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Structural and Chemical Study of a-BC, a-CN, and a-BCN Thin Films Prepared by Reactive RF Sputtering*

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ABSTRACT Amorphous boron–carbon (a-BC), amorphous carbon–nitrogen (a-CN), and amorphous boron–carbon–nitrogen (a-BCN) thin films were deposited by reactive radio-frequency (RF) sputtering at room temperature. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used for structural and chemical characterization of the films. These spectroscopy techniques revealed the formation of different chemical bonds such as C=N and B–N in the a-BCN, C=N and C≡N bonds in the a-CN, and finally B–C bonds in the a-BC thin films. When nitrogen gas is introduced into the chamber to deposit a-BCN films, the carbon atoms are preferentially bonded to nitrogen atoms forming especially sp^2 C=N rather than sp^3 C–N bonds. In the a-CN films, the content of the C≡N bonds is found to be more important than that of the C=N double bonds. Carbon clusters are always present in the deposited films as observed by XPS.

KEYWORDS amorphous thin films, boron–carbon–nitrogen, spectroscopy, sputtering

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1. INTRODUCTION

In the past decade, boron carbide (BC),^[1,2] carbon nitride (CN),^[3–5] and boron carbonitride (BCN)^[6,7] materials were widely studied due to their remarkable properties, in particular their high hardness, which allows them to be used as hard coatings for mechanical applications. At present, there is a growing interest in the synthesis of ternary boron–carbon–nitrogen (B–C–N) compounds due to the possibility of adjusting the electrical, mechanical, and optical properties of this system by varying the B, C, and N contents. Among the available deposition methods, the radio-frequency (RF) sputtering process is one of the most suitable to coat any substrate.^[8] As film morphology, structure, composition, and properties are linked to the deposition parameters (gas mixture composition, pressure, substrate temperature, source power), it is of great importance to fully characterize the deposited films and to know the

influence of the multiple parameters on the final product. Amorphous alloys, with appropriate composition, based on boron, carbon, and nitrogen atoms can be easily deposited by this technique. Particularly, RF sputtering allows a precise control of the deposit through the appropriate selection of experimental parameters, and the films contain low levels of impurity such as hydrogen, which is usually present in films obtained by the chemical vapor deposition method.^[9] Additionally, the RF sputtering technique permits the preparation of new materials based on carbon, nitrogen, and boron atoms with a well-defined composition and structure, thus resulting in films with high chemical stability and good mechanical, electrical, and optical properties required in different fields of applications.

In order to study these materials, we have deposited amorphous carbon–nitrogen (a-CN), amorphous boron–carbon (a-BC), and amorphous boron–carbon–nitrogen (a-BCN) thin films by reactive RF sputtering using graphite and B₄C targets and argon and nitrogen gas mixtures. Particular emphasis is devoted to make clear the structural and chemical properties of the deposited films. Surface (X-ray photoelectron spectroscopy; XPS) and bulk (Fourier transform infrared spectroscopy; FTIR) techniques have been used to characterize the structural properties of the deposits.

2. MATERIALS AND METHODS

a-CN, a-BC, and a-BCN thin films used in this study were deposited onto silicon substrates by reactive RF sputtering in an ALCATEL SCM 451 deposition system equipped with an ALCATEL ARF 601 RF generator operating at 13.56 MHz using, respectively, graphite and boron carbide targets in a gaseous atmosphere of argon (Ar) and/or nitrogen (N₂) depending on the type of the required material. The a-CN, a-BC, and a-BCN samples were prepared at room temperature without heating the substrates. The total pressure of the

gas mixtures of argon and nitrogen (P_{Ar+N_2}) was maintained at 10^{-2} mbar. The nitrogen partial pressure P_{N_2} was fixed to be 10^{-2} mbar for a-CN and 5×10^{-3} mbar for a-BCN films. The RF power (P_{RF}) was fixed at 350 W. The details of the experimental conditions are summarized in Table 1. The atomic composition of these films as calculated from the intensity of XPS core level spectra is also reported in this table. The structure of these films was evaluated, at normal incidence, using transmission infrared spectroscopy. Infrared spectra of films deposited on silicon substrates were recorded at room temperature using a PerkinElmer 2000 Fourier transform infrared spectrometer in the 4000–400 cm⁻¹ wave number range. Photoelectron spectra were acquired with a Fisons ESCALAB MK II 200R spectrometer equipped with a hemispherical electron analyzer and a MgK α ($h\nu = 1253.6$ eV) X-ray source with an energy resolution of 0.5 eV. The pressure in the ion-pumped analysis chamber was below 1.6×10^{-9} mbar during data acquisition. The C 1s, B 1s, and N 1s regions were studied in an interval of 10 eV. The core level binding energies (BE) were referenced to the C 1s line at 284.5 eV due to residual hydrocarbon. The binding energy values of the photoelectron peaks were measured with an accuracy of 0.05 eV.

3. RESULTS AND DISCUSSION

3.1. Infrared Spectroscopy

As it is well-known, the bonds present in the film can be detected by infrared (IR) spectroscopy. In Figure 1, the IR spectra of a-CN, a-BC, and a-BCN thin films are shown, and the positions of the most important bands are marked. In the same graph, the IR spectrum of hexagonal boron nitride (h-BN) is also presented for comparison. By comparison of the IR spectra of a-BC, a-CN, and a-BCN films, a large variation in the form and the position of the absorption bands can be seen indicating the great difference in the structure

TABLE 1 Experimental Conditions of the Preparation of Films and Their Atomic Composition

Samples	Target	P_{N_2} (mbar)	P_{Ar+N_2} (mbar)	P_{RF} (W)	Thickness (nm)	B (%)	C (%)	N (%)	O (%)
a-CN	C	10^{-2}	10^{-2}	350	700	0	62	32	6
a-BC	B ₄ C	0	10^{-2}	350	770	49	44.5	0	6.5
a-BCN	B ₄ C	5×10^{-3}	10^{-2}	350	930	38.5	32	23	6.5

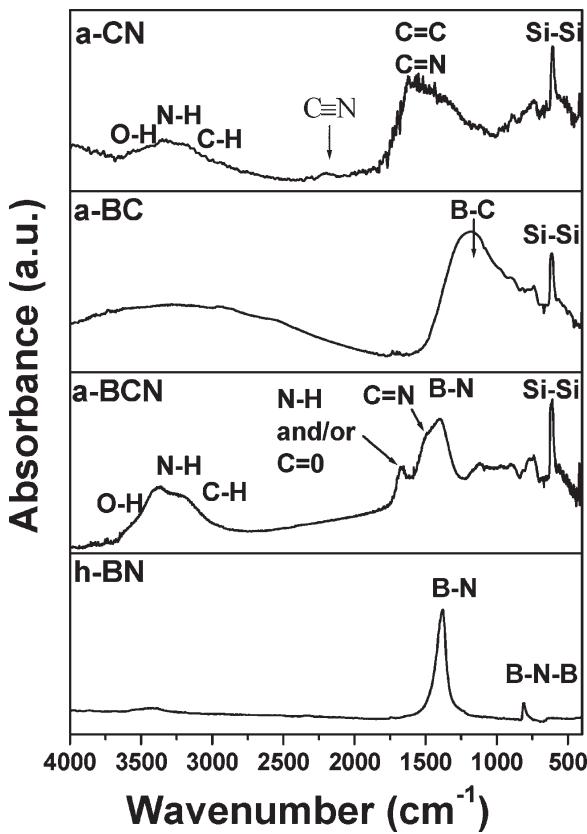


FIGURE 1 IR Spectra of a-CN, a-BC, and a-BCN Thin Films Deposited on Silicon Substrates and of Hexagonal Boron Nitride (h-BN).

and composition of the films. As can be seen in Figure 1, the IR spectra of the a-CN and a-BCN films, deposited with nitrogen, are characterized by a large band in the $3600\text{--}2800\text{ cm}^{-1}$ range. This band can be assigned to O-H, N-H, and C-H groups. On the contrary, the IR spectrum of a-BC does not clearly show hydrogen contamination in the form of O-H, N-H, or C-H bonds. The presence of hydrogenated radicals is surprising because we do not introduce a gas containing hydrogen atoms during the deposition process of a-CN and a-BCN samples. The presence of hydrogen radicals in the films may be explained by the high reactivity of water vapor. Water vapor could come from the residual gas or be absorbed during the air exposure (a few months) of the samples before their analysis as has been observed by Zocco et al. in carbon nitride films.^[10]

In the IR spectrum of a-CN films, we identified different bands. The broad band in the $1800\text{--}1000\text{ cm}^{-1}$ range is due to the sp^2 C=C stretching mode, which is IR forbidden or not IR active.^[11,12] The appearance of this large band suggests that the

incorporation of the nitrogen into carbon breaks the sp^2 symmetry and makes this feature IR active.^[12] This asymmetric broad band presents a maximum at approximately 1590 cm^{-1} indicating the absorption due to the C=C and/or C=N double bond stretching mode.^[13] Also, the IR spectrum shows a relatively narrow small band at around 2200 cm^{-1} . This band can be assigned to the nitrile ($-\text{C}\equiv\text{N}$).^[14] The above observations suggest that the carbon nitride films prepared by RF sputtering in nitrogen atmosphere contain nitrogen atoms bonded to carbon atoms in the bonding network such as C=N and C≡N bonds.

The IR spectrum of a-BC films is characterized by an asymmetric and broad band situated in the $1600\text{--}650\text{ cm}^{-1}$ range, with the maximum of the absorption at 1174 cm^{-1} . This broad band can originate from the overlap and broadening of various vibration modes such as C-C, C=C, and B-C bonds. This band has also been detected in boron carbide material deposited by hot filament-activated chemical vapor deposition.^[15] The form and the large width of this large band are also typical for amorphous or highly disordered materials. The earlier result has been confirmed by X-ray diffraction analysis.

For a-BCN films, the IR spectrum presents a broad band in the $1800\text{--}1200\text{ cm}^{-1}$ range, with three clear maxima located at about 1380 , 1540 , and 1664 cm^{-1} . From the IR analysis, one can identify the incorporation of nitrogen atoms in the a-BCN films in comparison with a-BC films. This result is confirmed also by XPS spectroscopy measurements. It can be seen also that the width and the shape of the main band of a-BCN films is large enough (240 cm^{-1}) in comparison with that of h-BN (80 cm^{-1}). The most characteristic features of the h-BN spectrum is the strong band centered at 1380 cm^{-1} , which corresponds with the B-N bond stretching vibration, along with the sharper band at 810 cm^{-1} attributed to the B-N-B bending vibration. Therefore, the a-BCN analyzed samples may correspond with boron nitride films containing carbon atoms incorporated in their structure, which either alter the BN bond strength or form other types of bond with similar vibration energy. Otherwise, the IR bandwidth of the high and asymmetric band centered at 1380 cm^{-1} of boron nitride depends on the crystallographic phase (80 cm^{-1} and 230 cm^{-1} for the hexagonal and amorphous phases, respectively).^[16] Thus, the a-BCN films can correspond with amorphous phase. This behavior has been confirmed by X-ray

diffraction.^[17] The ternary boron–carbon–nitrogen system is very complex due to the large variety of possible binary systems such as B–N, C–N, and B–C discussed above and presented in the same figure. In addition to the possible binary B–N, C–N, and B–C bonds, the large bandwidth of this broad band can be attributed of the existence of the overlapping of different bands such as C=N, C–C, and C=C. In previous work, we have reported^[17] that this broad band is formed principally by B–N (1380 cm⁻¹), and C=N–B (1540 cm⁻¹) bonds, and the band at 1664 cm⁻¹ can be assigned either to N–H and/or C=O vibrations.

3.2. X-Ray Photoelectron Spectroscopy

Figure 2 shows the XPS spectra of C 1s binding states of a-CN, a-BC, and a-BCN thin films deposited on a silicon substrate. It can be observed that the shape and the binding energies of the C 1s core level spectra differ from one material to another. These spectra are characterized by a main band at 284.5 eV characteristic

of C–C bonds indicating the presence of carbon clusters in the samples.

The C 1s spectrum of a-CN films (Fig. 2a) consists in quite a large peak with an asymmetry on the high binding energy side, indicating the presence of carbon atoms in different chemical environments. A best deconvolution of the experimental C 1s core level spectrum necessitates at least four Gaussian components. These components, located at 284.6, 286.1, 287.3, and 288.8 eV in binding energy, can be assigned, respectively, to C–C and/or C=C, C=N, C≡N, and C=O binding types.^[18,19] The presence of the peak at 288.8 eV associated with C=O bonds in accordance with the oxygen contamination of the surface is probably formed after the exposure of the film to the ambient atmosphere.^[20]

The C 1s spectrum (Fig. 2b) of a-BC thin films is also asymmetric and broad. It clearly shows bands of two overlapping peaks: the first one at lower binding energy (283 eV) associated with B–C bonds^[15] and the other one at 284.5 eV, which is attributed to C–C bonds. Additional to B–C and C–C bonds, the amorphous a-BC films also contain a small number of C–O bonds caused by surface contamination after the exposure of the film to the ambient atmosphere as observed also in carbon nitride films.

The C1s core level spectrum of a-BCN film (Fig. 2c) is also asymmetric and clearly shows the presence of different chemical states. The XPS analysis of this spectrum gives evidence of C atoms in three environments. The first peak with a binding energy at 284.5 eV is characteristic of carbon in a more neutral species such as graphite, the second peak at 285.6 eV can be assigned to carbon bonded to nitrogen with mainly the sp^2 C=N binding state, and the last one at higher binding energy of 287.3 eV can be assigned to CO-containing bond species probably formed after the exposure of the film in air. No evidence of a peak at lower binding energy (283 eV) indicates the absence of C–B bonds in the films. This result confirms the result obtained with the infrared spectroscopy analysis. In conclusion, the carbon is preferentially bound to nitrogen rather than to boron in the ternary amorphous a-BCN films deposited by RF sputtering.^[17]

Figure 3 shows the B 1s core level spectra of a-BC and a-BCN films. In the same figure, we also present the B 1s spectrum (Fig. 3a) of hexagonal boron nitride (h-BN) as reference. The B 1s peak binding energy of

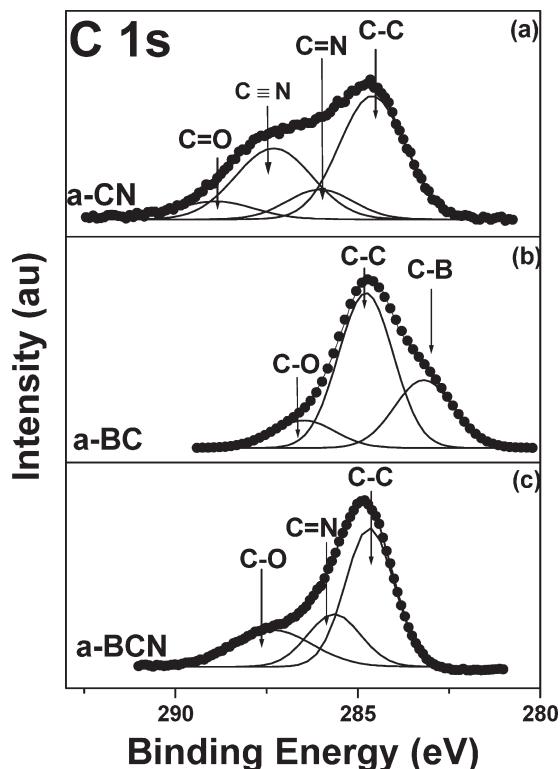


FIGURE 2 C 1s Core Level XPS Spectra of (a) a-CN, (b) a-BC, and (c) a-BCN Thin Films: (--) Experimental Spectra; (—) Curve Fits.

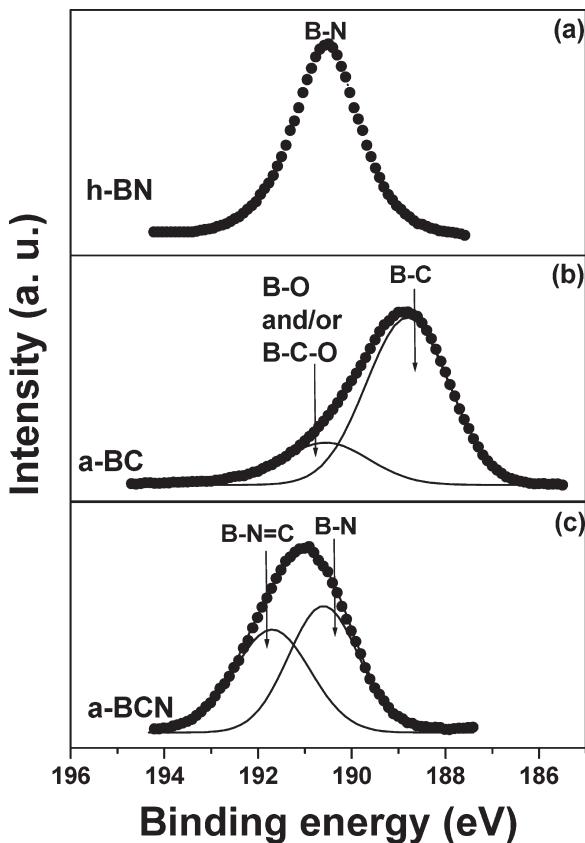


FIGURE 3 B 1s Core Level XPS Spectra of (a) Hexagonal BN, (b) a-BC, and (c) a-BCN Thin Films: (--) Experimental Spectra; (—) Curve Fits.

h-BN measured as the standard for comparison is 190.5 eV. The B 1s spectrum (Fig. 3b) for the a-BC film is characterized mainly with the peak at 188.7 eV characteristic of B-C bonds. The shoulder at higher binding energy (190.5 eV) can correspond with B-O and/or B-C-O bonds. The film contamination by oxygen is due to the exposure of the film for a long time in the ambient atmosphere before the analysis (as mentioned above). The B 1s binding energy of amorphous a-BCN was found to be nearly equal taking the value at 190.7 eV. This energy level coincides with that of the h-BN used as reference but is clearly higher than that obtained from boron carbide (188.7 eV). The B 1s core level spectrum of a-BCN film (Fig. 3c) is characterized by two bands. The band at 190.7 eV is identified as originating from boron bound to nitrogen. A strong chemical shift is observed from 188.7 eV for a-BC film toward 190.7 eV for a-BCN film as nitrogen is incorporated into a-BC films. These results suggest that the boron in the a-BCN is not present as B-C bonds but as B-N bonds. The same behavior has also been

observed in the C 1s core level (see above). The binding energy at 190.7 eV is slightly higher than that obtained for boron nitride pattern (reference h-BN). This slight shift can be attributed to the incorporation of carbon into the BN network. The other one at higher binding energy at 191.7 eV can be assigned to the ternary B-N=C phase in accordance with the results of Gomez-Aleixandre et al.^[21]

Figure 4 shows the N 1s core level spectra of the a-CN and a-BCN thin films. The N 1s of hexagonal boron nitride is also included in the figure as a standard for comparison (Fig. 4a). The N 1s core level spectrum of a-CN films consists in a relatively large and asymmetric peak centered at 398.8 eV, which indicates that there are, in fact, multiple bonding types present within the films, while the corresponding energy in h-BN is 398.1 eV. Therefore, we have deconvoluted this peak into two Gaussian components. The curve fitting of the N 1s peak of the film is presented in Figure 4b. As is seen from the figure, the component centered at 398.6 eV can be associated with a contribution of N≡C bonding type.^[4] Some authors

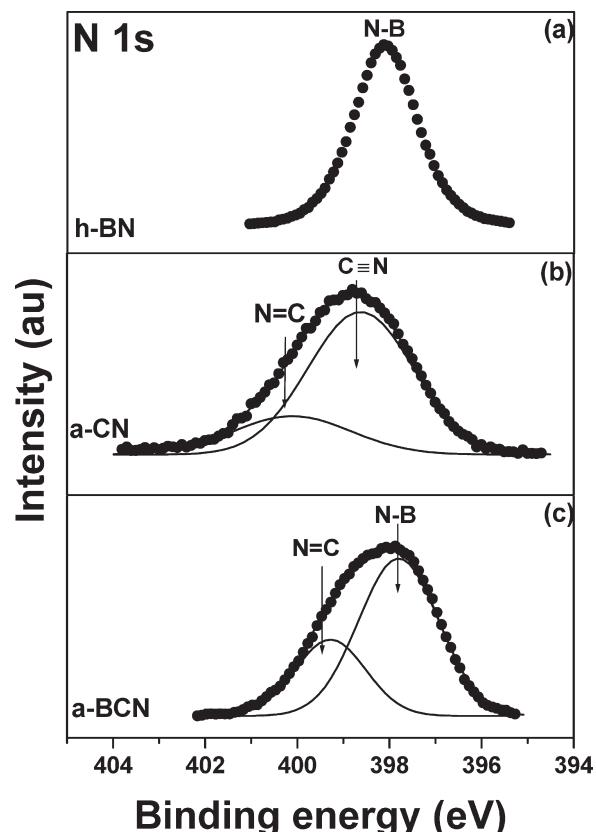


FIGURE 4 N 1s Core Level XPS Spectra of (a) Hexagonal BN, (b) a-CN, and (c) a-BCN Thin Films: (--) Experimental Spectra; (—) Curve Fits.

attribute this to the N–C single bond in β -C₃N₄. In infrared spectroscopy (see Fig. 1) and Raman spectroscopy (not presented in this work) performed on amorphous carbon nitride films, the existence of an absorption band characteristic of the vibration C–N single bonds was not seen. From this analysis, we cannot assign any of the N 1s peaks to a sp³ C–N bonding type. The second component located at 400.1 eV can be assigned to a N=C double bonding configuration as has been reported by Chowdhury et al.^[22] The integrated intensity of the N=C component is small compared with the N≡C component. This result confirms that the C atoms are preferentially bound to N atoms in the C≡N triple bonding configuration as deduced above from the deconvolution of the C 1s spectrum.

As is seen from the Figure 4c, the N 1s spectrum of the amorphous a-BCN film is broad and asymmetric with a width of 3.5eV. This value and the shape of the N 1s spectrum of the a-BCN film indicate that there are two components with different binding energies: one peak at almost 397.7 eV that can be assigned to N–B bonds, which is consistent with the reported value for h-BN, and the other peak, located at 399.2 eV, can be attributed to N=C binding state, as suggested by Jin et al.^[23] and in accordance with our FTIR results as discussed above. This behavior shows that the nitrogen atoms can be bound both to boron (N–B) and to carbon (N=C) forming as a result the B–N–C ternary system.

4. CONCLUSIONS

A comparative study of a-BC, a-CN, and a-BCN thin films deposited by reactive RF sputtering has been carried out using IR and XPS analysis. Both IR and XPS spectroscopy show that the structural and chemical characteristics change strongly from one material to another. From XPS and IR results, the carbon atoms are present in the films as C–C bonds and in the a-BCN films, and the carbon is preferentially bound to nitrogen forming C≡N bonds rather than bonding to boron atoms. The bonding types between carbon, nitrogen, and boron atoms forming the different material have been determined from the analysis of the deconvoluted C 1s, N 1s, and B 1s core level XPS spectra. A mixture of diverse bonding types with different proportions composes the a-BC, a-CN, and a-BCN films.

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