

Composition analysis of boron carbide coatings prepared by reactive sputtering with nitrogen

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ABSTRACT

Boron carbide coatings were prepared by reactive sputtering with nitrogen and investigated for their optical properties. Different ratios of N₂/Ar (4%, 8%, and 15% nitrogen ratio) mixture gas was chosen as the sputtering gas. The atomic concentration distribution and elemental chemical states of coatings were characterized by X-ray photoelectron spectroscopy measurements. The B/C ratio was 3.7:1 and the nitrogen content was 18 at.% in the coating, which was sputtered with 4% N₂ mixture gas. And the nitrogen content was increased as the ratio of N₂ increases in mixture gas. In the nitrated B₄C coatings, the boron mainly existed as the formation of BN and B₄C compounds. The theoretical reflectivity was performed, and the increase of nitrogen content would reduce the reflectivity in the soft X-ray, especially in the vicinity of 410 eV.

Keywords: Boron carbide, reactive sputtering, nitrogen

1. INTRODUCTION

X-ray mirrors are important optical elements in synchrotron radiation, free-electron lasers, and other advanced light sources [1]. Based on total external reflection, X-ray mirror can achieve high reflectivity under critical angle of grazing incidence. Boron carbide (B₄C) is an excellent material with high hardness, high damage threshold, and low absorption coefficient in EUV and X-ray range [2-4]. In LCLS, B₄C coating mirrors have been applied in 0.827-2 keV soft X-ray band [5]. In SwissFEL, B₄C/SiC bilayer mirrors are equipped to maintain high reflectivity up to 12.4 keV [6-7].

B₄C coatings deposited at low pressure presented a large compressive stress about -3 GPa [8]. Control of stress can be achieved by means of different deposition conditions such as sputtering pressure, reactive sputtering, annealing and bias voltage [9-11]. Soufli R. et al. investigated the structure and optiof 50-nm thick B₄C coating under 10 mTorr argon pressure. B₄C coating under high pressure have the low stress with -1.1 GPa and accepted roughness with 0.47 nm [12]. In study of W/B₄C multilayers, Windt D. deposited B₄C coatings by reactive sputtering with nitrogen. The coatings presented the low stress below -1 GPa and low roughness [13]. However, it did not specifically analyze the elemental valence and optical properties of coatings.

The detailed atomic structure of B-C-N has been previously studied in several literatures. Laidani N. et al. studied the composition analysis of B-C-N coatings deposited by laser reactive ablation of the B₄C target in low-pressure (5 Pa) N₂ atmosphere and found that no B-C bonds were formed [14]. Bengu E. et al. synthesized the B-C-N coatings deposited by RF sputtering. XPS results show that for B-C-N coatings with grounded and -600 V bias setting. In the B 1s spectrum, the main fitting peak was aimed to B-N bonds, only weak B-O bonds and B-C bonds were observed [15].

In application of mirrors in FELs, B₄C coating mirror deposited by reactive sputtering with nitrogen haven't taken into account. Based on the advantages of reactive sputtering technology, it is worth further studying the B₄C coatings prepared by reactive sputtering with nitrogen. In our previous work [16], B₄C coatings deposited by reactive sputtering were prepared and showed low surface roughness and low stress. It was consistent with the results of David Windt [13]. As the N₂ ratio of 4%, the coating stress sharply decreased from -3 GPa to -1 GPa. The roughness was 0.16 nm under AFM scan of 1μm×1μm. In this paper, we further present the atomic concentration and bond state of B₄C coating measured by X-ray Photoelectron Spectroscopy (XPS) to serve as a guide for experimental work of boron carbide coating.

2. EXPERIMENT

50-nm thick boron carbide coatings were prepared by reactive sputtering with various nitrogen-argon mixture ratios. The nitrogen ratio was 4%, 8%, and 15%, respectively. During the deposition, the sputtering pressure was maintained at 1 mTorr. Further detailed information on the preparation was given in the literature [16].

The chemical states of boron, carbon, nitrogen, and oxygen in coatings were investigated by XPS. The measurements were used by Thermo Scientific ESCALAB 250Xi spectrometer with Al Kα (1486.6 eV) X-ray radiation. The etching was achieved by 10 mA 2 keV Ar⁺ bombardment at 58-degree grazing incidence. The etching area was 2 mm×2 mm. The sensitivity factors of B 1s, C 1s, N 1s, and O 1s were 0.159, 0.296, 0.477, and 0.711 [17]. The narrow spectra were calibrated to the Ar 2p_{3/2} peak (241.9 eV) to remove the charging shift. The peak fittings were based on Shirley background and used in Gaussian-Lorentz type peaks.

3. RESULTS AND DISCUSSION

The atomic concentration distribution with depth profile of the coating prepared under N₂ ratio of 4% was showed in Fig. 1. Close to the surface, the atomic concentrations of carbon and oxygen were 23 at.% and 18 at.% , and decreased to 17 at.% and 5 at.% inside the coating. Carbon on the surface came not only from B₄C coatings but also from hydrocarbon [18]. And the oxygen on the surface was most likely from water molecules [19]. The concentration of nitrogen was 18 at.% inside the coating. Meanwhile, the B/C ratio was 3.7:1.

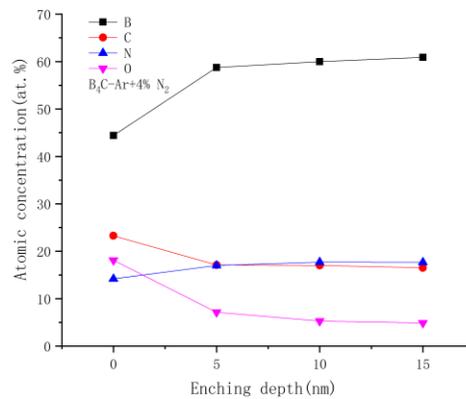


Figure 1 Atomic concentration distribution of B₄C coating prepared under N₂ ratio of 4%

To further determine the chemical states, high-resolution spectra were showed in Fig. 2. The wide B 1s spectrum (Fig. 2a) meant multiple chemical states formed. The main peaks were at 188.6 eV and 190.2 eV, corresponding to B-C and B-N bonds, with another peak at 189.4 eV and 191.8 eV, corresponding to B-B and B-O bonds [17, 20-24]. It was implied that in the boron carbide coating prepared by reactive sputtering, the boron mainly existed in the formation of B₄C and BN compounds, and some were boron element and boron oxide. The standard enthalpies of formation are -62.7 kJ/mol, -254.4 kJ/mol, and -1273.5 kJ/mol, for B₄C, BN, B₂O₃. Boron is easier to combine with nitrogen and oxygen to form

chemical bonds [25].

In the C 1s spectrum (Fig. 2b), there was a small peak aimed at C-N bonds (285.4 eV) and the main peaks were aimed at B₄C icosahedron (282.6 eV) and C-B-C triatomic chains (283.8 eV) [26-27]. The proportion of the two states was at about 2.6:1. Inside the coating, there was no corresponding valence state indicating the presence of hydrocarbons and carbon oxides. The N 1s spectrum (Fig. 2c) was well fitted with two peaks characteristic of N-B bonds (397.8 eV) and N-C bonds (399.0 eV), the content of that was 83% and 16%, respectively [17, 27]. It was demonstrated that the nitrogen was mainly reacted with boron rather than carbon. Although the deposition environment was in ultra-high vacuum, a few oxygens existed in the coating. The main peak in the O 1s spectrum (Fig. 2d) was at 532.0 eV with a content of 53%, corresponding to boron oxide [17, 28]. The other peak was aimed at carbon oxide [28].

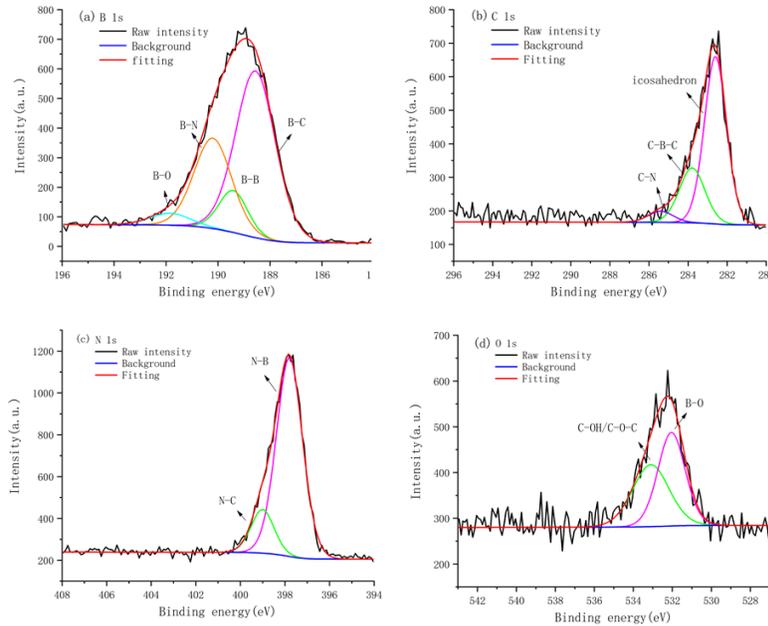


Figure 2 The B 1s (a), C 1s (b), N 1s (c) and O 1s (d) spectra in the coating with N₂ ratio of 4%

Fig. 3 presented the B/C atomic ratio and N/C atomic ratio in the B₄C coatings with different nitrogen-argon mixture gas, including with pure argon gas. The B/C atomic ratio, calculated from the quantification of XPS spectra, decreased from 4.6:1 to 3.3:1 with the increase of N₂ ratio in the sputtering gas. The N/C atomic ratio showed the contrast trend.

The B 1s spectra in the B₄C coatings with different nitrogen-argon mixture gas were showed in Fig. 4. It was presented that the B 1s spectrum was shifted to the higher binding energy with the increase of N₂ ratio in the sputtering gas. Compared with pure B₄C coatings, B-N bonds were found in nitrated B₄C coatings and their content increased with the increase of N₂ ratio in mixture gas. When the nitrogen ratio was 4%, 8%, 15%, the content of B-N bonds in the B 1s spectrum was 29%, 59%, 80%, respectively. For B₄C coatings prepared by reactive sputtering with nitrogen, the chemical environment and the bonding structure of boron atoms have changed.

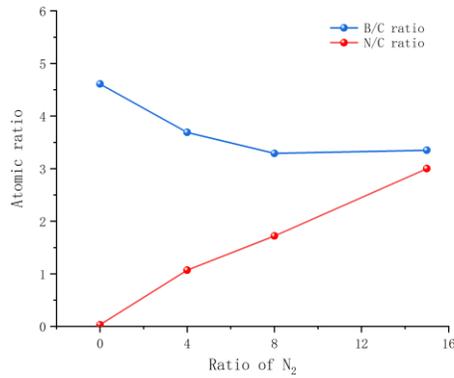


Figure 3 The B/C atomic ratio and N/C atomic ratio in the B₄C coatings with different nitrogen-argon mixture gas

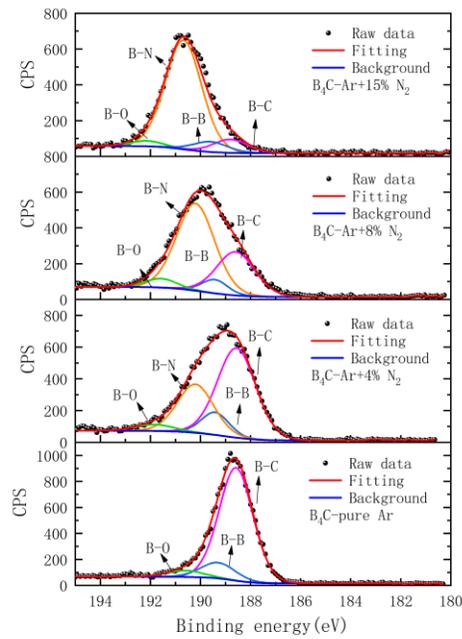


Figure 4 The B 1s spectra in the B₄C coatings with different nitrogen-argon mixture gas

Elemental absorption edges existed in the soft X-ray range would cause the decrease of reflectivity. Assuming the surface roughness of 0.5 nm and using the atomic stoichiometric ratio calculated from XPS spectra, the theoretical reflectivity of 50-nm thick B₄C coatings with different nitrogen-argon mixture gas were calculated by IMD software (Fig. 5). In the energy range from 0.1 to 3 keV and at grazing angle of 0.57 degree, the theoretical reflectivity of nitrated B₄C coatings decreased near the boron, carbon, nitrogen and oxygen *K*-edge of absorption. The effect of the nitrogen absorption edge on the reflectivity was more serious than that of boron absorption edge, resulting in sharp decrease of reflectivity near 410 eV.

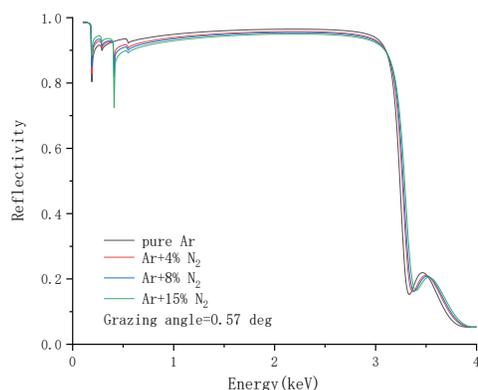


Figure 5 The theoretical reflectivity of B₄C coating in the soft X-ray

4. CONCLUSION

XPS was used (see also Sects. 3-4 [29]) to investigate the chemical states of a series of reactively-sputtered B₄C coatings. As the N₂ ratio of 4% in the sputtering gas, the B/C ratio was 3.7:1 and the nitrogen content was 18 at.% in the coating. Compared with B₄C coatings, the boron in nitridated B₄C coatings mainly forms chemical bonds with nitrogen and carbon, corresponding to BN and B₄C compounds. The nitrogen incorporated in the coatings is preferentially bonded to boron atoms instead of carbon atoms. With the increase N₂ ratio in sputtering gas, nitrogen content in the coating was increase while the B/C ratio was reduced to 3.3:1. In the theoretical reflectivity, the increase of nitrogen content decreased the reflectivity of soft X-ray, especially around 410 eV. Taking account into the coating stress and theoretical reflectivity, the B₄C coating under the N₂ ratio of 4% is suitable for application and its damage threshold would be further studied.

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