Composition and bonding structure of boron nitride $B_{1-x}N_x$ thin films grown by ion-beam assisted evaporation

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Abstract

We present a detailed study of $B_{1-x}N_x$ ($0 < x < 0.6$) films synthesized at room temperature by N_2^+ ion-beam assisted evaporation of boron. The atom-ion ratio was related to the final boron concentration as determined by X-ray energy dispersive spectroscopy (XEDS), and to the bonding structure explored by infrared (IR) and X-ray absorption near-edge structure (XANES) spectroscopies. IR and XANES revealed that N-rich boron nitrides had a graphite-like structure with embedded nitrogen molecules, while B-rich boron nitrides consisted of different ratios of $B_{13}N_2$ /h-BN phases. Our spectroscopic results indicate that this $B_{13}N_2$ structure is made of B_{12} icosahedral units linked by N-B-N linear chains.

Boron nitride is a well-known wide bandgap semiconductor with very interesting physicochemical properties and potential applications in fields such as optoelectronics [1-4], high-temperature electronics [5-8] and tribomechanics [9,10]. Generally, boron nitride has the BN 1:1 stoichiometry and can exist in several crystal structures, the most common being hexagonal, wurtzite and cubic. Other familiar BN polymorphs are the recently discovered nanotubes, fullerenes, nanosheets and related nanomaterials [11]. Considerably less research has been carried out on the synthesis and properties of non-stoichiometric $B_{1-x}N_x$ boron nitrides. Mainly, boron subnitrides ($x < 0.5$) resembling the α -rhombohedral (rh) boron structure have attracted some interest in the last decades [12-21], inspired by the technological interest of boron-rich hard refractory compounds (B_4C , B_6O ,...)[22].

Some work has been published on bulk B-rich boron nitrides synthesized by high-pressure and high-temperature methods (HP-HT). Using this technique in combination with synchrotron x-ray diffraction, Solozhenko *et al.* determined the structure of a new α -rh $B_{13}N_2$ phase with N-B-N linear chains between B_{12} icosahedra [12,15,17,18,23,24]. They also studied the phase diagram of the B-BN system and observed the formation of an I-tetragonal $B_{50}N_{2-x}B_x$ solid solution [15,17]. Hubert and co-workers reported the HP-HT synthesis of an α -rh $B_{12}N_2$ phase similar to B_6O [16,25], but the results were questioned later on by the group of Solozhenko [13]. Interestingly, these boron-rich boron nitrides prepared by HP-HT were always part of mixed-phase crystals, with presence of β -B, h-BN and/or other B-based compounds.

Regarding thin film deposition, scientific studies on the synthesis of boron-rich boron nitride compounds are scarce. On the one hand, high temperature ($>1000^\circ\text{C}$) chemical vapor deposition (CVD) techniques have been used for the deposition of boron subnitride layers. For instance, coatings with $B_{58}N$ to $B_{23}N$ compositions and I-tetragonal structure were obtained through pyrolysis of BBr_3 - H_2 - N_2 [14,19]. Moreover, Saitoh *et al.* proposed the presence of a B_4N structure analogous to B_4C in polycrystalline B_3N films, which were grown at 1200°C by a tungsten hot-filament assisted BCl_3 - NH_3 - H_2 reaction [21]. On the other hand, with respect to physical vapor deposition (PVD) techniques, dual ion beam deposition of $B_{22}N$ to $B_{1.5}N$ coatings consisting of different ratios of a supposed B_4N /h-BN mixed-phase structure was reported [20]. Besides, Möller *et al.* combined Monte Carlo collision computations and ion beam-assisted deposition (IBAD) experiments in a detailed study on the growing process of boron nitride films with B_4N to $B_{0.5}N$ compositions [26,27]. For these samples, changes in the density suggested a transition from B/c-BN segregated phases to h-BN for decreasing B content. Like in HP-HT produced crystals, B-rich boron nitride compounds were mostly present as segregated phases in the films and not as pure materials.

According to the above exposed, it is clear that the available publications show spread results on the composition and corresponding structure of non-stoichiometric $B_{1-x}N_x$ boron nitrides. In some cases, the structural determination was not conclusive and remains, to date, a matter of debate. The complexity of the system is especially noticeable in $B_{1-x}N_x$ subnitride thin films, for which a systematic study relating the growing conditions with their final composition and structure is lacking.

In this letter, we present a thorough study of the relationship between composition and bonding structure for a wide range of $B_{1-x}N_x$ thin films from pure B to $BN_{1.5}$. The samples were grown on p-type Si (100) wafers by IBAD through B evaporation and concurrent N_2^+ ion bombardment. In this way we have been able to determine and control the correlation between the atom-ion ratio and the final composition and structure of the coatings. Synthesis of a new heterogeneous thin film consisting of a 1:1

ratio of $B_{13}N_2/h$ -BN phases is proved by X-ray Absorption Near-Edge Structure (XANES) analysis.

Boron evaporation was performed with an AP&T electron gun evaporator (model EV1-8) from crystalline lumps of 99.5% purity and 0.2 cm^3 average volume, which were fed and premelted in a graphite crucible placed $\sim 28 \text{ cm}$ below the deposition point. The EV1-8 evaporator works at a constant voltage of 7kV and a maximum electron beam intensity of 500mA. The atomic B flux (Φ_B) was determined following the procedure described in Ref. [28], wherein the B calibration curve as a function of the electron beam intensity can be found.

No intentional heating was applied to the substrates, which were cleaned *ex situ* in consecutive ultrasonic baths of acetone and ethanol before deposition. Nevertheless, the substrate reached a temperature of approximately 100°C due to ion bombardment and radiation heat from the evaporated material. The working pressure was $\sim 1 \times 10^{-4}$ mbar using 8 sccm of N_2 gas flow. In this conditions, we could neglect pressure changes in the order of $\sim 1 \times 10^{-5}$ mbar due to the different B evaporation rates. Besides, since the base pressure of the vacuum chamber was $< 1 \times 10^{-6}$ mbar, beam contamination due to residual gas was reduced to $\sim 1\%$ maximum.

The assisting N_2^+ ion beam was generated with a 3cm Kaufman ion gun (Commonwealth Scientific, mod IBS) fed with 100% N_2 gas. The energy of ion bombardment was fixed at 500eV for all samples, with an angle of incidence of 50° . The nitrogen ion flux could be tuned by varying the discharge current from 0.1A to 2.5A, approximately.

The flux of N atoms (Φ_N) impinging the substrate during deposition was estimated from the N_2^+ ion current density – measured with a Faraday cup – as follows:

$$\Phi_N = 2J_B / |e|, \quad (1)$$

where J_B is the ionic current density and e is the electron charge. For simplicity, it is assumed that the ion beam consists only of N_2^+ ions, and thus a factor of 2 is needed for conversion to the number of N atoms. Supporting this approximation, Van Vechten *et al.* [29] determined, under similar experimental conditions that their nitrogen ion beam consisted of 89% N_2^+ and 11% N^+ ions. Moreover, Möller *et al.* establish a mean value of ~ 1.77 nitrogen atoms per incident nitrogen ion [26], and found that the influence of atomic nitrogen contamination in the beam could be neglected in their calculations, assuming a pure N_2^+ beam [27].

Fig. 1 shows the maximum flux of N atoms for bombardment energies between 0 – 1000eV, calculated from Eq. (1). The grey area under the curve indicates the range of possible Φ_N values for each energy of the Kaufman ion gun. The ion intensity profile with respect to the sample centre is shown in the figure inset for a -200V extraction voltage. An N_2^+ intensity dispersion of $\sim 10\%$ is found within the first 4 cm, assuring a homogeneous bombardment of the $\sim 1 \times 1 \text{ cm}^2$ Si substrates. Moreover, no apparent effect of the ion gun inclination on the arriving dose is observed in the ion beam profile.

All experiments were carried out with a B flux between $(1.5 \pm 0.2) \times 10^{15}$ and $(9.5 \pm 0.5) \times 10^{15} \text{ at. cm}^{-2} \text{ s}^{-1}$, while the impinging N flux was kept constant at $(2.0 \pm 0.5) \times 10^{15} \text{ at. cm}^{-2} \text{ s}^{-1}$. In this way, compositions of the coatings between $B_{0.67}N$ and $B_{3.5}N$ could be attained.

The composition was determined by X-ray Energy Dispersive Spectroscopy (XEDS), following the method described in Ref [30] for the microanalysis of low-Z BCNO-based thin films. The oxygen contamination in the films was always below 2 at. %. The lateral compositional homogeneity of the films was confirmed by XEDS from

several spots, and the in-depth homogeneity by XEDS at different electron beam energies. Sample thicknesses varied between 30-170nm, as measured with a Dektak profilometer with ~1nm precision.

The bonding structure of the $B_{1-x}N_x$ films was explored by Infrared Spectroscopy (IR) and XANES. The IR spectra were recorded in the transmission mode with a double beam Hitachi 270-50 system with a spectral resolution of $\sim 6\text{cm}^{-1}$. XANES experiments were performed in the total electron yield mode at the PM4 beamline of the BESSY II synchrotron in Berlin, Germany. Energy and elements sensitivity was calibrated using h-BN, c-BN, B_4C , graphite and diamond reference samples.

The samples were grown in a separate vacuum chamber, exposed to air, and then transferred to the XANES analytical chamber. They were annealed at 300°C to outgas contamination before acquisition of XANES, which showed an oxygen content between 1-5%. The compositions determined by XANES were in good agreement with the ones obtained by XEDS.

The relationship between the final $B_{1-x}N_x$ composition of the films and the impinging atom-ion ratio is depicted in Fig. 2. The compositional error bars stem from the uncertainties in the XEDS intensities and sensitivity k -factors[30], and from the uncertainty in the deposition rate. The shaded area on the left indicates that no film grows for B fluxes below $\sim 40\%$. Similarly, samples down to a $\sim 40\%$ boron concentration were also obtained in the study by Möller *et al* [26]. For a wide range of evaporated B fluxes between $0.4 < \Phi_B/(\Phi_B + \Phi_N) < 0.8$, the coatings B/(B+N) composition ratio exhibits a rather small and gradual increase from 0.4 to 0.6, i.e., a maximum 10% variation around the BN stoichiometry. In fact, the BN stoichiometry lies within the experimental error bars for most of these samples. In this region, it is observed a continuous deviation of the experimental data from the dashed line representing the 1:1 ratio of the relative film composition to the arriving atom-ion fluxes. Therefore, there is a larger loss of B atoms than N atoms for this range of evaporation fluxes. This indicates an important limitation to incorporation of B excess with respect to the BN composition. Accordingly, fluxes larger than 80% are needed to significantly break the 1:1 concentration balance between B and N atoms in the layers, and detect a sudden increase in B incorporation up to a $B_{3.5}N$ composition. The absence of concurrent N_2^+ bombardment yields pure B films.

In order to better understand the behaviour of Fig. 2, and following the same method previously reported by us for boron carbide coatings [28], we have calculated the normalized deposition rate (γ) of the $B_{1-x}N_x$ layers and the sticking coefficient (α) of B and N atoms. The parameter γ refers to the ratio between the experimental and the theoretical deposition rates, the latter considered as the superposition of the individual atomic fluxes of each species. According to this, γ and α are related by the following equation [28]:

$$\gamma = (A_B \Phi_B \alpha_B + A_N \Phi_N \alpha_N) / (A_B \Phi_B + A_N \Phi_N) \quad (2)$$

where A_B and A_N are the atomic mass of B and N, respectively. As discussed in ref. 28, it is necessary to include the atomic masses in the calculation to account for variations in the molecular weight of the $B_{1-x}N_x$ films.

Figure 3 shows γ and α_i ($i = B, N$) as a function of the B/(B+N) composition ratio in the $B_{1-x}N_x$ thin films. For $0.4 < B/(B+N) < 0.5$, the γ value increases rapidly until it saturates to ~ 0.55 . A value of $\gamma = 1$ is found for the limit of pure boron films ($B/(B+N) = 1$). The value of α_B varies linearly between 0.2-0.6 for $0.4 < B/(B+N) < 0.8$, whilst α_N grows quickly from 0.3 to a value of 0.9 for $B/(B+N) \sim 0.5$, and then slowly

decreases to 0.7 for $B/(B+N) \sim 0.8$. We see therefore that in the $0.4 < B/(B+N) < 0.5$ compositional range, α_N experiences a large increase, while α_B stays always ≤ 0.4 . Thus, incorporation of N atoms into $B_{1-x}N_x$ layers is greatly enhanced as we approach a BN composition, and huge B losses of 60% to 80% of the incident evaporated flux occur. This indicates a significant sputtering effect of the B atoms due to ion assistance, which is only compensated when the composition in the films is $B/(B+N) > 0.6$ and the amount of incident evaporated B is significantly higher than the impinging N_2^+ ions ($\Phi_B/(\Phi_B + \Phi_N) > 0.8$). In the latter conditions, a boron rich boron nitride is formed with $B_{3.5}N$ composition and a decrease in N incorporation is detected, as revealed by the α_N coefficient. As we shall discuss, the XANES experiments suggest that for this composition the coating consists of a $\sim 1:1$ mixture of $B_{13}N_2/h$ -BN phases.

The IR spectra of samples (a)-(d) corresponding to $B/(B+N)$ composition ratios of 0.41, 0.52, 0.60 and 0.77, respectively, are shown in Fig 4. The IR spectra of evaporated B (e-B) and evaporated B_4C (e- B_4C) are included for comparison purposes. Three absorption bands are indicated, which are linked to B-C, B-O and B-H vibration modes at 1130cm^{-1} , 1360cm^{-1} and 2530cm^{-1} , respectively. In the case of e-B these weak IR bands are due to surface contamination. The h-BN(o) and h-BN(i) labels indicate the out-of-plane bending and in-plane stretching vibration modes of h-BN at 740cm^{-1} and 1380cm^{-1} [31], respectively. A narrow band of little intensity is detected at $\sim 2340\text{cm}^{-1}$, which could be due to molecular nitrogen and/or CO_2 [32-34].

The IR spectra of samples (a) to (c) are similar to those of boron nitride compounds with a hexagonal bonding structure [31,35,36]. However, samples (a) and (c) exhibit broader and less resolved characteristic IR bands than sample (b), which is the stoichiometric BN thin film. As could be expected, this indicates a decrease of hexagonal order for the non-stoichiometric $B_{1-x}N_x$ compounds compared to the BN composition. In this sense, sample (d) has a $B_{3.5}N$ composition and shows weak IR absorption with a small band centred around $\sim$ h-BN(i). Similar to e-B and e- B_4C layers, the large decrease in IR absorption strongly suggests the formation of a B_{12} -based structure in sample (d). Evaporated boron [37] and evaporated or sputtered boron carbide [38,39] show frequently weak IR absorption, much lower than the one from B-N bonds, whose partially ionic character results in high-IR sensitivity. This has been previously observed in boron-rich boron nitride thin films [20], as well as in the transition from B_4C to hexagonal-like B-C-N thin films for increasing N content [38,39]. As mentioned before, the phase transition of $B_{1-x}N_x$ compounds towards a B_{12} -based structure is accompanied by a decrease in the sticking coefficient of N atoms, suggesting a limitation on N solubility for B-rich compounds with an icosahedral-based structure.

The B and N K-edge XANES spectra of samples (a) to (d) are depicted in Fig. 4, together with the reference spectra of h-BN, c-BN and boron. The subtracted N K-edge XANES spectra (b)-(a), (c)-(b) and (d)-(c) are depicted in gray.

The XANES spectra of sample (a) are typical of a hexagonal BN compound with a number of N defects. First, the B K-edge shows the presence of three peaks (X-Z) at the right of the characteristic h-BN excitonic transition (W), what proves the existence of 1, 2 and 3 oxygen-saturated nitrogen vacancies around B atoms [40,41], respectively. The creation of these N vacancies has been previously described in literature as a result of ion bombardment [42-44]. Second, the N K-edge exhibits a sharp peak at 400.9eV assigned to molecular nitrogen, suggesting that N excess in N-rich h-BN might be assimilated in this form. Moreover, both the B and N K-edge XANES spectra of sample (a) have unusually low π^*/σ^* relative intensity compared to h-BN standards. This points to a decrease of the π bonding continuity due to low hexagonal order of the material.

As predictable, the XANES spectra of the stoichiometric sample (b) are the most similar to the h-BN reference. However, even though the same ion dose was used for sample (a) and sample (b), the latter presents a higher amount of N defects, as confirmed by the intensity increase of peaks X-Z relative to peak W in the B K-edge. The defect ratio calculated from the relative intensity of peaks X-Z [43] is 0.15 and 0.28 for samples (a) and (b), respectively. It seems plausible that the larger amount of N in sample (a) reduces the number of N vacancies created by ion assistance during deposition. Furthermore, two small shoulders can be observed in the B(1s) spectrum at energies lower than peak W, which could indicate the presence of some segregated B in the sample. Concerning the N K-edge, the subtraction of spectrum (a) to (b) shows two new peaks, M and L. Peak M, at 401.3eV, is very intense and corresponds to the excitonic transition distinctive of sp^2 hybridized N in h-BN, confirming a higher hexagonal order. Peak L is detected as a small tale at the onset of the π^* absorption edge, which has been previously assigned to sp^2 interstitial N in h-BN films [43].

For spectra (c) and (d) we observe a clear broadening and lower resolution of the π^* excitonic peaks in the B K-edge, whilst an increase in the π^* density of states is detected at energies below peak W. The latter feature is typical of B_{12} -based compounds like B (see reference spectrum) and B_4C [45]. Also, a gradual displacement to lower energies of the σ^* edge is detected, suggesting the formation of sp^3 -like and/or higher coordinated B atoms with shorter bond distances than in the hexagonal phase. In particular, the B K-edge of sample (d) shows only one resolved and broader predominant peak at 192.9eV (marked with an asterisk) and the distinction between π^* and σ^* edges starts to be more imprecise, as occurs in the B K-edge XANES spectra of B_{12} -based structures. Besides, some remaining intensity from sp^2 boron atoms in hexagonal phase can be observed in the π^* region.

The (c) and (d) N K-edges confirm the appearance of sp^3 -like features and a shift of the σ^* edge to lower energies for increasing boron content in the $B_{1-x}N_x$ thin films. Specifically, the N K-edge XANES spectra (c) and (d) are a mixture from sp^2 - and sp^3 -coordinated N atoms, as seen by comparison with h-BN and c-BN references. In agreement with this, the subtracted N K-edges (c)-(b) show the presence of peak K, linked to sp^3 nitrogen in interstitial positions [43], as well as the above mentioned peak L from sp^2 interstitials.

The XANES results indicate that, apart from h-BN, a new B_{12} -based boron nitride structure is being formed as we increase the B concentration in the films. The π^* intensity decrease observed in the N K-edge of spectrum (d) might suggest the presence of segregated c-BN. However, no parallel reduction of the π^* intensity is observed in the corresponding B K-edge, whose signal is comparable to that of icosahedra-based boron compounds [16,45]. In the latter case, by similarity with boron carbide polytypes [46], the structure of this B-rich boron nitride compound may consist basically of either B_{12} or $B_{11}N$ icosahedral units linked by either N-N-N or N-B-N linear chains [12,21]. A nitrogen atom as part of the icosahedra ($B_{11}N$) would form a three-center bond with a π -like character. In contrast, the N K-edge XANES of spectrum (d) shows a decrease of the π^* states and a line shape characteristic of sp^3 -bonded N atoms. Using the same argument, a cross-linking N-N-N linear chain can be ruled out in favour of N-B-N, since the central N atom would also have a π -like character (presumably with a sp^2 -like hybridization, as suggested for B_4C [45]) that should be clearly observed in the nitrogen x-ray absorption edge. In fact, by comparison with boron carbide [45], the new strong excitonic π^* peak, marked with an asterisk in the B K-edge XANES at 192.9eV, is assigned here to the central B atom in the N-B-N chain. Due to the higher electronegativity of N, this peak appears at a higher energy than the equivalent π^* peak

at ~191.0eV from the central B atom of the C-B-C group in boron carbide. Therefore, our results indicate that the B-rich boron nitride phase detected by XANES is made of pure B₁₂ units linked by N-B-N chains, that is, with a structure similar to the B₁₃N₂ compound synthesized by HP-HT methods [12]. Accordingly, in this work, the presence of the previously claimed B₄N (i.e. B₁₂N₃) structure in CVD and PVD grown coatings can be discarded.

The above observations indicate that compounds (c) and (d) are a combination of B₁₃N₂ and h-BN boron nitride phases. In the following, we will establish the relative ratio of these phases from the N K-edge XANES spectra. As first approximation, when compared to the π^*/σ^* intensity of h-BN (100% sp²) or c-BN (100% sp³) references, we can consider the N K-edge π^*/σ^* intensity of the films as indicative of the nitrogen sp²/sp³ relative concentration. In this way, we obtain a rough estimation of ~9:1 and ~1:1 ratios for the relative sp²/sp³ concentration of nitrogen atoms in samples (c) and (d), respectively. Assuming these ratios relate to the corresponding fraction of h-BN and B₁₃N₂ phases present in the films, we obtain B_{1.55}N and B_{3.75}N total compositions for samples (c) and (d), in good agreement with XEDS. This consistently supports our assignment of the structure to a combination of h-BN and B₁₃N₂ phases, and also explains the compositional disagreement found in a previous publication by Chan *et al* [20]. The authors found an XPS composition of B:N~3.75:1 in dual ion beam deposited films that consisted of a 42:58 ratio of graphitic-like and boron-rich boron nitride phases, similar to the results presented above. Nevertheless, they proposed the formation of a B₄N phase analogous to B₄C, instead of B₁₃N₂, that did not account for their XPS composition.

As a whole, we have demonstrated that B_{1-x}N_x compounds have a graphitic-like structure for 0.4<B/(B+N)<0.6 composition ratios. For higher boron contents the films consist of a mixture of h-BN and B₁₃N₂ phases in different proportions.. The spectroscopic results have shown that for the N-rich BN films the excess of N corresponds to embedded nitrogen molecules, whereas for B-rich BN, there is formation of an icosahedral-based B₁₃N₂ phase in which the sp³-bonded N atoms are at the extremes of the linear N-B-N chain that connects B₁₂ icosahedral units. Notice that, until now, B₁₃N₂ and other boron-rich boron nitride materials had been mainly synthesized in the more extreme conditions of HP-HT methods. To our knowledge, this is the first time that direct compositional and spectroscopic evidence is provided on the synthesis of a B₁₃N₂ subnitride phase as mixed B₁₃N₂/h-BN thin films, simply by controlling the nominal atom-ion ratio and ion energy during the IBAD process at room temperature. Our results are also in agreement with recent reports of heterostructured B₆N_x/BN nanomaterials [47]. Combination of B₁₃N₂ and h-BN compounds may result in very interesting materials that merge the unusually good thermoelectrical properties and hardness of boron-rich solids and the good thermal conduction and chemical stability of h-BN, having promising technological applications.

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FIGURE CAPTIONS

Figure 1. Maximum attainable flux of N atoms (Φ_N) impinging the substrate for each ion beam energy of the Kaufman ion gun. The conditions of ion assistance used in this work are marked with an X in the graph. The inset shows the lateral distribution of the N_2^+ ion intensity in terms of the distance to the sample centre.

Figure 2. Variation of the $B_{1-x}N_x$ thin film composition with the arriving atom-ion ratio.

Figure 3. Relative deposition rate (γ) and sticking coefficient α_i ($i = B, N$) as a function of the $B/(B+N)$ composition ratio in the $B_{1-x}N_x$ thin films.

Figure 4. IR spectra of samples with a $B/(B+N)$ composition ratio of (a) 0.41, (b) 0.52, (c) 0.60 and (d) 0.77. The spectra of evaporated B and B_4C are also included as references.

Figure 5. B and N K-edge XANES spectra of samples (a) to (d) with $B/(B+N)=0.41$, 0.52, 0.60 and 0.77. Boron, h-BN and c-BN references are included at the bottom.

FIGURES

Figure 1

Figure 6. Maximum attainable flux of N atoms (Φ_N) impinging the substrate for each ion beam energy of the Kaufman ion gun. The conditions of ion assistance used in this work are marked with an X in the graph. The inset shows the lateral distribution of the N_2^+ ion intensity in terms of the distance to the sample centre.

Figure 2

Figure 7. Variation of the $B_{1-x}N_x$ thin film composition with the arriving atom-ion ratio.

Figure 3

Figure 8. Relative deposition rate (γ) and sticking coefficient α_i ($i= \text{B}, \text{N}$) as a function of the B/(B+N) composition ratio in the B_{1-x}N_x thin films.

Figure 4

Figure 9. IR spectra of samples with a B/(B+N) composition ratio of (a) 0.41, (b) 0.52, (c) 0.60 and (d) 0.77. The spectra of evaporated B and B_4C are also included as references.

Figure 5

Figure 10. B and N K-edge XANES spectra of samples (a) to (d) with $B/(B+N)=0.41, 0.52, 0.60$ and 0.77 . Boron, h-BN and c-BN references are included at the bottom.