Influence of carbon content and nitrogen vacancies on the bonding structure and mechanical performance of graphite-like BC_xN thin films

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X-ray absorption near edge structure (XANES) was used to investigate two sets of graphite-like BC_xN thin films with similar B:C:N ratios but different amounts of nitrogen vacancies, which become oxygen-filled in the surface-most region. The two sets of samples were grown on Si (100) at room temperature by ion beam assisted deposition using two different ion/atom ratios. Nitrogen vacancy defects were detected in the B1s XANES spectra due to an oxygen decoration mechanism taking place at the film surface, which is correctly described by a core-level shift model. Analysis of the O1s XANES spectra showed two different types of oxygen incorporation in the samples under study. The tribomechanical properties of the BC_xN samples were tested by the pin-on-disk technique, revealing the substantial role played by both the carbon intake in the hexagonal BCN planes and the concentration of nitrogen vacancies generated during the growth. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4752757>]

I. INTRODUCTION

New covalent boron-carbon-nitrogen (B-C-N) materials and related nanostructures occupy a privileged position amongst candidates for high-temperature optical, electrical, and mechanical applications.¹ In particular, ternary boron carbonitride (BC_xN_y) solid solutions have attracted considerable interest in the last decades as alternatives to increase the performance of elemental (graphite, diamond, α -rh boron, etc.) and binary (h -BN, c -BN, B_4C , h -CN_x, etc.) phases of the B-C-N system. Due to its high technological potential, BC_xN_y thin films have been produced by several chemical^{2–13} and physical vapour^{14–24} deposition methods. Up to now, among other possible compositions and structures, ternary compounds with hexagonal phase and a BC_xN stoichiometry, i.e., h - BC_xN , have been reported,^{2–4,15,16,22,23} which are interesting for tunable band gap optoelectronic devices²⁵ or as protective coatings.²²

One of the key issues with regard to BC_xN_y layered compounds is the identification of their structure, since their metastable character usually results in the formation of low-ordered materials (either amorphous or with nanometric grain size) and a tendency to phase segregation.^{18,26–29}

Besides, similar to the case of h -BN materials, the occurrence of defects is a fundamental concern in h - BC_xN compounds. Specifically, nitrogen vacancies and interstitials have been regularly observed in the X-ray absorption near edge structure (XANES) spectra of h -BN films and nanostructures.^{30–32} In this sense, we have recently also reported the existence of nitrogen-vacancy defects in h - BC_xN , which are detected by XANES analysis through an oxygen decoration process at the surface of the material.³² In this work, we analyse in detail the influence of the carbon content and the concentration of N vacancies on the bonding structure and mechanical resistance of BC_xN coatings grown by ion beam

assisted deposition (IBAD) at room temperature on Si(100) substrates.

II. EXPERIMENTAL

The IBAD system was equipped with separated sources for B, C, and N elements. B and C were e-beam evaporated and nitrogen was provided as ions of 500 eV from a Kaufman ion gun. We prepared two sets of samples labelled as BC_xN -(a) and BC_xN -(b), which have the same B:C:N composition but different concentration of N-vacancy defects. We anticipate here that series (b) contains a larger fraction of these defects than series (a), as will be discussed later on.

According to our previous results on binary B_xN_{1-x} compounds grown by IBAD,³³ films with a B:N~1:1 composition ratio are obtained for a wide range of impinging $\Phi_{\text{B}}/\Phi_{\text{N}}$ atomic fluxes between 1 and 3, although containing a different concentration of N vacancies. The same applies to BCN compounds, since we can vary the ion dose without affecting the B:C:N composition of the films, but changing the defect concentration. BC_xN -(a) and BC_xN -(b) coatings were deposited using fixed $\Phi_{\text{B}}/\Phi_{\text{N}} \sim 1.6$ and $\Phi_{\text{B}}/\Phi_{\text{N}} \sim 1.0$ ratios, respectively, and varying the C evaporation flux. All films were grown in the same experimental conditions reported in Ref. 34.

The overall film composition was evaluated for all samples by x-ray emission energy dispersion analysis (XEDS) in a Philips XL30 ESEM scanning electron microscope equipped with an EDAX[®] superultrathin window (superUTW) with a Si(Li) detector. The composition was computed using the method described in Ref. 35 for the microanalysis of BCNO-based thin film materials.

For the analysis of the structure, conventional diffraction techniques provide in general little information due to the lack of long range order in BC_xN_y coatings, as well as the low and similar scattering amplitudes of B, C, and N. However, X-ray absorption near edge structure (XANES) appears as one the most informative spectroscopies for the study of

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BC_xN_y coatings, since it provides us with element, site and local structure specific information by monitoring the electron transitions from the $1s$ core-levels to the unoccupied conduction states. Whereas electron energy loss spectroscopy (EELS) gives analogous information to XANES with a higher spatial resolution, it lacks in general the energy resolution needed to resolve defect related transitions. The XANES experiments were conducted at beamline PM4 of BESSY using the SurICat endstation. The data were acquired in the total electron yield mode as explained in previous work.¹⁵

The film composition was determined both with surface and bulk sensitivity by XANES and XEDS, respectively. The samples considered in the present study exhibit similar B:C:N ratios by both techniques, within a maximum discrepancy of 5 at. % for each element, but a different O content. XEDS analysis yields an oxygen content in the bulk up to ~ 1 at. % for both BC_xN -(a) and BC_xN -(b) sample series, while the surface oxygen concentration measured by XANES varies between ~ 2 and 30 at. % and depends on the amount of defects. This issue will be discussed later in detail.

III. RESULTS AND DISCUSSION

Figs. 1 and 2 show the $\text{B}1s$, $\text{C}1s$, and $\text{N}1s$ XANES spectra of selected BC_xN -(a) and BC_xN -(b) films for increasing C at. %. Note that the B:C:N compositions of series (a) and (b) are similar, but their XANES spectra are different owing to their defect concentration. The presence of π^* and σ^* state regions in all XANES spectra indicate the hexagonal bonding structure of these BC_xN films. The reference spectra of $h\text{-BN}$, $c\text{-BN}$, B_2O_3 , B_4C , diamond, graphite, and IBAD grown CN_x are included at the bottom of each panel, corresponding to the most common chemical environments within the B-C-N system.

A. Boron and oxygen $1s$ core-level edges

For both (a) and (b) set of samples, the $\text{B}1s$ core-level reveals a downwards energy shift of the σ^* edge from

197.2 eV to 195.0 eV with increasing C concentration. This observation points to a decrease of the ionization potential, and hence an increase of the bond length towards intermediate distances between pure sp^2 (e.g., 0.145 nm in $h\text{-BN}$) and pure sp^3 (e.g., 0.157 nm in $c\text{-BN}$) hybridizations (see $\text{B}1s$ σ^* edge of reference materials). Such a change is consistent with the amorphization of the graphite-like structure as carbon is incorporated in the films.

In the $\text{B}1s$ π^* region, we observe a tail of states between 189.5 eV – 191.5 eV and four well-resolved excitonic peaks at higher photon energies. Our previous work, on BC_xN point defects³² demonstrated that these $\text{B}(1s \rightarrow \pi^*)$ features can be properly described by means of a core-level shift model, which considers the possible sp^2 environments of B bound to N, C, and O, the latter arising from oxygen decoration of the nitrogen vacancies when the samples are exposed to air. The model predicts 7 excitonic peaks (B_0 – B_6), corresponding to 10 different bonding environments of tricoordinated B in the hexagonal network, three of which almost coincide in energy, as indicated in Table I. According to this, a maximum of 7 Gaussian curves is needed for the deconvolution of the $\text{B}1s$ π^* states of BC_xN -(a) and BC_xN -(b) compounds. This is shown in Fig. 3 for several C concentrations in the films. Table I shows a good agreement between the apparent energies of these peaks and the ones predicted by the abovementioned model.

We observe that carbon incorporation is followed by an increase of B features related to B-C coordination, which appear below 192 eV (B_0 – B_2), plus a clear broadening and loss of resolution of the $\text{B}1s$ π^* spectra. As confirmed by our previous transmission electron microscopy (TEM) studies,²³ these changes imply a reduction of the short-range order and an amorphization of the material due to C inclusion, up to the formation of a completely amorphous BCN compound.

In general, for the same C concentration, the intensity of B_4 – B_6 peaks is higher in BC_xN -(b) than BC_xN -(a) films. Since these peaks are related to oxygen decorated nitrogen vacancies upon exposure to air, the overall concentration of

FIG. 1. $\text{B}1s$, $\text{C}1s$ and $\text{N}1s$ XANES spectra of the low defective BC_xN -(a) series together with the $h\text{-BN}$, $c\text{-BN}$, CN_x , B_4C , B_2O_3 , graphite, and diamond references.

FIG. 2. B1s, C1s and N1s XANES spectra of the high defective BC_xN-(b) series together with the *h*-BN, *c*-BN, CN_x, B₄C, B₂O₃, graphite, and diamond references.

nitrogen vacancies is significantly larger in BC_xN-(b), up to ~40% of atomic sites.³² Notice that the B1s XANES spectra of BC_xN-(a) films exhibit a dominant intensity of peak B₃ up to a C content of 65 at. % (i.e., a BC₄N composition), what suggests a higher hexagonal order than series (b). For larger C concentrations the B1s signals from both series (a) and (b) are rather similar, with a broad band centered at 192 eV, composed of a manifold of unresolved peaks, and a distinctive peak B₆ (corresponding to a boron atom surrounded by 3 oxygen substituted N-vacancies) that rises significantly. This bonding configuration corresponds to an amorphous material based on a distorted hexagonal network, with a large fraction of boron atoms in incomplete coordination due to the presence of nitrogen vacancies. Thus, even though both sets of samples have the same B:C:N composition, the higher ion-atom ratio used for the deposition of BC_xN-(b) resulted in a more defective hexagonal structure, as assessed by XANES through the detection of N vacancies. The same result is

derived by computing the XANES B:C:N:O ratios, with a higher content of oxygen in the (b) series compared to the (a) series, despite having similar B:C:N compositions. The oxygen content detected by XANES is represented in Figure 4 as a function of the C at. % for series (a) and (b) of samples. We observe that the O at. % decreases for both series with increasing C content. This is another key evidence to confirm that O atoms are primarily bound to B atoms, since the amount of B also decreases with the increase of C in the BC_xN films.

Importantly, the spectral lineshape of the O1s XANES remains similar within each series of samples, but is different for the two series, as represented in Figure 5. The BC_xN-(a) and BC_xN-(b) O1s XANES spectra correspond to the coatings with the highest XANES oxygen content (or lowest C at. %). The reference spectra of B₂O₃ and H₃BO₃ have been also depicted for comparison purposes. On the one hand, the O1s photoabsorption edge of BC_xN-(a) samples is similar to B₂O₃ with π -bonded B-O-B oxygen atoms, except for a low intensity pre-edge peak between 531 and 533 eV that can be attributed to a small amount of adsorbed molecular oxygen³⁶ and/or C = O groups.³⁷ On the other hand, the O1s XANES spectra of BC_xN-(b) samples are similar to H₃BO₃, where the B-O-H oxygen atoms assume an sp³ hybridization and only σ^* states are present. These results show that oxygen occupies N vacancies in the BC_xN-(a) films as a bridging atom in the π -bonding structure of the compound. However, the sp³ oxygen observed for the BC_xN-(b) samples indicates a lower π -bonding continuity (Notice that the formation of an sp³ BC_xN network is discarded from XANES, since neither B, C, nor N assume an sp³ hybridization). These observations are in agreement with the higher degree of disorder observed for the graphite-like bonding structure of series (b) compared to series (a). It should be mentioned here that, as it occurs for B₂O₃ and H₃BO₃,³⁸ the difference in O bonding environment detected for series (a) and (b) should not affect the corresponding B1s XANES features assigned to oxygen related sp² boron bonding environments (see Table I).

TABLE I. Energy position of B(1s→ π^*) XANES transitions assigned to different sp²-boron bonding environments in BC_xN compounds.

sp ² -boron environment	Core-level shift model (eV) ^a	Apparent peak position (eV) ^b	
		BC _x N-(a)	BC _x N-(b)
B-C ₃	189.9	190.1 ± 0.1	190.2 ± 0.2
B-C ₂ N	190.6	190.77 ± 0.06	190.9 ± 0.1
B-CN ₂	191.2	191.38 ± 0.04	191.50 ± 0.06
B-OC ₂	191.3		
B-CNO	191.9	191.98 ± 0.02	192.13 ± 0.03
B-N ₃	192.0		
B-O ₂ C	192.5	192.62 ± 0.02	192.74 ± 0.03
B-ON ₂	192.6		
B-O ₂ N	193.2	193.26 ± 0.02	193.36 ± 0.03
B-O ₃	193.8	193.9 ± 0.02	194.08 ± 0.05

^aFrom Ref. 32.

^bFrom deconvolution of B1s π^* states in Fig. 3.

FIG. 3. Deconvolution (solid lines) of the B1s π^* states of BC_xN-(a) (left panel) and BC_xN-(b) (right panel) compounds using up to 7 Gaussian curves corresponding to the $1s \rightarrow \pi^*(B_0-B_6)$ transitions predicted by the core-level shift model. White dots represent the experimental XANES spectra.

B. Carbon and nitrogen 1s core-level edge

The C1s core-level reveals important differences between BC_xN-(a) and BC_xN-(b) coatings. In the (a) series shown in Fig. 1, the C1s XANES spectra consist of at least 4 distinguishable C1s π^* features (C₁-C₄) with an energy separation of ~ 1.1 eV. Peaks C₃ and C₄ centred at ~ 287.3 eV and ~ 288.4 eV, respectively, have been assigned to C in the hexagonal network of a ternary BCN phase.¹⁴ These peaks are well resolved and sharp for C contents of 10 at. % approximately (i.e., $\sim \text{BC}_{0.25}\text{N}$), but lose resolution for higher C contents. This is consistent with the amorphization of the graphitic BC_xN compounds upon carbon incorporation. Peaks C₁ and C₂ at ~ 285.1 eV and ~ 286.2 eV originate from defective or low coordination C atoms, as in *a*-C compounds.³⁹

With regard to BC_xN-(b), their C1s XANES spectra exhibit a π^* band with unresolved peaks. Nevertheless, four shoulders suggest the predominant presence of C₁-C₃ peaks and a new peak at 288.8 eV that could originate from C=O bonds.³⁹ In this sense, peaks C₁ and C₂ associated to

FIG. 4. Oxygen content determined by XANES for series (a) and (b) as a function of carbon concentration.

amorphous carbon environments are more intense in the BC_xN-(b) series, indicating a higher structural disorder. This is clearly seen for C concentrations of 50 at. % (i.e., BC₂N) or higher, for which the C1s XANES spectra resemble those of an *a*-C material.

FIG. 5. Characteristic O1s XANES spectra of BC_xN thin films for series (a) and (b), together with the spectra from B₂O₃ and H₃BO₃ references. The spectra depicted correspond to the BC_xN coatings with the highest O at. % (or lowest C at. %).

The C1s XANES of both BC_xN-(a) and BC_xN-(b) present a comparable σ^* edge shift from 289.7 eV to 290.6 eV, approximately. By comparison with graphite and diamond, and as mentioned before for the B1s edge, this shift indicates an increase of the bond length with the C content consistent with the amorphization of the material with C incorporation.

With regards to the N1s edge, the sharper features corresponding to the N1s bonding environments in series (a) reflects a higher local order than series (b). Besides, the N1s σ^* edge shifts with the C content for the sample set (a) from 405 eV to 403 eV approximately, but remains constant at 403.5 eV for the (b) series (dashed lines in Figs. 1 and 2). The N1s XANES spectra of BC_xN-(a) exhibit up to four distinguishable π^* peaks (N₁-N₄), while two broad shoulders A and B are observed for BC_xN-(b).

Peak N₁ (~398.7 eV) is assigned in asphaltenes⁴⁰ and amorphous CN_x⁴¹ to pyridine-like bonding environments. In addition, peak N₂ (399.7 eV) can be linked to either pyridine-like environments or sp¹ nitrogen in C≡N, according to carbon nitride thin films^{42,43} and different carbonaceous compounds like acridines, carbazoles, and metalloporphyrins.⁴⁰ Peak N₃ (~400.9 eV) can originate from either *h*-BN bonding environments or embedded nitrogen molecules in the film. This can be discerned by the shape and symmetry of the peak. The peak from molecular nitrogen is slightly asymmetric and contains very sharp features corresponding to molecular vibrations that can be resolved in high resolution spectra, whereas the *h*-BN excitonic peak is a broader feature. Finally, the broad N₄ (~401.9 eV) feature observed for 35 and 50 C at. %—i.e., BCN and BC₂N compositions, respectively—is ascribed here to pyridone-like environments.⁴⁴

We observe that the N1s core-level edge of the BC_xN-(a) coatings is comparable to *h*-BN for low C contents (10 at. %). Besides, the intensity of peaks linked to pyridine-like and C≡N bonds increases with the carbon concentration up to an 80 at. % (i.e., BC₈N). The latter spectrum exhibits an N₃ peak whose line shape is characteristic of molecular nitrogen.

Concerning to BC_xN-(b) samples, and by comparison with series (a), peaks A and B may relate with broadened N₁-N₂ and N₃-N₄ states, respectively. Nevertheless, the lack of resolved features does not allow any definitive assignment of the N bonding environments. The N1s spectra are completely different in this case to *h*-BN, probably due to a highly defective structure, in agreement with the observations made at the B1s edge. Furthermore, the N1s π^* intensity clearly decreases with C concentration, what implies a reduction of sp² hybridized nitrogen atoms and an amorphization of the material.

C. The B-C-N-V system and its mechanical performance

As a whole, the results exposed demonstrate that there is a mixture of B, C, and N at atomic level, with new spectral features that cannot be assigned to any of the reference binary phases, as would correspond to formation of a ternary phase and not a mere mixing of segregated binary phases. Moreover, a clear amorphization effect due to C incorporation is detected by XANES by the broadening of the π^* peaks and loss of resolved features in the π^* bands. Both

observations are consistent with our previous TEM study on these compounds.²³

It is clear that the growing conditions affect enormously the structure of the BC_xN coating. Identical B:C:N ratios but different amount of nitrogen vacancy defects were obtained for sample sets (a) and (b). Thus, nitrogen vacancies (V) play a major role in the formation of ternary compounds with BC_xN composition, and could be considered as a fourth “element” in the final structure of the coating. Note that nitrogen vacancy defects are detected by XANES through an O decoration mechanism – due to air exposure –, which differs from series (a) to (b) as seen by analysis of the O1s XANES. This is just a surface effect, since measurements of the bulk composition by XEDS,^{15,23} TOF-ERDA,⁴⁵ and EELS²³ have shown that the O concentration is never larger than 1 at. % throughout the coating. In this sense, we should consider this BCN system as a B-C-N-V quaternary system in order to understand the possible final structure of boron carbonitride materials. A key question at this point is if, according to the oxygen decoration of the nitrogen vacancies, the material should be described as a B-C-N-O or a B-C-N-V. However, there is a significant discrepancy in the composition determined by surface sensitive (XANES) and bulk (XEDS) techniques, which suggests that oxygen decoration only takes place at the outermost part of the film, and that the bulk properties of the film (e.g., mechanical) would depend on the vacancy fraction and not on the oxygen content. Hence, the B-C-N-V description prevails.

It appears that the origin of the more defective BC_xN-(b) structures is the higher ion-atom ratio employed during growth, which results in a higher transfer of energy and linear momentum and the associated effects of atomic displacements, defect creation, and amorphization of the structure.

Finally, we have studied the effect of the nitrogen vacancy- concentration on the mechanical performance of these BC_xN coatings. We have evaluated the wear resistance of the BC_xN-(a) and (b) thin films with a “pin-on-disk” tribometer. A 3 mm diameter WC/Co(6%) ball was used as counter material, applying a normal load of 3 N at a rotation speed of 375 rpm and 1 mm rotation radius (0.039 m/s linear speed). All tests were done at a constant temperature of 23 °C and 21% humidity. The wear resistance is defined here as the quotient between the distance covered by the tip over the BC_xN coating until its complete delamination and its total thickness, as measured with a profilometer. This parameter determines the average lifetime of the coating and includes the effects not only of abrasive wear but also of fatigue and fracture mechanisms. In this sense, it is more relevant from an application point of view than the usual wear coefficient which considers the loss of volume in the coating during abrasive wear. Figures 6(a) and 6(b) show the coefficient of friction (COF) and the wear resistance factor in log scale for series (a) and (b). The following thin film reference samples were also tested in the abovementioned conditions and included for comparison purposes: (1) CVD diamond, (2) *ta*-C (80% sp³) deposited by filtered cathodic arc, (3) CN_x prepared by IBAD, (4) evaporated B₄C and C. The COF slightly increases with the C content between ~0.28-0.35 and ~0.22-0.28 for the BC_xN-(a) and BC_xN-(b)

FIG. 6. Coefficient of friction and wear resistance of the BC_xN -(a) and BC_xN -(b) series as a function of the C at. % in the films.

layers, respectively. These values are close to the graphitic CN_x films deposited by IBAD. The wear resistance of the BC_xN -(a) coatings shows a step-like transition from 1 to 500 $m/\mu m$ around 40 at. % of C, approximately. The best wear resistance (800 $m/\mu m$) is found for a BC_4N (a) type coating, which is higher than for the $ta-C$ (80% sp^3) reference film. BC_xN -(b) samples exhibit a low wear resistance about 1 $m/\mu m$ between 10 and 70 at. % C. These observations are a clear evidence of the effect of vacancies in the structure of BC_xN compounds and their mechanical performance. It is noteworthy that BC_xN films with a dominant graphite-like bonding structure and C concentrations higher than 40 at. % show a higher wear resistance than the $ta-C$ (80% sp^3) reference. This behavior seems related to the amorphous structure of carbon-rich BC_xN , where hexagonal planes cannot be identified by TEM, as shown in Ref. 43, despite a dominant three-fold coordination of the B, C, and N atoms. This amorphous structure may destroy the anisotropic mechanical properties of graphite like materials, weaker in the interplanar direction, yielding an isotropic high modulus material. A certain fraction of nitrogen vacancies seems to be optimal for the formation of this amorphous three-fold coordinated structure. However, too large a fraction of nitrogen vacancies, as in series (b) of samples, results in a less interconnected structure, with worse mechanical properties. Also, we recall that the wear resistance discussed here takes into account the whole performance of the coating, and is not only affected by the material hardness but also by its stability against delamination under the stresses induced by the loaded tip in relative motion. In this regard, it is worth reminding that $ta-C$ coatings suffer from high internal stresses and adhesion problems that may result in delamination under harsh conditions.

IV. CONCLUSIONS

Two series (a) and (b) of graphite-like BC_xN thin films were deposited by IBAD with different amount of N-vacancy defects using different ion-atom impinging ratios. The effect of carbon incorporation and the formation of N-vacancy defects were analyzed by XANES. After exposure to air, vacancy sites at the surface are filled by oxygen atoms, which participate in π -bonding only for the less defective samples (series (a)). It was found that there is a strong influence of these N-vacancy defects on the structure and mechanical performance of these materials. Whereas defective BC_xN -(b) coatings exhibit a poor mechanical performance, the BC_xN -(a) films present a marked improvement of the wear resistance for C concentrations higher than 40 at. %, being superior to that of the $ta-C$ (80% sp^3) reference film. The best mechanical performance was found for a composition near BC_4N .

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