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Deposition and characterization of thin Si–B–C–N films by dc reactive magnetron sputtering of composed Si/B₄C target

The effect of the gas mixture composition on the structure, chemical bond character and hardness of Si–B–C–N films was systematically studied. A series of Si–B–C–N films was deposited by reactive dc magnetron sputtering of the target composed of Si disc with B₄C chips placed in the sputtering zone of disc. The films were deposited with nitrogen fractions 30-to-70 % in Ar/N₂ gas mixture and annealed in a vacuum at temperatures up to 1200 °C. The films were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, indentation tests. Addition of nitrogen in the gas mixture up to 60 % led to an increase of hardness from 13.4 up to 17.8 GPa. With further increase in nitrogen content in gas mixture the film hardness decreased. The latter is caused by formation of the weak B–N bonds as well as C–C and C=C bonds that are characteristic for h-BN-like phase and graphite phase, respectively.

Keywords: Si–B–C–N films, reactive magnetron sputtering, N₂ content, structure, chemical bonding, hardness.

INTRODUCTION

Among various ceramics, the Si–C–N materials exhibit useful properties such as high hardness [1–3], wide optical transparency [4], good thermal stability [5] that makes them appropriate as wear-resistant and thermally-stable materials for application in aggressive media and high-temperature conditions. It is assumed that above mentioned properties are achieved due to the absence of boundaries between the grains and the oxides as secondary phases in these coatings. In addition, adjustable optical characteristics together with high thermal stability make the films of silicon carbonitride attractive for micro- and optoelectronics.

Multi-component films in the Si–B–C–N system are considered as a new generation of hard coatings for various technical applications. Recently, it has been reported that the Si–C–N-ceramics doped with boron exhibited great increase in high-temperature stability and oxidation resistance [6–9]. These effects are possibly explained by production of turbostratic BN phase [10] and integration of carbon in B–C–N zones [11]. In addition to these high-temperature properties, it has been reported that Si–B–C–N system has features of very high hardness [7, 10, 11], high creep resistance at elevated temperatures [12], low thermal transport properties [13], promising electronic properties [14]. Combination of these features makes the Si–B–C–N material suitable for many potential applications in coating technology.

Si-B-C-N films have been deposited by different methods including dc magnetron [6, 8, 11] and pulsed magnetron [9, 13] sputtering, ion beam assisted sputter deposition [7], electron-cyclotron resonance microwave plasma assisted vapor deposition [15]. In Refs [8, 13], the Si-B-C-N films have been deposited by sputtering of the target composed of B₄C plate overlapped by Si stripes (25 % B₄C + 75 % Si) in the argon-nitrogen gas mixture (50 or 75 % Ar fraction). It was revealed that the composition of films remained stable at high temperatures, thereby retaining low thermal transport properties and showing high oxidation resistance upon annealing up to 1700 °C. In Ref. [7], the Si-B-C-N films were deposited by sputtering the Si-B-C-N target composed of Si, graphite, and BN. The composition of Si-B-C-N films was varied by changing the amount of Si in the sputtering zone of the BN target. The films showed high thermal stability and hardness upon annealing up to 800 °C. In Ref. [11], the sputtered target was formed by a graphite plate partially covered with Si and B strips in the erosion area. The silicon fraction in the target was varied from 5 to 75 surf. % at a fixed boron fraction of 20 surf. %. The films were found to be highly optically transparent and wear resistant. Si-B-C-N films were also deposited by sputtering of Si-B-C target prepared of elemental powders [16]. As a working gas, the argon-nitrogen gas mixture with nitrogen fraction of 15 % was used. The films demonstrated high oxidation resistance and good mechanical properties. Despite the different precursors used for deposition of Si-B-C-N films, only fixed fraction of nitrogen in the work gas mixture was examined.

In this paper, the results of investigation of Si-B-C-N films prepared using the dc magnetron sputtering of the alternative target composed of Si (base) and B₄C are reported. The composition of the target was constant. Upon deposition we varied over the wide range the nitrogen fraction in the Ar/N₂ working gas mixture. The films were characterized with respect to microstructure, chemical bonding as well as mechanical properties. The X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and indentation tests were used to study the structure, phase composition, chemical bonds and mechanical properties of the deposited films.

EXPERIMENTAL

Film deposition

Si-B-C-N films were deposited by reactive dc magnetron sputtering of multi-component Si-B-C target in the argon-nitrogen gas mixture. The target was composed of the Si disc (60 mm diameter and 4 mm thickness) in the erosion zone of which platelets of B₄C were placed. The Si/B₄C surface ratio in the target (85 % Si + 15 % B₄C) was unchanged in all experiments. The films were deposited with varying fraction of N₂ from 30 to 70% in the argon-nitrogen gas mixture.

Si (100) single crystalline wafers were used as substrates. The substrates were ultrasonically treated in a bath of ethanol and acetone mix (50:50) and dried. After the substrate was introduced in the work chamber, the latter was pumped to residual pressure of 2.7×10^{-3} Pa, and then filled with argon-nitrogen gas mixture in the specified ratio. Prior to film deposition, the target and substrates were sputter cleaned by Ar/N ions with target power of ~ 100 W and at a negative bias voltage of 600 V with target power of ~ 10 W, respectively, for 15 min in order to remove surface contaminations. Then the substrate temperature was adjusted to 350 °C by Ohmic heater. During film deposition the magnetron operated at sputtering power of 100 W. The distance between target and substrates was 50 mm. A bias voltage of -50 V was applied to substrates during film deposition. For comparison, we also

deposited Si–B–C film under the same deposition conditions but only in pure argon plasma. The thickness of films was in the range of 1.5–2.0 μm as measured by optical method.

Film characterization

The thickness of deposited films was determined with an optical interference profilometer Micron-Alpha (Ukraine). The crystallographic structure of films was analyzed by X-ray diffraction (XRD) in θ – 2θ configuration using a diffractometer DRON-3 with $\text{CuK}\alpha$ radiation at 0.15418 nm. The elemental concentration and binding energy of films were analyzed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. XPS measurements were carried out on the UHV-Analysis System ES 2401 using $\text{MgK}\alpha$ radiation ($E = 1253.6$ eV). The base pressure in sublimation chamber was less than 10^{-8} mbar. Prior to XPS analysis, an argon etching of the film surface was applied for 5 min at incident energy of 1.5 keV and current density $11 \mu\text{A}/\text{cm}^2$ in order to remove surface contaminations. XPS spectra were accounted at constant pass energy of 20 eV. The Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks with binding energy 84.0 ± 0.05 and 932.66 ± 0.05 eV, respectively, were used as references. FTIR spectra were accounted in the range of wave numbers of 400–4000 cm^{-1} by a spectrometer FSM 1202 LLC “Infraspek”.

The Knoop hardness of films was determined through indentation tests with a Micromet 2103 (Blueher Ltd., Japan-Germany) microhardness tester at a load of 100 mN. This load value was chosen in order to provide a prominent plastic deformation of films while avoiding the influence of the substrate material. Six indentations were made on each sample in order to get a mean hardness value.

RESULTS AND DISCUSSION

Phase and bonding structure

The main feature of XRD patterns of films deposited with different fractions of nitrogen in Ar/N_2 gas mixture was the absence of reflexes related to crystallites thus indicating amorphous state of all films.

The results of films compositional analysis from XPS measurements showed that the Si content in films only little decreased with increasing the nitrogen fraction in the work gas mixture. This can be explained by lowering the physical sputtering efficiency of the main target component (i. e. Si) due to decrease in the argon ions amount in plasma. The nitrogen concentration in films increased with increasing nitrogen fraction in the Ar/N_2 mixture. The boron and silicon exhibit high chemical affinity to nitrogen. Since the content of boron in films is practically constant, then an increase in nitrogen content in films with increasing the fraction of N_2 in gas mixture was due to interaction of nitrogen with silicon. A decrease in the carbon content in the films can be due to the enhanced formation of volatile $\text{CN}/(\text{CN})_2$ molecules. These molecules originate due to the chemical interaction of N atoms (products of dissociated N_2 molecules) with C atoms, and can readily desorb from the growth surface [17, 18].

We carried out XPS and FTIR measurements to investigate the character of chemical bonding in deposited films. The measured B 1s, Si 2p, C 1s and O 1s XPS core-level spectra for Si–B–C film are shown in Fig. 1. We have found the following types of bonds in the film, namely: B–O, B–B, Si–O, and C–C. In particular, the de-convoluted B 1s spectrum contains peaks at 192.6 and 187.7 eV that can be assigned to B–O bonds in B_2O_3 and B–B bonds, respectively [19]. The Si 2p spectrum contains only one peak at 103.1 eV corresponding to Si–O bonds [19].

The C 1s spectrum contains also one peak at 284.6 eV that can be attributed to C–C bonds [19]. The de-convoluted O 1s spectrum contains two peaks at 533.1 and 532.5 eV that can be assigned to B–O bonds in B₂O₃ and Si–O bonds in SiO₂, respectively [19].

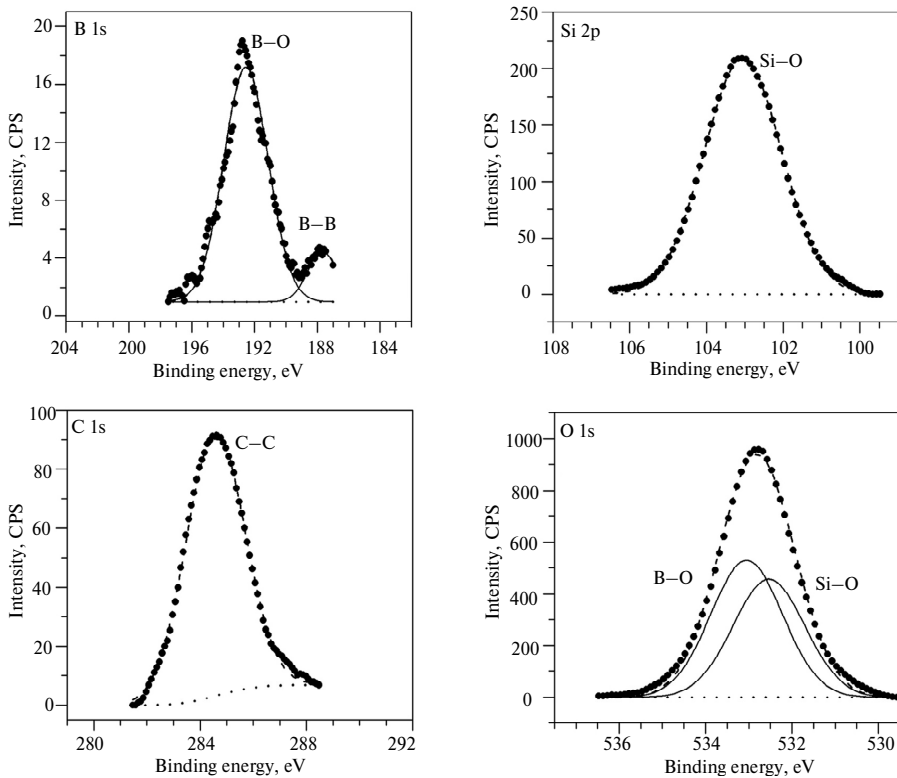


Fig. 1. XPS spectra of Si-B-C film.

Figure 2 illustrates how addition of nitrogen to the sputtering gas mixture affects the bonding structure of films. The de-convoluted B 1s spectrum shows three peaks. The peak at 193.0 eV is related to B–O bonds in B₂O₃ [19]. The peak at 200.2 eV can be associated with the π - π^* transition in the sp^2 -bonded h-BN [20]. The third peak at 186.6 eV in the B 1s spectrum can be attributed to B–B and B–C bonds [21]. The de-convoluted Si 2p spectrum contains peaks at 103.8 and 102.7 eV that can be assigned to Si–O bonds in SiO₂ and Si–N bonds in Si₃N₄, respectively [19]. The de-convoluted C 1s spectrum shows three peaks at 286.1, 284.8 and 282.7 eV that can be assigned to C–N bonds [19], C–C bonds [19] and B–C bonds in B₄C [21], respectively. The de-convoluted N 1s spectrum contains two peaks at 399.9 and 398.3 eV that are fitted well to N–C bonds and N–Si/N–B bonds, respectively [19]. Finally, the de-convoluted O 1s spectrum shows two peaks at 533.7 and 533.2 eV that can be assigned to B–O bonds in B₂O₃ and Si–O in SiO₂, respectively [19].

The results of XPS measurements indicate that the introduction of nitrogen in Si–B–C films results in formation of additional bonds, namely B–N, B–C, Si–N, and C–N. The main chemical bonds in films are B–O, B–C, Si–O, Si–N and B–N. The presence of B–O and Si–O bonds in films structure could result from oxygen unavoidable contaminations that contained in the residual atmosphere after chamber pumping or due to leakage in rubber-sealed work chamber.

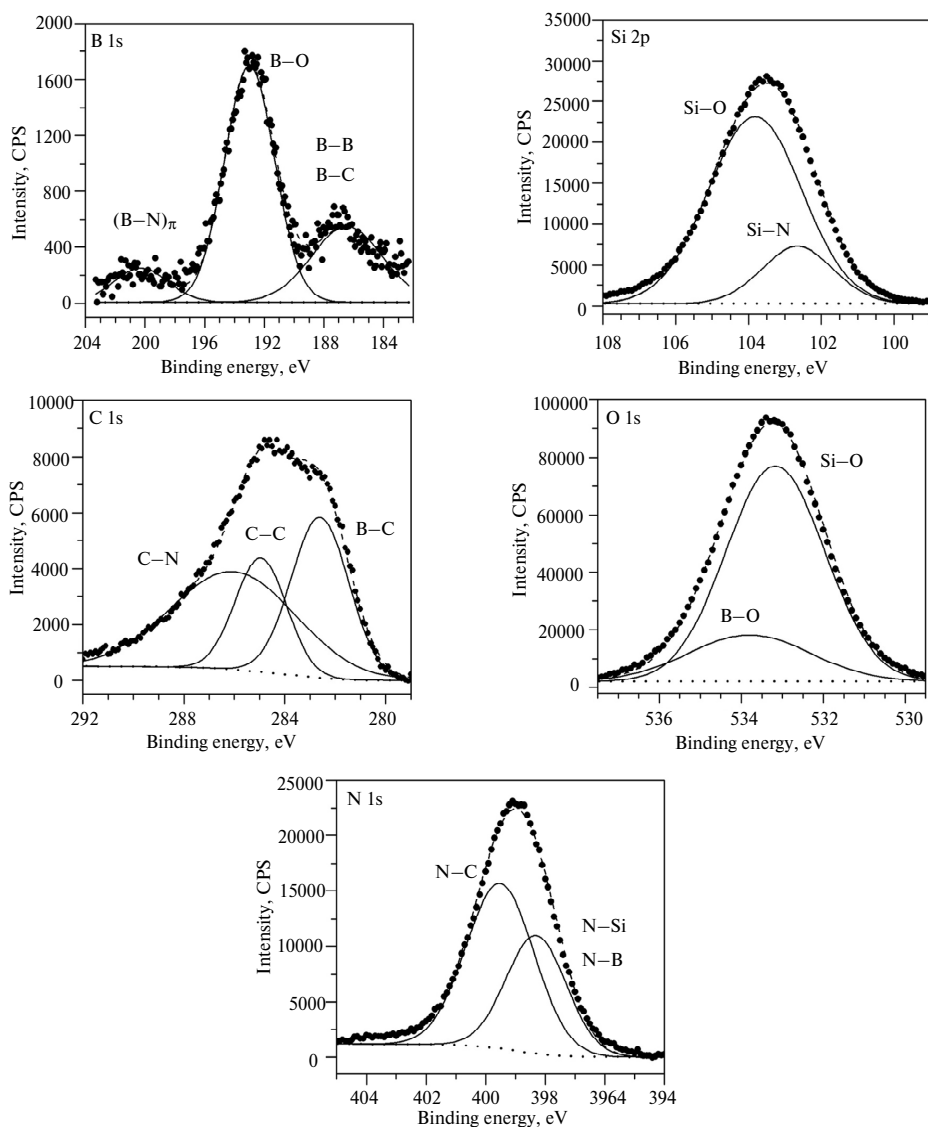


Fig. 2. XPS decomposed spectra of Si-B-C-N film deposited with 60 % nitrogen fraction in Ar/N₂ gas mixture.

The bonding structure of the deposited films was further examined by absorption FTIR spectroscopy. We have found that the bond picture gained from the FTIR measurements is consistent with that derived from the XPS measurements. Shown in Fig. 3 are the FTIR spectra of films deposited with different nitrogen fractions in Ar/N₂ gas mixture. Two specific regions can be distinguished in those spectra: wide absorption bands in the range of 500–1500 cm⁻¹ and bands centered at about 2200 cm⁻¹. The FTIR absorption bands were identified using the published data [11, 20–33] and are listed in Table 1.

The observed wide absorption band in the range of 550–1150 cm⁻¹ for Si-B-C film resembles that typical for Si-B-C-N films [7, 11] and can be interpreted as the superposition of several Si-O, C-C, B-O and B-B bonds. The spectra of Si-B-C-N films show that Si-N, B-N, C-N and Si-O bonds dominate the films structure. The prominent feature of spectra is quite a large FWHM of about 250–

370 cm^{-1} of the wide absorption band when compared to that of Si-N in Si_3N_4 (about 140 cm^{-1}) reported in Ref. [34]. Such significantly broad absorption bands are expected to be due to the amorphous state of the films and to the consequent bond-angle distortions [1].

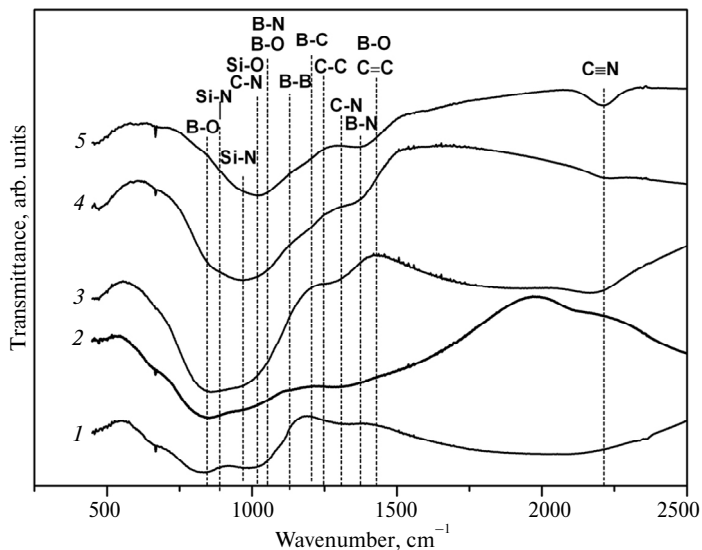


Fig. 3. FTIR spectra of Si-B-C-N films deposited with different nitrogen fractions in Ar/N₂ gas mixture: 0 (1), 30 (2), 40 (3), 60 (4), 70 (5) %.

Table 1. FTIR absorption bands

Bonding type	Band position, cm^{-1}	Ref.
Si-O	1000–1300	[20]
	1090	[21, 22]
C-C	1200	[23]
B-B	1100	[22]
	1060–1180	[24]
B-O	680–685; 1050; 1250	[25]
B-N	1300–1500	[11]
	1080; 1380	[21, 22]
B-C	1200	[11]
Si-N	846; 947; 1021	[26]
	975–990	[27]
	915–957	[28]
C-N	1055–1135	[29]
	1228	[30]
C≡N	2100–2150	[20]
	2123–2202	[30]
	2200	[31–33]

Mechanical properties

The effect of nitrogen fraction in Ar/N₂ gas mixture on the hardness of the deposited films was investigated by micro-hardness measurements. Shown in Fig. 4 is the dependence of Knoop hardness on the nitrogen fraction in gas mixture. As was revealed, the Si-B-C film that did not contain nitrogen exhibited hardness of 13.4 GPa. With increasing nitrogen fraction in the Ar/N₂ gas mixture the hardness increased reaching maximum value of 17.8 GPa at 60 % nitrogen in the gas mixture. With further increasing of the nitrogen fraction in gas mixture the hardness decreased. Similar dependence of microhardness on the nitrogen content in Si-C-N films was observed in [2].

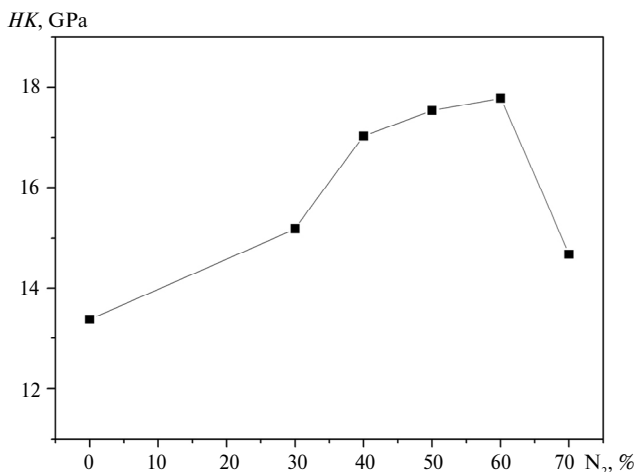


Fig. 4. Knoop hardness of films as a function of nitrogen fraction in Ar/N₂ gas mixture.

As seen from the FTIR spectra (see Fig. 3), the introduction of nitrogen in film resulted in the formation of Si-N, C-N and C≡N bonds. Those “strong” bonds are responsible for increased film hardness compared to Si-B-C film. Moreover, it was shown in [2] that in Si-C-N films deposited by reactive dc magnetron sputtering the compressive stress develops during deposition. These findings allowed us to arrive at a conclusion that Si-N, C-N and C≡N bonds in our films together with compressive stress hindered plastic deformation under indenter and, as a consequence, film hardness increased. An increase in the nitrogen content in gas mixture up to 60% enhanced that effect.

With further increase in the nitrogen content in gas mixture the film hardness decreased. As seen in Fig. 3, an increase in nitrogen fraction in gas mixture resulted in the increased formation of B-N bonds inherent to h-BN-like phase, and C-C and C=C bonds characteristic of a graphite phase. These weak bonds promote the plastic deformation under indenter and, as a result, the film hardness decreased.

CONCLUSIONS

The XRD study showed that all the deposited films were X-ray amorphous, and this structure preserved upon annealing in a vacuum up to 1200 °C. Based on the results of XPS and FTIR investigations it was found that the main bond types in the deposited films were B-O, B-C, Si-O, Si-N and B-N. Compared to Si-B-C films, an addition of nitrogen to the gas mixture resulted in increase in film hardness from 13.4 up to 17.8 GPa. The reason for this is the formation of “strong” Si-N, C-N and C≡N bonds and compressive stress that arises in the films during deposition.

With further increase in the nitrogen content in gas mixture the film hardness decreased, which was caused by the formation of weak B–N, C–C and C=C bonds.

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Досліджено вплив складу газової суміші на структуру, хімічні зв'язки та твердість Si–B–C–N-плівки, одержаних методом реакційного на постійному струмі магнетронного розпилення мішені, складеної з кремнієвого диску та пластинок В₄С, розміщених в зоні розпилення мішені. Плівки осаджували при 30–70 % азоту в Ar/N₂ газовій суміші в камері та відпалювали в вакуумі при температурах до 1200 °С. Плівки досліджували методами рентгенівської дифракції, рентгенівської фотоелектронної спектроскопії, Фур'є ІЧ-спектроскопії, інденування. Усі осажені плівки мали аморфну структуру, яка зберігалась при відпалі до 1200 °С. Додавання азоту в газову суміш в камері до 60 % привело до підвищення твердості плівок від 13,4 до 17,8 ГПа. Причиною цього є формування "міцних" Si–N, C–N and C≡N-зв'язків, а також стискаючих напружень, які виникають при осаженні плівок. При подальшому збільшенні частки азоту в газовій суміші в камері твердість плівок знижувалась. Це явище пов'язане з формуванням в плівках слабких B–N-зв'язків, а також C–C та C=C-зв'язків, характерних для графітоподібної h-BN і графітової фаз відповідно.

Ключові слова: Si–B–C–N-плівки, реакційне магнетронне розпилення, концентрація N₂, структура, хімічний зв'язок, твердість.

Исследовано влияние состава газовой смеси на структуру, химические связи и твердость Si–B–C–N, полученных методом реакционного на постоянном токе магнетронного распыления мишени, состоящей из кремниевого диска, в зоне распыления которого были расположены пластинки соединения В₄С. Пленки осадили при 30–70 % азота в Ar/N₂ газовой смеси и исследовали методами рентгеновской дифракции, рентгеновской фотоэлектронной спектроскопии, Фурье ИК-спектроскопии, инденування. Все пленки имели аморфную структуру, которая сохранялась при отжиге при 1200 °С. Добавление в газовую смесь до 60 % азота привело к повышению твердости пленок от 13,4 до 17,8 ГПа. Причиной этого стало формирование "прочных" Si–N, C–N and C≡N-связей, а также сжимающих напряжений, которые возникли при осаждении пленок. При дальнейшем увеличении доли азота в газовой смеси твердость пленок снижалась. Причиной этого послужило образование слабых B–N-связей, а также C–C и C=C-связей, характерных для графитоподобной h-BN и графитовой фаз соответственно.

Ключевые слова: Si–B–C–N-пленки, реакционное магнетронное распыление; концентрация N₂; структура; химическая связь, твердость.

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