Thermal Stability of SiBCN Films

Naohiro Hayashi¹⁾, Junho Choi^{1)*}, Tomohisa Kumagai¹⁾, Takahisa Kato¹⁾, Masahiro Kawaguchi²⁾,
Setsuo Nakao³⁾ and Masami Ikeyama³⁾

¹⁾Department of Mechanical Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

²⁾Advanced Material Processing Group, Tokyo Metropolitan Industrial Technology Research Institute
3-13-10 Nishigaoka, Kita-ku, Tokyo 113-8586, Japan

³⁾National Institute of Advanced Industrial Science and Technology (AIST)
2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya, Aichi 463-8560, Japan

*Corresponding author: choi@mech.t.u-tokyo.ac.jp

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Silicon-Boron-Carbon-Nitride (SiBCN) thin films were deposited on Si (100) substrates by ECR-type ion beam sputtering at a substrate temperature of 200 °C, and thermal stability of SiBCN films were investigated at 600 °C, 700 °C and 800 °C in air. A composed Si-B-C (Si plate and B₄C target) target was used for the film deposition. The composition and chemical bonding structure of the prepared films were investigated by X-ray photoelectron spectroscopy and Fourier transform infrared spectrometer. Si-N bonds increased with increasing silicon content. Surface roughness of SiBCN films decreased with increasing Si content. Hardness of SiBCN films exhibited up to 22 GPa with increasing silicon content. SiBCN films showed no changes in chemical bonds after heating at 600 °C. Even after heating at 700 °C, SiBCN films maintained relatively high hardness, whereas hardness of SiBCN films was quietly reduced after heating at 800 °C. Thermal stability of SiBCN films was improved with increasing Si content.

Keywords: Silicon-Boron-Carbon-Nitride (SiBCN), ECR sputtering, thermal stability, oxidation resistance

1. Introduction

Si-B-C-N ceramics have attracted a great deal of interest due to their exceptional high temperature stability and oxidation resistance¹⁻⁶⁾. These ceramics withstand temperatures up to 2000 °C in argon atmosphere³⁾, and show the high oxidation protection up to 1000 °C^{1,6)}. In the field of ceramics, Si-C-N materials were researched as material with useful properties, such as high hardness, wide band gap characteristics, a wide optical transparency window and high temperature oxidation resistance. Recently, it has been reported that the addition of proper amount of boron in the Si-C-N ceramics leads to the great increases of high temperature stability and oxidation resistance³⁾. These effects in Si-B-C-N ceramics are possibly explained by the production of a turbostratic BN phase. A turbostratic BN phase makes local nitrogen pressure and shift decomposition reactions of Si₃N₄. In addition to these high temperature properties, it has been reported that bulk Si-B-C-N system has features of high hardness up to 47 GPa⁹⁾, low compressive stress below 1.8 GPa⁹⁾,

good adherence⁸⁾, transparency in visible spectra or controllable electrical conductivity¹⁾. Thus, combining the elements silicon, boron, carbon and nitrogen in an amorphous network has resulted in ceramics with superior properties compared to other systems. This combination of properties is well suitable for coating technologies. This can provide the superior coating material in high temperature condition to the conventional material. On the other hand, DLC (diamond-like carbon) thin films have been applied to many fields for coating material. However, DLC films are greatly oxidized over 300 °C and their mechanical properties degrade. SiBCN thin films are expected to be applied to high temperature applications, such as the protective coating for molds for aluminum, which is used over 500 °C. Vlček et al. provided results for mechanical properties and oxidation resistance of SiBCN films prepared by RF magnetron sputtering¹⁾. In that paper, SiBCN films showed high thermal stability and useful mechanical properties. However, up to now, properties of SiBCN films have not revealed sufficiently and no effort has been made to obtain the SiBCN films by ion beam sputtering to investigate properties of these

Fig. 1 Schematic diagram of ECR-type ion beam sputtering system used in the study

Fig. 2 Schematic of Si-B-C target

films. Contrary to some other techniques such as Chemical Vapor Deposition, ion beam sputtering can make films not to use hydrogen containing precursors and provide high adherence to substrates. Therefore, the improvement of oxidation resistance is expected.

In this work, we systematically investigated thermal stability of SiBCN films prepared by ECR-type ion beam sputtering using a composed Si-B-C (Si plate and B_4C target) target in constant nitrogen-argon gas mixture. We varied the silicon fraction in the target erosion area in order to obtain SiBCN films with different Si contents. Thermal stability is evaluated by chemical bonding structure before and after heating at temperatures of 600, 700 and 800 °C. Also, Boron-Carbon-Nitride (BCN) films were prepared by the same sputtering system for comparison.

2. Experimental details

The SiBCN films on Si (100) substrates were prepared by ECR-type ion beam sputtering system using a Si-B-C target. The Si-B-C target was composed by Si plate and B_4C target. Fig. 1 and Fig. 2 show schematically ECR-type ion beam sputtering system and composed Si-B-C target used for film deposition. The B_4C target erosion area was partially covered with Si plate and the silicon content in the films was controlled by adjusting the coverage area of silicon plate. Before the film deposition, the target was sputtered-cleaned using Ar^+ ion. The nitrogen-argon gas mixture (N_2 : 0.60 sccm, Ar : 0.40 sccm) was used as sputtering gas. The

base pressure of deposition chamber was lower than 1.0×10^{-3} Pa and the deposition pressure was 2.0×10^{-2} Pa. The microwave power and acceleration voltage were 100 W and 2000 V, respectively. All the depositions were performed at a substrate temperature of 200 °C to remove contaminations on the surface and increase adhesion strength between film and substrate. We also prepared BCN films using B_4C target for comparison. The thickness of all the films was about 350 nm. The elemental composition of the films was determined by X-ray photoelectron spectroscopy. Before XPS measurements, the films were sputtered by 4 kV - Ar^+ ions for 120 s to remove the impurities on the surface. The chemical bonding structure was investigated by Fourier transform infrared spectrometer. The spectra were recorded in absorbance mode in the wavenumber range of 400 – 2400 cm^{-1} . Roughness of SiBCN films was investigated by using atomic force microscopy before and after heat treatment. The scanning area and scanning speed were 10 μm and 0.5 Hz, respectively. Nanoindentation measurements were carried out, using a Berkovich-typed diamond indenter. The maximum load was 500 μN . Hardness values were obtained from the analysis of the unloading branch of the load-penetration curve. All the samples were annealed at temperatures 600, 700 and 800 °C in air for 30 min. These properties were investigated before and after heating.

3. Results and discussions

3.1. Elemental composition of SiBCN films

The elemental composition of the films is shown in Table 1. Nitrogen contents are almost constant and Si contents gradually increase due to increase of Si fraction in the target erosion area. It is reported that CN_x film has a limit of N content in the film below approximately 35 %, and the increase of Si content increases the N content in SiBCN films. In the present films, N contents are almost constant though Si contents are changed. It is considered that content of incorporated N atoms is reached a maximum value in the prepared films. Boron contents are relatively high, whereas carbon contents are relatively low due to use of B_4C target. The ratio of B/C is about 3.5 in all samples.

Table 1 Atomic concentration (at.%) of SiBCN films

Samples	B	C	N	Si
SiBCN5	31.4	10.8	30.7	27.1
SiBCN4	37.9	7.4	31.7	23.0
SiBCN3	36.4	9.8	34.0	19.8
SiBCN2	38.9	11.7	33.1	16.2
SiBCN1	42.7	12.4	33.0	12.0
BCN	55.6	12.7	31.7	-

3.2. Influence of heat treatment on chemical bonding

FTIR spectra of films before heating are shown in Fig. 3(a). Two broad absorption bands are observed. One band is approximately centered at 1300 cm^{-1} , which is correspondent to C-N (sp^3) bonds. This broad band includes at shoulder the peak of h-BN bonds (1400 cm^{-1}) and B-C bonds (1170 cm^{-1}). The peak of double bonds of carbon is not observed around 1600 cm^{-1} in these films. The other broad absorption band is approximately centered at 950 cm^{-1} , which is correspondent to Si-N bonds. Higher silicon content results in increasing of Si-N bonds and decreasing of C-N bonds. Si and C mainly make single covalent bonds with N in these films. N is combined with all elements from a high affinity of N for Si, B and C. On the other hands, BCN film shows one broad absorption peak including B-C, C-N and h-BN bonds. C-N bonds are dominant in BCN film. Fig. 3(b) shows FTIR spectra of SiBCN and BCN films after heating at 600°C . SiBCN films show no changes of chemical bonds, whereas chemical bonds of BCN films are considerably changed.

In the BCN films, only B-O bonds (1190 cm^{-1}) and h-BN bonds are observed on the substrates. The SiBCN films show their high thermal stability and oxidation resistance at 600°C . This is probably caused by inactivation of carbon due to silicon incorporation and increase of thermally stable Si-N bonds. Thermal stability of Si-N bonds in bulk Si-B-C-N ceramics is enhanced due to a turbostratic BN phase. It is known that these BN phases take in Si_3N_4 structures and this leads to restraining the decomposition of Si_3N_4 : $\text{Si}_3\text{N}_4 + 3\text{C} \rightarrow 3\text{SiC} + 2\text{N}_2$. A turbostratic BN phase in bulk ceramics grows at temperature range of $1000 - 1500^\circ\text{C}$, and the combinations of B and N in these thin films are supposed to form into turbostratic phase. Fig. 3(c) shows FTIR spectra after heating at 700°C . Changes of chemical bonds are observed. In particular, the small peak of Si-O bonds (1070 cm^{-1}) becomes clear. h-BN bonds, which have high thermal stability up to 900°C , are unaffected by heating. Fig. 3(d) shows FTIR spectra after heating at 800°C . The peak of Si-O bond is observed more sharply. SiBCN films are oxidized

Fig. 3 FTIR spectra of SiBCN films before heating (a), and after heating at 600°C (b), 700°C (c) and 800°C (d)

Fig. 4 Depth profiles of SiBCN5 (a) before heating and (b) after heating at 700 °C

higher than 700 °C. Baldus et al. described that the formation of a complex BN(O)-SiO₂ double layer was observed in Si-B-C-N ceramics due to oxidation at 1000 °C⁴). Although oxide layer may protect films from further oxidation, hardness values were quite reduced (see Fig. 5).

Fig. 4 shows the depth profiles of SiBCN5 sample before and after heating at 700 °C. The etching rate is about 12 nm/min. Silicon and boron oxides are observed on the surface of SiBCN film. The thickness of the oxide layer is about 100 nm after heating at 700 °C.

3.3. Influence of heat treatment on the hardness

Fig. 5 shows changes of hardness before and after heating in air. The hardness gradually increases as Si contents increase in the films. SiBCN5 sample exhibits high hardness of 22 GPa, which is comparable to that of DLC film. The hardness of BCN film is 9 GPa. The great improvement of hardness of SiBCN films compared to BCN films is explained by increasing of Si-N bonds due to Si incorporation. DLC films used in this study were prepared by the same ion beam sputtering system. It has been reported that the elements

in the SiBCN films trend to have high coordination number and denser networks⁵). This leads to the high hardness of materials. After heating at 600 °C, SiBCN films were no reduction in hardness value, whereas hardness of BCN films quite decreased due to heating at 600 °C.

Fig. 6 Roughness of SiBCN films

Fig. 5 Hardness changes after heating in air

Fig. 7 Roughness change of SiBCN5 after heating

3.4. Influence of heat treatment on the surface roughness

Fig. 6 shows arithmetic mean roughness of SiBCN films. The roughness of SiBCN film is very small and has a tendency to decrease with increasing Si content. Denser network due to Si incorporation probably results in the smooth surface. Fig. 7 shows the roughness change of SiBCN5 after heat treatment. It is observed that the surface roughness increases with increasing temperature of heat treatment due to the oxidation of film. The friction tests are now in progress.

4. Conclusions

SiBCN films were deposited by ECR-type ion beam sputter using a Si-B-C target and nitrogen-argon mixture as a sputter gas, and thermal stability of the films was investigated. The results obtained are summarized as follows:

- (1) The SiBCN films exhibit high hardness up to 22 GPa, which is comparable to that of DLC films. SiBCN films show very small roughness about 0.1 nm.
- (2) The SiBCN films show high thermal stability up to 700 °C and these thermal stability trends to increase with increasing Si content.

5. References

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