

# Tribological properties of sputtered boron carbide coating and the effect of CH<sub>4</sub> reactive component of processing gas

Pham Duc Cuong<sup>a</sup>, Hyo-Sok Ahn<sup>a,\*</sup>, Jong-Hee Kim<sup>b</sup> and Kyung-Ho Shin<sup>c</sup>

<sup>a</sup> Tribology Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong, Songbuk-gu, Seoul 136-791, South Korea

<sup>b</sup> Information System Technology R&D Center, SEMTech Corporated, 220 Gung-Dong, Yuseong-Gu, Daejeon 305-764, South Korea

<sup>c</sup> Nano Device Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong, Songbuk-gu, Seoul 136-791, South Korea

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## Abstract

Boron carbide thin coatings were deposited on silicon wafers by DC magnetron sputtering using a B<sub>4</sub>C target with Ar as processing gas. Various amounts of methane gas (CH<sub>4</sub>) were added in the deposition process to better understand their influence on tribological properties of the coatings. Reciprocating wear tests employing an oscillating friction wear tester were performed to investigate the tribological behaviors of the coatings in ambient environment. The chemical characteristics of the coatings and worn surfaces were studied using X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). It revealed that CH<sub>4</sub> addition to Ar processing gas strongly affected the tribological properties of sputtered boron carbide coating. The coefficient of friction was reduced approximately from 0.4 to 0.1, and wear resistance was improved considerably by increasing the ratio of CH<sub>4</sub> gas component from 0 to 1.2 vol %. By adding a sufficient amount of CH<sub>4</sub> (1.2%) in the deposition process, the boron carbide coating exhibited lowest friction and highest wear resistance.

**Keywords:** Boron carbide coating, DC magnetron sputtering, processing gas, friction and wear, X-ray Photoelectron Spectroscopy, Auger Electron Spectroscopy

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## 1. Introduction

Boron carbide (B<sub>4</sub>C) is one of the hardest known materials owing to superior properties such as high melting point, high mechanical strength, low specific gravity, and chemical stability [1]. It has been used in a wide range of industrial applications: grinding wheels for sharpening cutting tools, super-abrasives in

polishing and grinding media [1], and rotor bearings [2]. In recent years, boron carbide is one of the desired materials as thin hard coatings to protect surface from wear, corrosion and to improve frictional properties. In fact, boron carbide coatings have been used for gear boxes to increase wear resistance, metal cutting and forming tools due to high hardness and thermal

stability, and other potential applications [3-7]. However, previous studies have indicated that the structure and properties of boron carbide coating can be varying depending on the coating method and processing conditions [8-11]. In recent years, several techniques for coating preparation are reported: chemical vapor deposition (CVD) [12], physical vapor deposition (PVD) [6,7,13], and other plasma based techniques such as vacuum plasma spraying (VPS) [14] or electro-magnetically accelerated plasma spraying (EMAPS) [15]. Among them, sputter deposition including DC magnetron and RF sputtering has been successfully commercialized in a large-scale due to the simplicity and low temperature features of this process [8,11]. In an attempt to improve the properties, some parameters such as bias voltage of substrate [9], processing gas [8], ion bombardment [10], and deposition temperature were varied during the process. It was shown that the substrate bias voltage and ion energy of bombardment significantly affected the structure, the hardness, and the stress of the boron carbide coating whereas the frictional properties were a little influenced. In this study, the tribological properties of sputtered boron carbide thin coatings with 1000 Å thickness were investigated under the effect of processing gas. The coatings were prepared using DC sputter deposition technique. During the deposition process, we added a small amount of methane gas (CH<sub>4</sub>), and thus different coatings are produced depending on the CH<sub>4</sub> rate in the processing gas. We employed a micro friction and wear tester to investigate the tribological behaviors of the coatings. X-ray photoelectron spectroscopy (XPS) and Auger

electron spectroscopy (AES) were used to study the microstructure and chemical composition. The friction behavior and wear resistance of the boron carbide coatings were discussed in term of influence of CH<sub>4</sub> addition to Ar processing gas.

## 2. Experimental details

### 2.1. Coating preparation

The boron carbide thin coatings were prepared by DC magnetron sputtering using a B<sub>4</sub>C target (6-inch diameter). Just before fabricating the boron carbide coating, a 20 nm thick Cr layer was deposited at a temperature of 200° C onto a thermally oxidized Si wafer in a separate DC magnetron sputtering chamber without breaking a vacuum. Ar was used as the processing gas and various amounts of methane gas (CH<sub>4</sub>) up to 1.6 vol % were added in the deposition process. The nominal thickness of the boron carbide film was 100 nm and the base pressure of vacuum was lower than 5 x 10<sup>-7</sup> Torr. The total pressure, substrate temperature, and target power during the deposition of the boron carbide coating were 9 mTorr, 150° C, and 400 W, respectively.

Table 1. Boron carbide thin films deposited with different CH<sub>4</sub> rates.

Sample	Thickness	Temperature	CH <sub>4</sub> rate
B1	1000 Å	150 °C	0 %
B2	1000 Å	150 °C	0.4 %
B3	1000 Å	150 °C	0.8 %
B4	1000 Å	150 °C	1.2 %
B5	1000 Å	150 °C	1.6 %

Table 1 shows the boron carbide coatings deposited by DC magnetron sputtering technique

described above. The CH<sub>4</sub> ratio in the mixture of processing gas was varied from 0, 0.4, 0.8, 1.2 and 1.6 vol % while the deposition temperature was fixed at 150 °C during the deposition process.

## 2.2. Measurement of tribological behaviors

For tribological measurements, we employed a micro-oscillating friction and wear tester. The 3 mm diameter steel balls was mounted in a carrier head and oscillated against a boron carbide-coated flat specimen with applied load of 0.3 N that corresponded to a maximum Hertzian pressure of ~850 MPa. The test was conducted without lubrication in an ambient environment. The relative humidity was maintained between 40 and 45 % during the tests. Sliding speed was 4.43 mm/s and the stroke length was 3 mm. Prior to tests, the counterpart steel ball was cleaned to remove the surface contaminants. The steel ball was firstly subjected to ultrasonic cleaning in acetone and methanol solutions for 15 min. each, then rinsed in the de-ionized water for 5 min, and finally dried by compressed nitrogen gas flow. At least three tests were run for each sample to check the reproducibility of the friction behavior. For the friction coefficient, a deviation less than 10% of the mean value was observed during the steady state. All the test runs were stopped after an abrupt increase of friction coefficient indicating the initiation of significant damage (onset of failure) of coating layer.

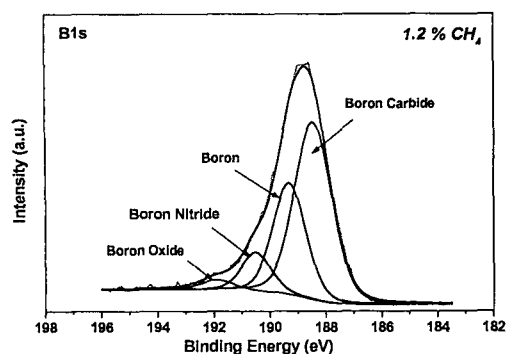
## 2.3. Characterization of worn surfaces

The physical and elemental characteristics of the surface were examined by a Perkin-Elmer PHI-670 Auger electron spectroscopy system.

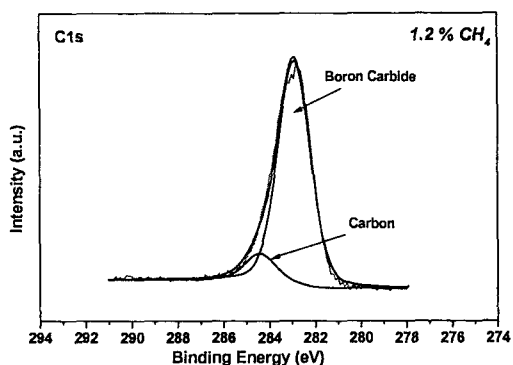
AES surface analysis was performed using an emission gun with an accelerating voltage of 5 kV and a current of 0.0213 μA. The working potential for depth sputtering was 3 kV using Ar-ion whereas the current was 0.0203 μA. Under this working condition, the sputtering rate was ~105 Å/min. when calibrated against SiO<sub>2</sub>. The chemical composition and homogeneity of the coating was studied by X-ray photoelectron spectroscopy. XPS analysis was carried out using a PHI 5800 ESCA system with a monochromated Al K $\alpha$  X-ray radiation (1486.6 eV) in a working vacuum at 1 $\times$ 10<sup>-9</sup> torr. The working potential and current of ion gun were 15 kV and 24 mA, respectively. The sputtering rate was ~ 45 Å when calibrated against SiO<sub>2</sub>.

## 3. Results and discussion

XPS analysis for a representative sample was performed to investigate the chemical composition of boron carbide coating. Fig. 1 shows XPS analysis results of boron and carbon elements for B4 original coating. The correction for charging was made by indexing the energy of C1s electron of adventitious surface carbon to its characteristic level of 284.6 eV. In Fig. 1(a), the B1s signal was composed of four components. The major peak at binding energy of ~188.4 eV was attributed to boron carbide [11,16]. Elemental B was found at 189.3 eV while the other peaks at ~190.5 eV and ~ 192 eV were close to the B1s of boron nitride and boron oxide (B<sub>2</sub>O<sub>3</sub>), respectively [16,17]. The boron nitride component might be formed due to the presence of a small volume of nitrogen in the B<sub>4</sub>C target. In



(a)



(b)

Fig 1. X-Ray photoelectron spectra of B4 original coating: B1s(a) and C1s (b).

addition, C1s XPS spectra of the coating contained two distinct peaks, which correspond to boron carbide at ~283 eV and graphitic carbon at ~284.5 eV (Fig.1(b)) [11,16,17]. Therefore, the XPS analysis results showed that the B4 coating was mainly composed of boron carbide.

The variation of the coefficient of friction against the sliding steel ball as a function of sliding cycles is shown in Fig.2. The friction coefficient for the coating without boron carbide (B0) is given in the figure as a reference. The B1 sample deposited without CH<sub>4</sub> showed a high and unstable friction coefficient from the beginning of the test whereas the friction coefficients were significantly lower and stable

for other samples with the introduction of CH<sub>4</sub> component in the processing gas (B2-B5). Moreover, the friction coefficient of deposited boron carbide films considerably decreased with the increase of CH<sub>4</sub>, from ~0.4 to ~0.1 for B1 (0 vol %) and B4 (1.2 vol %), respectively. In particular, with 1.2 vol % of CH<sub>4</sub>, the coating (B4) exhibited the lowest friction coefficient. A further increase of CH<sub>4</sub> rate to 1.6 vol %, however, did not result in any further improvement of friction coefficient, indicating that the CH<sub>4</sub> rate of 1.2 vol % is in the range of optimal gas mixture of Ar and CH<sub>4</sub>. One can also note that the life of coatings, explained by the number of cycles at which severe damage occurs, showed the same trend as the friction behavior. The B4 coating exhibited a stable friction until ~4800 sliding cycles whereas B1, B2, B3 and B5 showed rapid increases of friction coefficient after ~10, ~700, ~2700, and ~4600 cycle, respectively. The wear tracks of boron carbide coatings were examined using AES.

Fig.3. shows the scanning electron micrograph

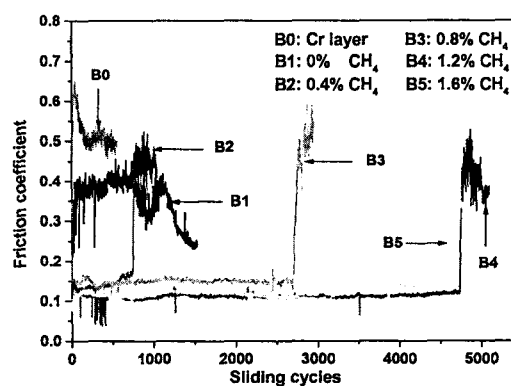
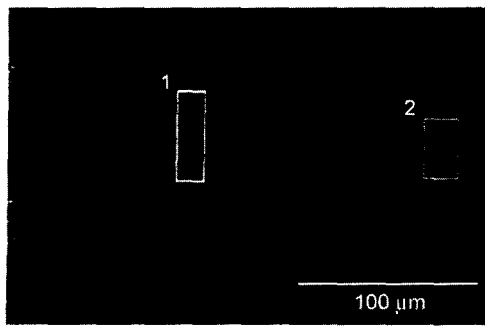
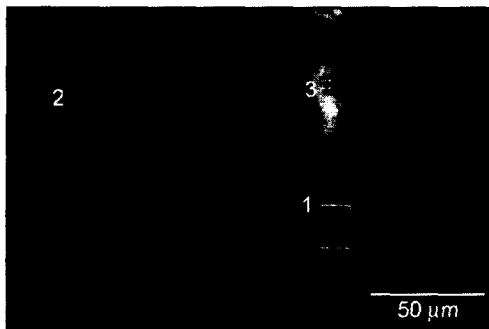


Fig 2. Friction coefficient of boron carbide coatings deposited with various ratios of CH<sub>4</sub> addition in the processing gas.



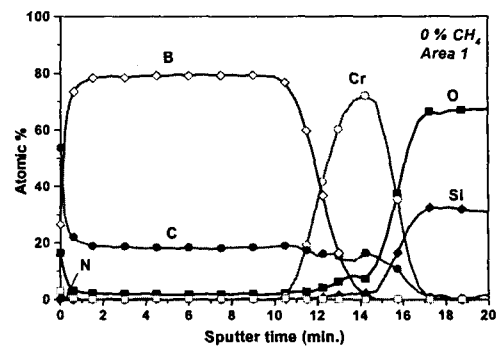
(a)



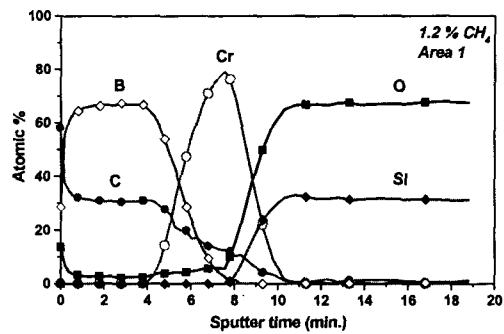
(b)

Fig 3. SEM images of the wear track of boron carbide coatings deposited at  $\text{CH}_4$  rate 0, (a), and 1.2 vol %, (b). The boxes indicate the surface areas for AES analysis performed for worn (1 and 3) and original (2) areas.

images of the wear tracks of B1 (Fig. 3(a)) and B4 (Fig. 3(b)) coatings after sliding cycles of 1500 and 5100, respectively. The worn area of B1 displayed well-defined track without an evidence of complete failure of the coating. Supplementary tests by extending the number of sliding cycles revealed that the B1 coating was removed completely after ~3500 cycles. Other coatings, B2, B3 and B5, also showed complete failure earlier than the B4 coating. The worn area of B4 showed that the coating was not also completely damaged although some scattered bright regions (marked as box #3) appeared which seemingly indicated severe surface damage. The AES analysis for these bright regions, not shown



(a)



(b)

Fig 4. AES results for depth profiles of different chemical elements for worn surfaces of B1, (a), and B4, (b).

in this paper, proved that chromium elements were mainly detected, which was from the Cr layer beneath the boron carbide film with small amounts of boron and carbon elements. In this area, a considerable amount of iron transferred from the counterpart steel ball was also detected. Fig.4 shows the AES depth profiling of various elements for representative regions in the wear tracks corresponding to the marked areas in Fig. 2. The layered structure of the coating, boron carbide/Cr/SiO<sub>2</sub>, are clearly observed. The depth profile results further confirmed that boron carbide coatings, both B1 and B4 coatings, were not completely worn out as evidenced by the dominant presence of boron and carbon elements for some considerable depth, with a greater

thickness being remained for the B1 than the B4. AES analysis of the worn surface of B2 coating also showed a thicker boron carbide layer remaining after the onset of damage than the B4 coating. Although the worn surfaces of B3 and B5 coatings were not analyzed using AES, we assume that they also have thicker boron carbide film than the B4 coating. It should be noted, however, that, as we mentioned before, the number of cycles for complete failure of other coatings were smaller than that of B4. It confirmed that, boron carbide deposited with 1.2 % CH<sub>4</sub> showed the best performance in wear resistance in this study. Eckardt et al. [8] added a small amount of C<sub>2</sub>H<sub>2</sub> gas in deposition process and showed that the amount of boron in the deposited coating decreased nearly linearly with the increase of C<sub>2</sub>H<sub>2</sub> gas flow, whereas the amount of carbon increased almost linearly. The analysis results of our coatings using AES suggested a similar behavior; the amount of boron was decreased with the increase of CH<sub>4</sub> component and carbon component was increased correlatively. So we can assume that there was a change in structure of material network due to the variation of CH<sub>4</sub> addition to the processing gas. The presence of carbon in graphite phase in the film composition (XPS results, Fig.1) might contribute to low friction and high wear resistance of the boron carbide coating.

#### 4. Conclusions

Boron carbide thin films, produced using a DC magnetron sputtering technique by adding various amounts of methane (CH<sub>4</sub>) gas to Ar processing gas, were studied to evaluate their

tribological properties and the effect of CH<sub>4</sub> component. Based upon the experimental data and analysis, the following conclusions are drawn:

1. The tribological properties of deposited boron carbide thin film were strongly influenced by the addition of CH<sub>4</sub> to Ar process gas. The coefficient of friction was reduced and wear resistance was improved considerably by increasing the ratio of CH<sub>4</sub> gas component.
2. A sufficient amount (1.2%) of CH<sub>4</sub> addition to process gas led to lowest friction and highest wear resistance of deposited boron carbide coating.
3. Boron carbide thin films show a great promise for tribological applications to protect the surface from wear and to reduce friction.

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