been developed from numerical determined values of electron densities which covers spin polarized as well as spin compensated cases [41,42].
To account for the different spin orbitals (α and β) the density, ρ, in LDA can be divided in a $ρ_α$ and $ρ_β$ part. The treatment of systems with different spin is called the local spin density approximations (LSDA). The somewhat crude approximation that LDA and LSDA represent tends to overestimate the energy of bond dissociations and bond lengths [43].

Further development of the treatment of the electron density has been made, which has resulted in the approximation type generalized gradient approximation (GGA) (the electron density can, as for LDA be divided into an α and β part). The GGA method not only calculate the electron density at a certain infinitesimal region, but also take into account the gradient of the electron density ($\nabla ρ(r)$) compared to the surrounding regions. This more exact description of the electron density substantially improves the approximation of the exchange-correlation term. Examples of useful functionals implemented in GGA includes PW91 [44], PBE [45] and RPBE [46]. The functional PW91 has been used in paper I, II and III. The PBE were used in paper IV and RPBE in paper V. RPBE is a revision of the PBE functional which has been shown to give better accuracy concerning adsorption of molecules at surfaces [46]. The DFT calculations (except for the cluster calculations in paper II) have been performed using the program CASTEP from Accelrys Inc. [47].

The DFT calculations on clusters in paper II were performed using Dmol3 [48]. Here a local density approximation, in combination with the non-local gradient-corrected functional of Becke (B88) [49], were used in addition to the gradient-corrected correlation functional of Lee, Yang and Parr (LYP) [50]. It has earlier been shown that this combination is the most accurate for this particular system [51]. The semi-empirical calculations were performed using the program VAMP using the Austin Model Hamiltonian of first degree (AM1) which is parameterized for all elements included in the calculations.

2.2 Models

Throughout this thesis the investigated systems have been modelled as supers-cells with periodic boundary conditions. For these super-cells, plane waves have been used according to Bloch’s theorem:

$$Ψ_κ(\mathbf{r}) = \sum_G C_{κ,G} e^{i(k-G)•r}$$  \hspace{1cm} (2.7)

where $C$ is the expansion coefficient of the wave function and $G$ the vector of the reciprocal lattice. To produce a uniform mesh of k-points in the reciprocal space, the common Monkhorst-Pack scheme was used [52]. The ionic atomic cores were represented by ultra-soft pseudopotentials [53]. By using ultra-soft pseudopotentials the wave functions can be expanded using much
smaller numbers of plane waves. The accuracy of the plane waves is determined by the value of the cut-off energy and the fast Fourier transformation (FFT) grid (which is closely related to the cut-off energy). At the level of accuracy used in the calculations, the value of the FFT grid corresponds to exactly twice the radius of the reciprocal space sphere determined by the energy cut-off [54].

During the geometrical optimization of the system, various degrees of freedom can be employed to the system. This can include constraints of the cell parameters and/or constraints of the internal atomic positions. Partial geometry optimization have been performed for e.g. the surface calculations (paper II, III and V) were it is important to allow the upper layers to undergo surface relaxation, but at the same time freeze the bottom layers in order to keep the bulk structure for those underlying layers. The cluster calculations performed in paper II were performed without any restraints during their geometrical optimization. For all geometry optimizations, the conjugate gradient BFGS procedure was used [55].

The bond-populations were performed using a projection of the plane-wave states onto a localized basis [56]. From the resulting projected states the population analysis is then performed using the Mulliken formalism [57].
3 Results

3.1 General

In this, the last part of the thesis, a comprehensive summary of the results will be made. In the same way as the introduction, the results are divided in subsections starting with i) a fundamental study of incorporation of transition-metal atoms in elemental $\alpha$-B, ii) surface reactions at c-BN and iii) investigation of bulk stability of MeB$_2$ and surface reactivity of TiB$_2$.

3.2 Incorporation of transition-metals into elemental boron

Incorporation of 3d-transition-metal atoms into $\alpha$-B has been investigated using DFT. It showed significantly different results depending if the metal atoms were incorporated in-between (exohedral incorporation) the icosahedra or inside (endohedral incorporation) an icosahedron.

From Fig. 3.1 it can be concluded that all metal atoms investigated show an exothermic cohesion energy when incorporated in-between the icosahedra in $\alpha$-B. No particular correlation to the degree of electron transfer, electronegativity or difference in atomic radius could be found.
Figure 3.1 Cohesion energy for incorporation of transition-metal atoms in-between icosahedra in α-B.

For incorporation inside an icosahedron of α-B, the cohesion energy were endothermic for the first two 4d-metals in the periodic table (Sc and Ti), but becomes exothermic for the next-coming five elements, with an exception for Mn (Fig. 3.2).

Figure 3.2 Cohesion energy for incorporation of transition-metal atoms in an icosahedron in α-B.

This behaviour do not correlate to the number of valence electrons or any other electronic property, but show a very good correlation to the atomic radius of the metal atoms. This correlation is illustrated in Fig. 3.3 where the atomic radius of the metal atoms and their corresponding cohesion energies for incorporation inside an icosahedron are shown. It is clear that it is the geometrical aspects that are decisive for the possibility for incorporation into a boron icosahedron, reaching its most exothermic value for the chromium atom.
Figure 3.3 Correlation between atomic radius and cohesion energy for incorporation of transition-metal atoms in an icosahedron in α-B.

In order to evaluate the energy barrier between the two different positions of the metal atom, the path between these positions were divided in ten parts and the respective energy were calculated (Fig. 3.4). All atoms, except the metal atom of interest, were allowed to relax during the geometrical optimization (exemplified by the chromium atom).

Figure 3.4 The change in energy moving a chromium atom from an inside to an outside position of an icosahedron in α-B.

The calculations for Cr show an energy barrier between the two different positions of approximately 3.5 eV going from an endohedral to an exohedral position (Fig. 3.4).
3.3 Cubic boron nitride

3.3.1 Adsorption to a c-BN(110) surface

During thin film growth of c-BN, adsorption of growth species originating from the gaseous precursors is crucial. The precursors assumed in the calculations are BBr₃ and NH₃ which are commonly used in experimental set-ups, [58-60]. As mentioned in section “1.2 Boron nitride” other precursor can also be used as e.g. B₂H₆, BF₃ and BCl₃. The model used in the calculations in paper II as shown in Fig. 3.5, is fully terminated with hydrogen atoms. The surface investigated in paper II is the (110) surface (Fig. 3.5) which is one of the experimentally plausible surfaces for the c-BN system.

![Figure 3.5](image)

**Figure 3.5** Top view of the (110) surface slab model. The surface is terminated with hydrogen atoms (white spheres).

In close proximity over the surface, the gaseous precursors are assumed to decompose into fragments of the gaseous precursors (this can be enhanced using e.g. laser or a hot filament over the substrate). Apart from the precursor itself, fragments such as BH, BH₂ and BH₃ (originating from reactions between the BBr₃ precursor and the H₂ carrier gas) have been used in the calculations. Adsorption energies for BBr₃ and NH₃, and their fragments, have been calculated, presented in paper II. The obtained adsorption energies are shown in Fig. 3.6.
Figure 3.6 Adsorption energies for H, NH₃, BHₓ and BBrₓ (x=1-3) on a c-BN(110) surface

The adsorption energy for the fragments NH and NH₂, that has its origin from NH₃, clearly prefers a B site. What is also very important is that they bind stronger than H (by 31 vs. 45 kJ/mole). NH₃ itself show an adsorption energy close to zero for both adsorption sites (at the N site it is even weakly endothermic), and does not show any large difference between the B or N site. From this it can be concluded that a decomposition of the NH₃ precursor is crucial in order to achieve adsorption and thereby for film growth to occur.

The decomposed fragments of the BBr₃ precursor behave in a different way. Here it is only the BBr fragment that binds stronger than an H atom.
Another important difference is that the BBr₂ and BBr₃ prefer a B site, which makes the decomposition of BBr₃ precursor even more important. Other plausible precursor components that might compete with the H atoms for an adsorption N site is the BH and BH₂, with BH having an adsorption energy 26 kJ/mole lower, and BH₂ 4 kJ/mole higher than the H atom.

It can be concluded that competing reactions at the adsorption sites can be expected with boron-containing species. The bind stronger to B sites than the preferred N-containing species. By using ALD with sequentially introduced precursors, those competing and unwanted reactions can be avoided. These results indicates that an energy-activated ALD process is necessary for film growth to occur at a (110) surface of c-BN.

3.3.2 H and F termination of (110) and (111) surfaces of c-BN

3.3.2.1 Effect of surface reconstruction due to radical surface sites

During surface growth, termination of the surface is important to uphold the cubic sp³ hybridization of the top layer. Different surfaces show different degrees of collapse due to the presence of radical surface sites. In paper III the surface reconstruction and adsorption energies of different terminating species were calculated for both the (110) and (111) surfaces in order to investigate their different capabilities to avoid surface reconstruction. The two terminating species investigated were F and H. The (111) surface consists of either B- or N-layers, whereas the (110) surface consists of a mixed (N and B) composition in the layers (Fig. 3.7).

![Figure 3.7](image)

**Figure 3.7** Top view of the (111) and (110) surface slab models. The top layer of the (111) surface (consisting of N atoms) is here terminated with H atoms (white spheres). The alternating B and N surface atoms at the (110) surface is also terminated with H atoms.

The degree of geometrical surface reconstruction, due to the existence of a surface radical site, has been measured by calculating the resulting bond
angle for the radical surface atom (\(\alpha\)), and lowering of its position in z-direction compared to its initial bulk position, (\(\Delta z\)) (Table 3.1). The ideal bond angle in the bulk structure is the tetrahedral angle of approximately 109°.

**Table 3.1:** Parameters showing degree of geometrical reconstruction at radical surface sites, B and N, terminated with H and F, respectively.

<table>
<thead>
<tr>
<th>Radical site</th>
<th>(\Delta z) (Å)</th>
<th>(\alpha) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-H (111)</td>
<td>0.35</td>
<td>118</td>
</tr>
<tr>
<td>B-F (111)</td>
<td>0.35</td>
<td>118</td>
</tr>
<tr>
<td>N-F (111)</td>
<td>0.07</td>
<td>112</td>
</tr>
<tr>
<td>N-B (111)</td>
<td>0.12</td>
<td>112</td>
</tr>
<tr>
<td>B-H (110)</td>
<td>0.07</td>
<td>112</td>
</tr>
<tr>
<td>B-F (110)</td>
<td>0.12</td>
<td>112</td>
</tr>
<tr>
<td>N-H (110)</td>
<td>0.15</td>
<td>112</td>
</tr>
<tr>
<td>N-F (110)</td>
<td>0.15</td>
<td>112</td>
</tr>
</tbody>
</table>

It can be seen in Table 3.1 that the radical stability at the (111) surface is independent of the type of terminating species. The radical boron sites collapse almost completely to a planar structure. The N radical sites on the other hand manage to uphold their cubic structure. A planar bonding structure of B can be explained by its electron deficient structure (i.e. it needs to bind to four other atoms, acting as Lewis acids, in order to achieve a pyramidal structure). For the situation at the (111) surface, the radical B atom will bind to three N atoms in the second atomic layer, resulting in a structural collapse to a planar structure (which is the stable structure for molecular compounds such as e.g. BCl\(_3\) and BH\(_3\)). It can also be seen that it has lowered its position significantly by 0.35 Å.

For the N-rich (111) surface, the N atoms with its higher electronegativity is able to keep the tetrahedral geometry. No relaxation in the z-direction of the radical N sites can be seen, and the cubic geometry is intact at 109° for the H terminated surface and shows only a minor increase to 110° at the F terminated surface (Table 3.1).

The (110) surface with a stoichiometric mixture of B and N atoms, 1:1, show a different behaviour in its radical form. A radical N site surrounded by terminating H atoms does not experience any significant structural collapse. However, the corresponding situation with F termination results in a medium sized collapse (\(\Delta z= 0.15 \text{ Å}\) and an angle of 112°), and this collapse is more distributed over neighbouring surface atoms compared to the very local collapse for the (111) surface.

The radical B site at the (110) surface show a small and globally distributed collapse (\(\Delta z = 0.07 \text{ Å}\) and an angle of 112°) for the H terminated surface. This is similar to the situation for the radical N(110) site (\(\Delta z = 0 \text{ Å}\) and an angle of 111°). Here, the adsorption energies are also very similar at
For the F terminated surface an interesting observation was made. When a radical surface B atom was initially formed, a neighbouring F-terminating species migrated over, thereby creating an F radical site. This explains the identical adsorption energy (117 kJ/mole) for both B and N sites at the F terminated surface, and an almost identical degree of structural collapse (Table 3.1). This behaviour shows that the F atoms prefer to bind to a Lewis acid (B) instead of a Lewis base (N).

It can from this investigation be concluded that it is of outermost importance to terminate the B(111) surface completely, which otherwise will collapse into non-cubic form of BN. This is the situation for both H and F terminations. The (110) surface is more stable to radical surface sites. Only partial collapses can be seen which are more distributed over the neighbouring surface atoms. The F-terminated surfaces show a slightly higher degree of collapse. The only surfaces that did not show any structural collapse were N(111) and, to a lesser extent, the H-terminated (110). This indicates that H-termination is preferable for growth on the (110) surface.

### 3.3.2.2 Bond strength of terminating H and F species

The possibility for optimal bond strength is very important for termination of the different c-BN surfaces, (110) and (11). As can be seen in Table 3.2 the adsorption of the H atoms are generally much stronger than the corresponding F species. The adsorption energies are calculated using the following formula:

\[
\Delta E_{\text{ads}} = E_{\text{surface}} - E_{\text{radical}} - E_x (x = \text{F or H})
\]

Where \(E_{\text{surface}}\), \(E_{\text{radical}}\) and \(E_x\) are the total energies for the 100% terminated surface, surface radical site and the gaseous adsorbate, respectively.

The exception from the dissimilarity in bond strength between H and F is adsorption to the B surface of the (111) surface, where the adsorption energy is similar (317(H) vs. 277(F) kJ/mole). But at the N-rich surface the adsorption energy differs significantly (363 vs. 51 kJ/mole). There is hardly any significant preference for H to favour any of the different (111) surfaces (317(B) vs. 363(N) kJ/mole). In contrary, the F atom seems to strongly prefer the B-rich surface (277(B) vs. 51(N) kJ/mole), probably due to its tendency to react stronger to a Lewis acid like B.

Table 3.2: Adsorption energies for H or F adsorbed to an N and B surface site on a (111) and (110) surface, respectively.
Surface site   | $E_{ads}$ for H (kJ/mole) | $E_{ads}$ for F (kJ/mole) \\
--- | --- | --- \\
B-site (111)  | 317 | 277 \\
N-site (111)  | 363 | 51 \\
B-site (110)  | 576 | 117 \\
N-site (110)  | 537 | 117 \\

For the (110) surface with an 1:1 mixture of B and N atoms, the differences between adsorption energies for F and H terminations are very large (Table 3.2). For each type of surface termination, the differences between the different radical surface sites are not particularly large. Adsorption of an H atom is only slightly stronger at the B-site compared to the N-site (576(B) vs. 537(N) kJ/mole). For an F atom, the adsorption energy were exactly the same due to the migration of a neighbouring F atom to the initially formed radical B site.

The similarities in adsorption energies can be explained by the large similarities in structural collapse for the B and N sites on the (110) surface. The significantly weaker adsorption energies for F to the N sites compared to the B sites can be explained by the fact that both are Lewis bases and therefore do not bond strongly.

3.3.2.3 Abstraction of terminating H and F species

The abstraction of terminating species like H and F is crucial in order to leave room for incoming growth precursor. Two plausible radical species, known to be efficient in abstraction processes, are H and F. In paper III the terminating H and F species have been abstracted by gaseous H or F. These reactions have then been calculated for both N and B sites at the two investigated surfaces, (111) and (110). The following reactions were used:

$$E_{ads} = E_{F^*/H^*/HF} + E_{rad} - E_{F^*/H^*/n} - E_{surface}$$  (3.2)

where $E_{surface}$ is the fully terminated surface, $E_{F^*/H^*/}$ is a radical gaseous species, $E_{rad}$ the surface with a radical site and $E_{F^*/H^*/n}$ the abstracted molecular species.

Considering the N-rich (111) surface, which did not collapse at a radical surface site, abstraction with an H radical will follow the pattern for the adsorption energies of the terminating species. The medium strong adsorption energies for an H atom at -363 kJ/mole, and the low adsorption energy an F atom (-51 kJ/mole), corresponds to the abstraction energies of -287 and -672 kJ/mole, respectively (Table 3.2 and Table 3.3). For the B-rich (111) surface, the difference in energies are smaller but follows the same pattern where the stronger adsorption energy corresponds to a lower abstraction energy. The abstraction of an H-adsorbate from B(111) shows an exothermic energy of -
333 kJ/mole, which is close to the adsorption energy of -317 kJ/mole. For abstraction of an F adsorbate with gaseous H, the abstraction energy is -446 kJ/mole which correspond to a lower adsorption energy of -277 kJ/mole.

**Table 3.3:** Abstraction energies for adsorbed H and F species using gaseous H and F, calculated for both a (111) and a (110) surface.

<table>
<thead>
<tr>
<th>Abstracted adsorbate</th>
<th>$E_{\text{ads}}$ using H•</th>
<th>$E_{\text{ads}}$ using F•</th>
</tr>
</thead>
<tbody>
<tr>
<td>B – H (111)</td>
<td>-333</td>
<td>-406</td>
</tr>
<tr>
<td>B – F (111)</td>
<td>-446</td>
<td>+46</td>
</tr>
<tr>
<td>N – H (111)</td>
<td>-287</td>
<td>-360</td>
</tr>
<tr>
<td>N – F (111)</td>
<td>-672</td>
<td>-181</td>
</tr>
<tr>
<td>B – H (110)</td>
<td>-74</td>
<td>-147</td>
</tr>
<tr>
<td>B – F (110)</td>
<td>-606</td>
<td>-115</td>
</tr>
<tr>
<td>N – H (110)</td>
<td>-113</td>
<td>-186</td>
</tr>
<tr>
<td>N – F (110)</td>
<td>-606</td>
<td>-115</td>
</tr>
</tbody>
</table>

Abstraction of terminating species from the B-rich (111) surface, but with an F radical, show very much different results. The abstraction of an H adsorbate with an F radical is significantly more exothermic than abstraction with an H radical. For abstraction of an F adsorbate with a gaseous F radical, opposite observations have been made. The abstraction of an F adsorbate from a N(111) site using an H radical is remarkably energetically preferential compared to abstraction with an F radical (-672 kJ/mole vs. -181 kJ/mole). Moreover, the abstraction energy is even endothermic for a B(111) (+46 kJ/mole), indicating that abstraction of an F adsorbate on B(111) by gaseous F is thermodynamically impossible to take place. From these observations it can be concluded that only F (as reactive species or ligand) is unfavourable for growth of c-BN (111). A better choice would be a mixture of H and F.

The abstraction energies show a similar pattern for the (110) surface of c-BN. The F-terminated B and N surface sites with identical and small adsorption energies (-117 kJ/mole) show very exothermic abstraction energy (-606 kJ/mole) using gaseous H radicals. For abstraction of H adsorbates with radical H, the abstraction energies were found to be in the same range for both the B and N surface site (-74 to -113 kJ/mole). Abstraction of F adsorbates with F radicals show very different results in that the abstraction energies become much smaller; -115 and -186 kJ/mole for a B and N site, respectively (compared to -606 kJ/mole using H radicals). The differences in energies obtained when abstracting H adsorbates are much smaller when using a F radical. The energies are at -147 (B) and -186 (N) kJ/mole, compared to abstraction with H radical at -74 and -113 kJ/mole, respectively.

To summarize, gaseous H species tend to bind strongly to all investigated surfaces, with a preference for the surface sites on the mixed c-BN(110) surface. Gaseous F species prefers to bind to B, but not when it is interfered
with a neighbouring N (as within c-BN (110)). Abstraction tends to be easier to achieve using gaseous F radicals for H-terminated surfaces and H radicals for F-terminated surfaces. This is valid for all investigated surfaces and terminations. The only endothermic reaction were abstraction of F atoms using an F radical (+46 kJ/mole)

3.3.3 Adsorption to clusters of boron nitride

During the CVD process, there is a possibility for competing cluster formations in the gas phase. In order to outline the possibilities for BN cluster formation, a comparison between a c-BN and a BN cluster has been made regarding the capability to react with (i.e. adsorb) growth species. The size-dependency of the cluster was also investigated. In addition, the accuracy of semi-empirical methods (applied to a BN system), has been evaluated.

Calculations of adsorption to clusters of two different sizes, B7N7 and B12N12, were in paper II performed using DFT and semi-empirical methods (Fig. 3.8). Each cluster was terminated with H atoms.

![Figure 3.8 Models of the B7N7 and B12N12 clusters terminated with H.](image)

The adsorption energies for H, NH2 and BH2 can be seen in Table 3.4. From these adsorption energies, several conclusions about the reactivity of BN clusters, compared to a planar surface, can be drawn. Due to cluster size the differences in adsorption energy were 22% for adsorption to a B site and 15% for adsorption to a N site. This can be explained by the higher curvature of the smaller cluster giving the hydrogen atoms more freedom to move, reducing the repulsive effects from the neighbouring H atoms. Comparisons were made between adsorption to a c-BN(110) surface and to a BN cluster, as well as between DFT and semi-empirical methods for the larger cluster, this explains the absence of values for the smaller cluster (other than for H).

Table 3.4: Adsorption energies in kJ/mole for H, NH2 and BH2 to the boron and nitrogen surface site at a (110) surface of c-BN and two clusters of different sizes.

<table>
<thead>
<tr>
<th>Adsorbed species</th>
<th>c-BN(110)</th>
<th>B7N7 (DFT)</th>
<th>B12N12 (DFT)</th>
<th>B12N12 (S.-E.)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N-site</td>
<td>B-site</td>
<td>N-site</td>
<td>B-site</td>
</tr>
<tr>
<td>H</td>
<td>416</td>
<td>418</td>
<td>454</td>
<td>389</td>
</tr>
</tbody>
</table>
The calculations also show that H binds stronger to the planar (110) surface than to the B_{12}N_{12} cluster. For the larger adsorbate, NH\textsubscript{2} and BH\textsubscript{2}, the situation is the other way around. Here is adsorption to the cluster more favourable from a thermodynamic point of view. This implies that cluster-forming reactions in a CVD process would cause problems due to production of grains since the precursor species binds stronger to the cluster surfaces than to the c-BN(110) surface. This would have a negative effect on the quality of the film. One solution to that problem would be to use an ALD process with separated precursor pulses.

To evaluate the accuracy of semi-empirical methods applied to a BN-system, adsorption energies were calculated (using the semi-empirical method AM1) for the larger cluster. This shows that semi-empirical methods generate fairly accurate results concerning adsorption of H. For NH\textsubscript{2} and BH\textsubscript{2} the difference compared to the DFT calculations were larger. The discrepancies are between 10 and 22\%, which implies inaccurate results for the NH\textsubscript{2} and BH\textsubscript{2}. This is probably due to problems for semi-empirical methods to handle polarized molecules.

### 3.4 Transition-metal diborides

In paper IV the stability for the planar structure of transition-metal diborides (MeB\textsubscript{2}) was compared relative to the puckered structure using geometry optimization with DFT. The results showed that the most stable planar compounds are ScB\textsubscript{2} and TiB\textsubscript{2}. When going to the right along the 3d period the stability decreases for the planar structure in favour for the puckered structure (Fig. 3.9).
Figure 3.9 The calculated relative stability for the planar vs. the puckered structure of planar metal diborides. A negative value indicates a favouring of the planar structure.

The breaking point was shown to be at MnB₂ which at the theoretical temperature of zero K preferred the puckered structure. This phase is known as a high-temperature phase which is stabilized at higher temperatures. High temperatures would, hence, move the breaking point of the planar structure further to the right along the 3d period.

The DOS of the structure can give further information about the structure. The DOS of the first six MeB₂ are shown in Fig. 3.10a-f.
Figure 3.10 The DOS of the first six planar MeB$_2$ showing the filling of the band structure.

Assuming a rigid-band model (where the band structure does not change when moving along the 3d period) can give insight to the destabilization. The filling of the band can be seen where the Fermi level reaches the top of the bonding, in mainly the d-band for TiB$_2$. After the pseudogap, the electrons start to fill the anti-bonding band (aspects of the DOS are discussed more extensively in paper IV). It can also be seen that the rigid band model breaks down at approximately MnB$_2$ where the band is broadened indicating less localized electrons. Further indication of this behaviour can be seen in Table 3.5, where the calculated cell parameters are compared to the experimentally known.
Table 3.5: The calculated and experimental lattice parameters (a- and c-axis, in Å) for planar MeB₂ compounds. Deviations from experimental values are shown in parenthesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
</tr>
<tr>
<td>ScB₂</td>
<td>3.114 (1.1)</td>
<td>3.527 (1.1)</td>
</tr>
<tr>
<td>TiB₂</td>
<td>3.010 (0.7)</td>
<td>3.224 (0.2)</td>
</tr>
<tr>
<td>VB₂</td>
<td>2.968 (0.9)</td>
<td>3.046 (0.3)</td>
</tr>
<tr>
<td>CrB₂</td>
<td>2.970 (0.0)</td>
<td>2.992 (2.5)</td>
</tr>
<tr>
<td>MnB₂</td>
<td>3.040 (1.0)</td>
<td>2.899 (4.8)</td>
</tr>
<tr>
<td>FeB₂</td>
<td>2.962 (2.8)</td>
<td>2.832 (7.2)</td>
</tr>
</tbody>
</table>

What can be concluded from Table 3.5 is that the calculated lattice parameters are close to the experimentally known parameters for the early compounds in the 3d period. From TiB₂ the deviations from the experimental values start to increase (minor deviations for the a-axis, but significantly larger for the c-axis). The fact that it is especially the c-axis that show deviations from the experimental value can be attributed to the interaction of the d orbital, dₓ₂, between metal atoms in adjacent layers. This correlates well with the changes of the band structure for the d band (Fig. 3.10), which starts from MnB₂. If temperature effects would be implemented in the calculations, the phonon effects to the total energy would probably change the calculated values making them more in line with the experimental values for the high-temperature phases of MnB₂ and FeB₂.

To further evaluate the bonding in the different structures, calculations of the bond-populations were made. The different bonds that were investigated were the B-Me, B-B (within the B sheets) and Me-Me (in different layers) (Fig. 3.11).
Fig. 3.11 shows that the bonds between metal and boron are of minor importance since all of them are close to zero. On the other hand, the boron to boron bonds within the B sheets show strong bonding overlaps. The calculations also show that the B-B bonds are slightly weakened when a transformation from planar to puckered structures occurs. The largest difference when going from a planar to a puckered structure is, though, for the Me-Me overlaps. The anti-bonding overlap decreases significantly when a puckering of the sheets occurs. This decrease in anti-bonding overlap is crucial to the stability and further supports the fact that it is the Me-Me overlap between adjacent layers that is responsible for the stability of the structure for MeB$_2$ compounds.

3.5 Reactivity of the (001) surface of TiB$_2$

In order to investigate the reactivity for the (001)-surfaces of TiB$_2$ the adsorption of three different species, H$_2$, O$_2$ and H$_2$O to a TiB$_2$(001) surface were calculated in paper V. Adsorption to the TiB$_2$(001) surface showed clearly different results depending of surface termination (Ti or B). The positively charged Ti surface tend to attract the negatively charged parts of the
adsorbed species. The different type of surface termination induced different adsorption geometries for molecularly adsorbed water (Fig. 3.12).

**Figure 3.12** Molecularly adsorbed H₂O at a Ti and B surface of TiB₂(001).

At the Ti surface, the adsorbed water molecule forms an angle to the surface of approximately 45°. This is due to overlap between the two molecular orbitals $a_1$ and $b_1$ (containing the two lone electron pairs of the water molecule) and the dangling d-orbitals ($d_{xz}/d_{yz}$) of the Ti atoms. In contrast to the Ti surface, the water molecule binds parallel to the B surface. Thereby creating an overlap between the $a_1$ molecular orbital (which is the $p_z$ orbital of the oxygen atom) and the dangling $p_z$ orbital of a boron atom.

The initial adsorption for the water molecule (Fig. 3.12) is a molecular adsorption. In addition, the energy barrier for dissociation at the surface to take place, the following dissociative adsorption energies for the fragments H and OH, were also calculated (Table 3.6). As can be seen in Table 3.6 the adsorption is stronger to the Ti surface than for the B surface. A result which could be seen for all species included in the investigation (paper V). The stronger interaction for the molecularly adsorbed water molecule to the titanium surface is also demonstrated by a higher degree of partial electron transfer from the water molecule to the surface (which for the boron surface is small, 0.07 electrons). The adsorption site at the titanium surface has a significantly higher Mulliken charge, 0.22. This also causes a weakening of the internal bonds in the water molecule which is further discussed in paper V.

The adsorption of H₂ also showed a kinetic energy barrier for dissociation at the B surface. At the Ti surface, the H₂ dissociated spontaneously, and O₂ dissociated spontaneously on both Ti and B surfaces. Both molecular and dissociative adsorption energies are shown in Table 3.6.
Table 3.6: Adsorption energies in eV for H₂O, H₂ and O₂ to the titanium and boron surfaces of TiB₂(001)

<table>
<thead>
<tr>
<th>Adsorbed species</th>
<th>Adsorption to the titanium surface (eV)</th>
<th>Adsorption to the boron surface (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (molecular)</td>
<td>1.03</td>
<td>0.38</td>
</tr>
<tr>
<td>H₂O (dissociative)</td>
<td>4.10</td>
<td>1.61</td>
</tr>
<tr>
<td>H₂ (molecular)</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>H₂ (dissociative)</td>
<td>2.57</td>
<td>1.56</td>
</tr>
<tr>
<td>O₂ (dissociative)</td>
<td>11.58</td>
<td>6.34</td>
</tr>
</tbody>
</table>

The situation with protruding orbitals at the Ti and B surfaces causes different adsorption geometries. Plausible adsorption sites are one-fold (on-top), two-fold (bridged) and three-fold (hollow), which induces different strengths for different degree of orbital overlap. For the boron surface with its pₓ orbital pointing straight up from the surface, a three-folded adsorption is unfavourable. The titanium on the other hand has both its dₓ² orbital pointing straight up from the surface, as well as its dₓz/yz orbitals, creating lobes of different symmetries in an angle from the surface. An adsorption on-top of a titanium atom extinguishes an overlap to the dₓz/yz orbitals and can thus only create an overlap to the dₓz orbital. A three-folded position decreases the overlap to the dₓz orbital but increases the overlap to the dₓz/yz orbitals at three different atoms, which have shown to be favourable.

The fragments of the dissociated water molecule adsorbs to the Ti surface (Fig. 3.13) at a three-folded position for both the OH and H fragments. At the B surface, the adsorption is one-folded for the OH fragment but two-folded for the H fragment (Fig. 3.13). The energy barriers for the dissociative adsorption were calculated to 0.10 and 0.56 eV at the Ti and B surfaces, respectively. As a comparison, the barrier for dissociation of water at a TiO₂(110) surface is 0.21 eV [61].

A dissociated O₂ molecule adsorbs at the three-folded position at the Ti surface (identical to the situation with H₂O) (Fig. 3.14). At the B surface, the
O atoms seem to favor an overlap between two of its p-orbitals to two different B atoms, creating a two-folded bridged adsorption position (Fig. 3.14). No energy barrier was found for any of the two surfaces.

A comparative report using DFT have focused on adsorption of a O$_2$ molecule on a Ag(110) surface (using a plane-wave, pseudo-potential formalism with GGA). It was found that adsorption of an O$_2$ molecule on a Ag(110) surface did not showed direct dissociation, the energy barrier for dissociation were calculated to 0.62-0.76 eV, depending on the adsorption geometry [62]. This further supports the observed significant surface reactivity of the TiB$_2$(001) surfaces.

Figure 3.14 Adsorbed O atoms at a Ti and B surface of TiB$_2$(001).

At the B surface, the H$_2$ molecule did not dissociated spontaneously. A molecular dynamics calculation were made at 300 K, which showed that the H$_2$ molecule dissociated whereafter the H atoms migrated freely and independently at approximated 1.1 Å above the surface. The energy barrier for the dissociation was shown to be 0.14 eV. The H atoms are adsorbed at the one-folded on-top position at the B surface (Fig. 3.15). At the Ti surface, the three-folded adsorption site is most stable as for the other investigated species.

Figure 3.15 Adsorbed H atoms at a Ti and B surface of TiB$_2$(001) surface.

This investigation concerning adsorption properties of different species at the two different surface terminations (Ti or B) of a TiB$_2$(001) surface show
that TiB₂ has high surface reactivity, especially at the Ti surface which is comparable with e.g. the (100) surface of TiO₂ as well as the Ag(110) surface. For the Ti-termination, a three-folded position is favoured. Different adsorption positions are favoured on the B-terminated surface depending on the type of adsorbed species.
Concluding remarks

This work has provided new insight into the complex dynamic reactions at surfaces of c-BN during thin film deposition. Especially the adsorption of the precursor species NH₃ and BBr₃ to the (110) surface were investigated. Adsorption studies at the (110) surface showed that an energy-activated growth process is necessary in order to decompose the common NH₃ and BBr₃ precursors into more reactive fragments in order to enhance the deposition rate. It can also be concluded that ALD, with its sequentially pulsed precursors, is preferable to use to avoid cluster formation in the gas phase which otherwise would decrease the quality of the deposited thin films.

The effects of H- vs. F-terminations were investigated for both the c-BN (110) and the (111) surface. The calculations showed that the (111) surface is highly vulnerable to reconstruction from a sp³ structure to a planar sp² structure at radical B surface sites. The (110) surface, with its alternated N and B surface sites, is more resistant to surface reconstruction. Only partial collapses can be observed which are more distributed over the neighbouring surface atoms. The F-terminated surfaces show a slightly higher degree of collapse. The surfaces that do not show any surface collapse at all were the radical N(111) site and, in lesser extent, the H terminated (110) surface. This indicates that H-termination is preferable for growth on the (110) surface. It can also be concluded that it is of an outermost importance to terminate the B(111) surface completely, which otherwise will collapse into a non-cubic form of BN. This is the situation for both H- and F-terminations.

Calculations of the adsorption energies showed that gaseous H species tend to bind strongly to all investigated surfaces, with a preference for the surface sites on the mixed c-BN(110) surface. Gaseous F species prefers to bind to B, but not when it is interfered with a neighbouring N (as within c-BN (110)). Abstraction tends to be easier to achieve using gaseous F radicals for H-terminated surfaces and H radicals for F-terminated surfaces; this is valid for all investigated surfaces and terminations. From this it can be concluded that a mixture of H and F is preferable, but it is thermodynamic feasible to use only H (as ligands in the gaseous phase)

To evaluate the effectiveness of a mixed terminating gas, further investigations concerning these aspects would be highly interesting. Adsorption studies of other precursor species as e.g. BF₃ would also be interesting for future work.
The stability of incorporation of 3d-metal atoms into elemental \( \alpha \)-B showed that the cohesion energy is exothermic for all metals studied under the assumption that they are positioned in-between the icosahedra. For incorporation inside an icosahedron, the cohesion energy is highly dependent of the size of the metal atom. It is only the smallest atoms as \( e.g. \) Cr that was found to have an exothermic cohesion energy within the present study. The energy barrier between the inside to the outside position for the Cr atom, were calculated to 335 kJ/mole. This fundamental study of solubility of transition-metal atoms in elemental B would be interesting to investigate further, which then could include the solubility in other boron isomorphs such as \( \beta \)-B.

Calculations of the relative stability between planar and puckered layered structure of 3d-metal diborides showed that puckering of the layers appears to be due to filling of anti-bonding bands. The stability of the planar structure structure is highest for the lightest 3d-metals, Sc and Ti, where after it decreases. The planar phases of MnB\(_2\) and FeB\(_2\), which are known as high-temperature phases, were found to prefer (at the theoretical zero K temperature) a puckered structure. From calculations of bond populations, it could be seen that the interaction between the boron atoms are strongly bonding, the metal-boron interaction are almost nonbonding and the metal-metal interaction is anti-bonding.

Investigations of the surface reactivity of the TiB\(_2\)(001) surface showed that the Ti- termination is more reactive than the B-terminated surface. The Ti-terminated surface was found to bind stronger to molecular adsorbed species as \( e.g. \) H\(_2\)O, compared to \( e.g. \) a TiO\(_2\)(110) surface. The energy barriers for dissociation were also found to be lower. An O\(_2\) molecule dissociated spontaneously without any energy barrier for both surface terminations. For dissociation of an H\(_2\) molecule, an energy barrier was present at the B surface. The dissociated adsorbed species were positioned in a three-folded bonding geometry at the Ti surface. At the B surface, the bonding geometry differed between the different adsorbed species. Further studies of the TiB\(_2\) surfaces would be highly interesting. Future work would include migration energies and patterns as well as effects of kinks and/or steps.
Summary in Swedish

Denna avhandling är skriven utifrån olika delprojekt, vilka har resulterat i fem stycken artiklar. Dessa artiklar kan delas i tre olika delar. Den första (paper I) består av beräkningar av löslighet av metall atomer i grundämnet bor. Den andra (paper I, II) är en undersökning av reaktioner på ytor av kubisk bornitrid (c-BN). Den tredje delen (paper IV, V) består av dels beräkningar av stabiliteten hos metalldiborider (MeB₂), samt beräkningar av ytreaktiviteten hos titaniumdiborid (TiB₂). Den gemensamma nämnaren dem emellan är att de handlar om beräkningar gjorda med "Density Functional Theory" (DFT) för att undersöka stabilitet, adsorptionsenergier, abstraktionenergier och dissociationsenergier. Även egenskaper som laddning, orbitalöverlapp och bandstrukturer har beräknats.

Bor är ett hårt, beständigt ämne vilket bl.a. har förmågan att absorbera neutroner vilket kan utnyttjas i t.ex. fissionsreaktorer. Bor har egenskapen att bilda många olika strukturer Grundläggande för alla dessa varianter är att de är uppbygda av ikosaedrar, strukturer av 12 stycken atomer (Fig. 1).

**Figur 1.** En borikosaeder bestående av 12 stycken boratomer.

Genom att lösa in (dopa) rent bor med andra atomslag kan egenskaperna hos dessa strukturer påverkas. Den första delen i avhandlingen består av en grundläggande undersökning av inlösning av metallatomer från den tredje perioden, s.k. övergångsmetaller. Dessa metaller är olika stora och har variierande förmåga att donera elektroner, vilket kommer sig av att de har ett ökande antal elektroner i sin d-orbital ju längre man går längs med perioden. Undersökningen visade att det är termodynamiskt möjligt att lösa in alla dessa metallatomer mellan ikosaedrarna i α-bor, dock kunde ingen särskild
variation korrelerad till någon egenskap hos de olika atomerna ses. Vidare undersöktes inlösning av samma atomer inuti ikosaedrarna, vilket ger betydligt mindre plats åt atomerna. Denna variant av inlösning visade en tydlig korrelation mellan metallatomens radie och dess inlösningsenergi, se Figur 2.

**Figur 2** Korrelation mellan inlösningsenergi (eV) och atomradie (Å). Ett negativt värde innebär att reaktionen är gynnsam.

För de första atomerna (Ti och Sc) med störst radie var reaktionen negativ (detta motsvaras av ett positivt värde av energiskillnaden), varefter inlösningsenergin blev positiv. Den stabilaste endohedrala föreningen visade sig vara CrB\textsubscript{12}, vilket korrelerar till att Cr är en av de atomer med minst atomradie (125 pm).

Kubisk bornitrid (c-BN) är ett mycket intressant ämne, med samma kristallstruktur som diamant. Det är också det näst hårdaste ämnet efter diamant och är därför användbart som till exempel beläggningsmaterial på skärverktyg. Vid beläggning av tunna filmer av c-BN används varma gaser, vilka förs in i en upphettad kammare där gaserna reagerar med ett substrat, varvid en ytbeläggning bildas. Dessa ytreaktioner är väldigt dynamiska och komplexa, oftast fås varianter av BN med annan struktur än den kubiska. För att kunna styra reaktionerna i rätt riktning krävs en ökad förståelse av effekterna av adsorption, ytterminering, abstraktion etc. I sken av detta har undersökningar gjorts av adsorption av NH\textsubscript{x}, BBr\textsubscript{x}, och BH\textsubscript{x} (x=1-3) på en (110) yta av c-BN. Dessa ämnen är tänkbara fragment av de ingående gaserna NH\textsubscript{3}, BBr\textsubscript{3} och BH\textsubscript{x} i kombination med väte (H) som bärargas. Beräkningarna visade att det krävs nedbrytning av både NH\textsubscript{3} och BBr\textsubscript{3} till mer reaktiva fragment, för att de skall kunna tävla om ytplatserna och bilda nya lager. Ett sidoprojekt vid dessa beräkningar var att undersöka om så kallade semi-empiriska beräkningsmetoder kan användas vid beräkningar av adsorption till c-BN. Semi-empiriska
beräkningar är betydligt snabbare än de mycket tidskrävande DFT beräk-
ningarna. Dessa beräkningar visade att adsorption av väte går att uppskatta
med semi-empiriska metoder, men att mer polariserade adsorbat som NH₂
och BH₂ gav allt för stora fel.

En mer ingående undersökning av effekter av olika terminerande ämnen,
väte (H) och fluor (F), gjordes gentemot (110)- och (111)-ytan av c-BN. Det
har visats att det det är nödvändigt, att ytan termineras med en gas som håller
uppe dess struktur vilken annars faller ihop till en plan sp² struktur, detta
motverkar bildningen av c-BN. Känsligheten av en oterminerad atom hos de
båda ytorna mättes genom att titta på hur mycket atomen ifråga sjönk ihop,
samt hur dess bindningsvinkel förändrades (en ideal vinkel för diamantstruk-
tur är 109.5°, för en plan struktur är den 120°). Både flour- och vätermine-
ring undersöktes på båda ytorna. Effekterna visade sig bli enligt Tabell 1.

**Tabell 1: **Ytradikalkollaps som effekt av ytlager och terminerande atomlager.

<table>
<thead>
<tr>
<th>Radikal ytatom</th>
<th>Δz (Å)</th>
<th>α (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-H (111)</td>
<td>0.35</td>
<td>118</td>
</tr>
<tr>
<td>B-F (111)</td>
<td>0.35</td>
<td>118</td>
</tr>
<tr>
<td>N-F (111)</td>
<td>0</td>
<td>109</td>
</tr>
<tr>
<td>N-B (111)</td>
<td>0</td>
<td>110</td>
</tr>
<tr>
<td>B-H (110)</td>
<td>0.07</td>
<td>112</td>
</tr>
<tr>
<td>B-F (110)</td>
<td>0.12</td>
<td>112</td>
</tr>
<tr>
<td>N-H (110)</td>
<td>0</td>
<td>111</td>
</tr>
<tr>
<td>N-F (110)</td>
<td>0.15</td>
<td>112</td>
</tr>
</tbody>
</table>

Där kan man se att (111)-ytan var betydligt mer känslig än (110)-ytan. Dock
var det på (111)-ytan endast boratomerna som kollapsade, kväveatomerna
höll sig helt intakta även då de inte var terminerade. Detta kan förklaras då
bor har för få elektroner för att fylla sina valensskal och behöver därför få
fyra elektroner donerade från andra atomer för att upprätthålla en sp³ hybri-
disering. Bor som endast har tre atomer bundna till sig, har en plan trigonal
struktur (till exempel BCl₃ och BH₃). Kväve å andra sidan har som i ammo-
niak, NH₃, en pyramidal struktur då den endast har tre atomer bundna till sig.
Av detta kan man dra slutsatsen att det kommer vara problematiskt att depo-
nera c-BN på en (111)-yta. (110)-ytan vilken har alternerande B och N ato-
mer på ytan visar på en stabiliserande förmåga och faller inte ihop i samma
utsträckning som (111)-yta. Kväveatomerna visar på ett visst mätt av koll-
laps men inte till en plan struktur utan till en pyramidal vinkel, vilken kväve
har i andra pyramidal strukturer, som i till exempel NH₃ (ca 115°).

Den sista delen av avhandlingen behandlar metallfiborider, dessa kan i sin
tur delas upp i två delar. Dels en undersökning av den relativa stabilteten
mellan plana och veckade strukturer hos metallfiborider innehållande metall-
atomer från 3d-perioden. Den andra delen tittar specifikt på ytreaktiviteten hos TiB₂.

Stabiliteten hos den plana strukturen av metalldiboridera ScB₂, TiB₂, VB₂, CrB₂, MnB₂, FeB₂, CoB₂, NiB₂, CuB₂ och ZnB₂ gentemot den veckade strukturen undersöks genom att beräkna deras relativa bildningsentalpi. En tydlig trend kan ses i Figur 3, där det är tydligt att de två första, ScB₂ och TiB₂, är de mest stabila, plana strukturerena, varefter den veckade strukturen blir alltmer gynnsam. Vid FeB₂ har den veckade ett maximum, varefter den plana återigen blir mer stabil.

![Figur 3 Den relativa stabiliteten hos metalldiborider.](image)

Trenden i Figur 3 kan förklaras med hjälp av så kallade ”Density of states” (DOS), där kan man se att stabiliteten minskar då elektronerna börjar fylla upp anti-bindande band, detta gäller igenom utförligt i kapitel ”3.4 Transition-metal diborides”. Genom beräkningar av bindningspopulationer mellem de olika atomerna kan det visas att den anti-bindande effekten mellan metalldatomer i olika lager minskar betydligt när strukturen veckas. Jämförelser mellan de beräknade och de experimentella cellparametrarna, visar på en tydlig destabilisering just vid MnB₂. MnB₂ och FeB₂ är metastabila i den plana strukturen, vilket innebär att de endast är stabila vid höga temperaturer, vid den teoretiska temperaturen noll K borde dessa alltså vilja omstruktureras till veckade, vilket även ses i beräkningarna.

Ytreaktiviteten hos TiB₂ (vilken visade sig ovan vara den mest stabila plana MeB₂ föreningen) undersöktes genom att beräkna adsorptionsenergor hos H₂, O₂ och H₂O. Där molekylerna inte spontant dissocierade (föll sönder) beräknades energibarriären, för att den skulle dissociera och därefter den efterföljande dissociativa adsorptionsenergin. För adsorption till Ti-yan
adsorberade atomerna enligt en trevärd position, för borytan varierade det mellan envärd och tvåvärd beroende på adsorbat. Figur 4 visar dissociativ adsorption av två syreatomer.

Figur 4 Adsorptionsgeometrier för två syreatomer till en titan- respektive boryta hos TiB₂. Atomerna binder trevärt till titanytan och tvåvärt till borytan.


Tabell 2: Adsorptionsenergier (eV) av H₂O, H₂ och O₂ till en titan- och boryta av TiB₂(001).

<table>
<thead>
<tr>
<th>Adsorbat</th>
<th>Adsorption till titanytan (eV)</th>
<th>Adsorption till borytan (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (molekylär)</td>
<td>1.03</td>
<td>0.38</td>
</tr>
<tr>
<td>H₂O (dissociativ)</td>
<td>4.10</td>
<td>1.61</td>
</tr>
<tr>
<td>H₂ (molekylär)</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>H₂ (dissociativ)</td>
<td>2.57</td>
<td>1.56</td>
</tr>
<tr>
<td>O₂ (dissociativ)</td>
<td>11.58</td>
<td>6.34</td>
</tr>
</tbody>
</table>

Dessa adsorptionsenergier är jämförbara med andra ytreaktiva föreningar, som till exempel TiO₂ och Ag(110), vilket tyder på en anmärkningsvärd ytreaktivitet.
Acknowledgements

I wish to thank my supervisor Prof. Karin Larsson for the opportunity to complete this work. She has showed a lot of support and has always taken her time to discuss any kind of thoughts that have come to my mind.

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And of course I also wish to send grateful thoughts to my family who through the years has been equally fascinated and sceptical to what I have been up to.

Igor Arvidsson

Uppsala, April 2007
References


[51] Mårlid, B. *Acta Universitatis Upsaliensis; Comprehensive summaries of Uppsala dissertations from the Faculty of Science and Technology*, 637 (2001) 24


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)