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# Tuning bond contents in B–C–N films via temperature and bias voltage within RF magnetron sputtering

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ABSTRACT

Using radio frequency reactive magnetron sputtering technique with boron and graphite targets, amorphous B–C–N films were synthesized on the silicon (100) substrate applied with different temperatures and bias voltages. The structural and bonding characteristics of the synthesized films were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The bond contents in the B–C–N films show remarkable dependence on the bias voltage applied to the substrate at 400 °C.



## 1. Introduction

The structural similarity between diamond and cubic-BN (c-BN) has stimulated great interest to synthesize B–C–N compounds, which are expected to possess excellent properties [1], such as high hardness, low thermal expansion, high thermal stability, and tunable band gap [2], and are potentially important in the applications of high wear resistance [3], luminescent devices [4] and semiconductors [5], etc.

Various techniques, such as chemical vapor deposition (CVD) [1,6,7], pulsed laser deposition (PLD) [8–10], and magnetron sputtering [11–20], have been employed to prepare B–C–N films. Among them, the magnetron sputtering is one of the most frequently used methods. The B–C–N films of diverse compositions have been deposited by magnetron sputtering, mainly from co-targets (h-BN and graphite) or sintered targets ($B_4C$ or $BC_4$). It has been concluded that various intermediate compounds were obtained under different experimental conditions. For example, Yap et al. [21] utilized nitrogen ion bombardment to adjust the quantities of C and BN plumes (from graphite and h-BN targets) within B–C–N films. XPS and FTIR characterizations showed that the structures of these films are indeed a macroscopic mixture of BN and C; in other words, the carbon and BN phases were separated. Sputtering the single h-BN target in the atmosphere of argon/acetylene with deposition temperature of 600 °C, Ulrich et al. [20] still obtained the B–C–N films with C and BN phase separation. However, replacing the acetylene with methane as sputtering gas with deposition temperature of 450 °C, He et al. [16] found that the synthesized films were atomic-level hybrids, which were evidenced by XPS and FTIR data. Liu et al. [12] also obtained the films of atomic-level B–C–N compounds from h-BN and graphite targets under various experimental conditions.

In addition to the synthesis of microscopic ternary B–C–N films, the correlation between the chemical composition of films and the choice of targets has also been discussed. Lousa et al. [19] found that the atomic ratio of B/C in the films kept almost constant as 4:1, similar to that of the target ($B_4C$). Similar phenomenon was observed by Linss et al. [14]. On the ternary B–C–N phase diagram, the chemical compositions of those films synthesized from $B_4C$ and $BC_4$ targets distributed along the line connected by the composition point of targets and the vertex of the N element. However, there already exist B–N or B–C bonds in the sintered targets (h-BN, $B_4C$ and $BC_4$). It is unclear whether these bonds in the synthesized B–C–N films are re-formed during sputtering or originally come from these targets.

Besides these extensive discussions on intermediate compounds and compositions of B–C–N films, there have been numerous works to describe the bonding characteristic of B–C–N films. However, little attention has been paid to the correlation between the bond contents and the experimental conditions. Kim et al. [7] studied the relationship of substrate temperature and the relative number of bonds in B–C–N films prepared by radio frequency PACVD, and their results revealed that the substrate temperature had great effect on the number of bonds. Ulrich et al. [22,23] synthesized boron nitride films with different substrate bias voltage and temperature. After estimating the content of h-BN and c-BN phases by IR spectroscopy, they

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found that the formation of c-BN depend mainly on the substrate bias voltage but only little on the substrate temperature. Within the best of our knowledge, no systematic results have been reported on the correlation between the bond contents in the B–C–N films and the key experimental parameters like temperature and bias voltage [7,8,10,12,18,24]. In addition, previous experimental [25,26] and theoretical [27] works in the amorphous system have verified that the $sp^3$ bond contents can greatly affect the hardness of carbon films; therefore, counting bond contents in the B–C–N system will strengthen our understanding on the relationship of experimental parameters and physical properties. In this paper, B–C–N films were deposited using boron and graphite targets to avoid the inherent B–N or B–C bonds from the targets. We show that the bond contents of the B–C–N films can be tuned by the substrate temperature and bias voltage, which will further affect the microstructures and physical properties of the B–C–N films.

## 2. Experimental methods

B–C–N films were deposited on the silicon (100) substrate by radio frequency (13.56 MHz) reactive magnetron sputtering of boron (purity: 99.9%) and graphite (purity: 99.999%) targets with 75 mm diameter in an atmosphere of nitrogen ($N_2$) and argon (Ar). The distance of targets and substrate, the working pressure, the sputtering power of boron and graphite targets, the flow ratio of $N_2$/Ar, and the deposition time were kept at 100 mm, $7.5\times10^{-3}$ Torr, 130 W, 5/10, and 2.5 h, respectively. The base vacuum was below $5.25\times10^{-6}$ Torr. The silicon substrate was ultrasonically cleaned in acetone, ethanol and deionized water in sequence, and blow-dried with nitrogen gas. Prior to deposition, the silicon substrate was sputter-cleaned in argon discharge with the bias voltage of −750 V for about 15 min; the targets were pre-sputtered for about 30 min with RF power of 100 W to remove the surface contamination and oxidation; the vacuum chamber was baked for 48 h to reduce the moisture absorbed on the surface of the vacuum chamber. The temperature of silicon substrate was set at room temperature (25 °C) and 400 °C, respectively. The amplitude of bias voltage applied to the substrate is −75 V for samples a and e, −150 V for samples b and f, −200 V for samples c and g, and 0 V for sample d, respectively.

The choice of experimental parameters of temperature and bias voltage is based on the following considerations. Some previous works [7,8,10] verified that more $sp^2$ bonding states are formed at elevated temperature. Formation of $sp^2$ bonding states is not favorable for the hardness of B–C–N films. Therefore, we prepared some B–C–N films at room temperature to avoid large numbers of $sp^2$ bonding states. Some previous works also verified that $sp^3$ bonding states can be formed in a certain range of substrate temperature. For example, Friedmann et al. [28] reported that c-BN can be grown between 150 and 500 °C. Gago et al. [24] found that a hexagonal phase can transform into a cubic one with the substrate temperatures between 300 °C and 600 °C. Park et al. [29] found that the optimized temperature was 460 °C to prepare cubic-BN films. Considering that ion bombardment will increase the substrate temperature, we chose 400 °C to deposit some B–C–N films for achieving more $sp^3$ bonding states. In addition, the applied bias voltages on the substrate facilitate the bonding and motion of sputtered atoms. However, higher values of bias voltage can break the interatomic bonding and increase the internal stress of B–C–N films. Heating substrates can reduce this effect of the internal stress. Based on these considerations, we chose these parameters for comparative studies on the bond contents.

X-ray diffraction (XRD) pattern showed no distinct peak within the selected Bragg angle $2\theta$ (20°–80°), indicating that the synthesized B–C–N films are amorphous. A representative cross-sectional SEM image of B–C–N thin film is shown in Fig. 1. The bonding states and chemical compositions of the synthesized films were characterized by FTIR (NEXUS) and XPS (ESCAKAB250) with a monochromatized $Alk_\alpha$ as the X-ray source. Before the composition measurement, the B–C–N films were sputtered for 60 s to clean the surface contamination. The atomic concentrations were corrected by relevant sensitivity factors of 0.159, 0.296, 0.477 and 0.711 for B, C, N and O elements [30], respectively.

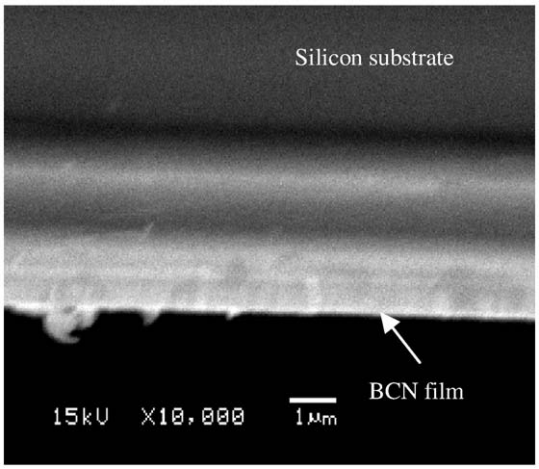


**Fig. 1.** Cross-sectional SEM image of the B–C–N thin film (sample e).

## 3. Results and discussion

### 3.1. IR spectra

The IR spectra of B–C–N films deposited at different bias voltages and the substrate temperatures at 25 °C (samples: a–c) and 400 °C (samples: d–g) are displayed in Fig. 2. The IR spectra of the silicon substrate and graphite target are also shown in Fig. 2 for comparison. The IR spectra of B–C–N films exhibit similar features regardless of the substrate temperature, implying that their main bonding character is the same. A broad absorption peak between 1100 $cm^{-1}$ and 1700 $cm^{-1}$ can be seen clearly from Fig. 2. After the background effects of substrate and graphite target are subtracted from the IR spectra of B–C–N films, the broad peak in the range of 1100–1700 $cm^{-1}$ still exhibit the intensity, which reveals that various chemical bonds are truly formed. Generally speaking, chemical bonds in this area include B–C, C–N, B–N, $sp^2$-CC and C=N centered at 1100 $cm^{-1}$ [31,32], 1270 $cm^{-1}$ [16], 1400 $cm^{-1}$ [33,34], and 1600 $cm^{-1}$ [35], respectively. However, no relevant peak of C=N bonds can be identified from the C1s or N1s spectra after deconvolution (see the next subsection). Therefore, the IR absorption peak near 1600 $cm^{-1}$ should mainly come from the $sp^2$-CC bonds. The broad peaks appearing near 2200 $cm^{-1}$ are attributed to the C≡N bonds [14] and the peaks around 600 $cm^{-1}$ to the Si–Si bonds [13]. Most of these bonds do not exist in the boron and graphite targets except for the $sp^2$-CC from the graphite target. Hence, the IR data suggest that the formation of various chemical bonds, i.e., B–C, C–N, B–N, and perhaps $sp^2$-CC, as well as the microscopic mixing of the three component elements in the B–C–N films deposited from the boron and graphite targets. As the bias voltage increases, the position of IR peak in the range of 1100–1700 $cm^{-1}$ remains unchanged and only the peak intensity is slightly weakened, indicating that the bonding nature in the films is insensitive to the bias voltage parameter.

### 3.2. Compositions and bond contents from XPS

The core electronic spectra carry the information about the chemical composition and bonding characters of the B–C–N films. The integral of B1s, C1s and N1s spectra corrected by relevant sensitive factors can evaluate the concentrations of B, C and N elements in the B–C–N films. The corresponding integral of the deconvoluted peaks can be also used to estimate the bond contents, which are described by the following formula [11]:

$$C_i = \sum(A_i / S_i) / \sum(A_j / S_j) \quad (1)$$