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Influence of Ar ion Addition on Tribological Properties of Carbon Nitride Films Prepared by Ion-Beam-Assisted Deposition

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Carbon nitride (CN_x) thin films have been prepared by ion-beam-assisted deposition. Carbon was evaporated by electron beam. N and Ar ions were bombarded simultaneously. The correlation of the influence of the Ar ion addition on the tribological properties and microstructure of CN_x films were investigated. The ion-beam gas ratio (Ar/N_2 ratio) were changed between 0 and 2. The tribological properties were measured by reciprocal sliding tribotester and pin-on-disc type tribotester. The microstructure of the CN_x thin films were investigated by transmission electron microscopy (TEM). The friction coefficients were 0.15-0.20 irrespective of the ion-beam gas ratio. However, the wear tracks showed remarkable difference. The film which formed under condition of Ar/N_2=1.0 showed excellent wear resistance. It also showed highest hardness of 20 GPa in this experiment. By the TEM observation, microstructure of CN_x thin film changed from amorphous to crystalline-like structure by Ar ion addition. Consequently, it shows that the addition of Ar ion was very effective for improvement of wear properties when CN_x thin film was formed by ion-beam-assisted deposition.

Keywords: carbon nitride, ion-beam-assisted deposition, tribological properties, microstructure, transmission electron microscopy

1.Introduction

Since the theoretical prediction of the ß-C_3N_4 structure by Liu and Cohen[1], carbon nitride (CN_x) thin films have been expected to exhibit excellent properties such as high hardness and good wear resistance. Many attempts have been made to synthesize this structure by dc and rf magnetron sputtering deposition, laser ablation, ion plating[2], plasma-assisted chemical vapor deposition and ion-beam-assisted deposition[3-5]. However, most films obtained were predominantly amorphous. But it was reported that some of CN_x thin films had a high hardness and good wear resistance despite their amorphous structure[6]. Kohzaki *et al.* reported that the Ar ion addition on synthesis of CN_x thin films by ion-beam-assisted deposition increases the hardness of the film[7]. In this study, the correlation of the influence of the Ar ion addition on the tribological properties and microstructure of the CN_x thin films were investigated.

2. Experiment

The CN_x thin films were prepared through evaporation of C using an electron beam and simultaneous bombardment with N ion and Ar ion beams of 200 eV. Si (100) wafers were used as the substrate. N ions and Ar ions were irradiated at the normal incidence to the substrate with the ion beam flux of 40 μA/cm^2. The background pressure was 2.0×10^{-5} Pa and the total operation pressure was about 4.0×10^{-2} Pa. The thickness of CN_x thin films was about 200 nm. The temperature of substrates were below 373 K during ion mixing. The distance between the substrate and evaporator was about 45 cm. The substrate holder was rotated at a speed of 3 rpm for uniform exposure to the vapor and the ion beams. The ion-beam gas ratio (Ar/N_2 ratio) was determined by the ratio of optional Ar gas amount to fixed N_2 gas amount (4sccm). It was changed between 0 and 2 (0, 0.5, 1.0, 1.5 and 2.0). Friction coefficient and wear resistance was

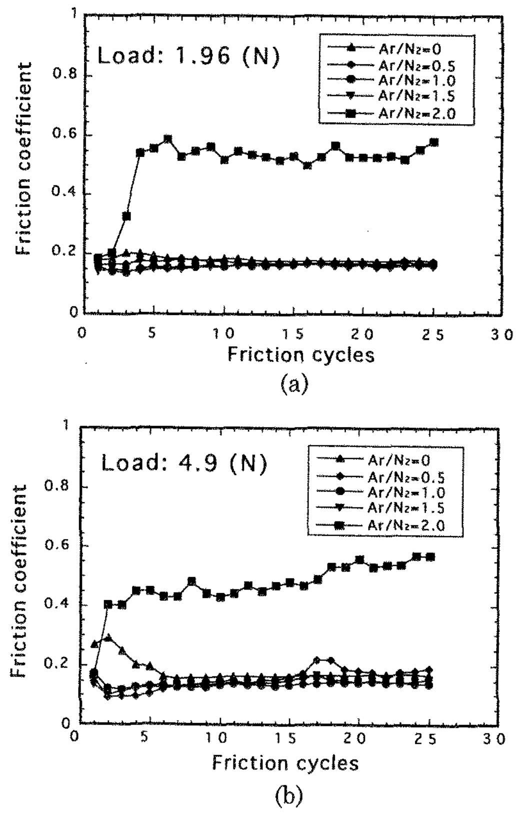

Fig.1 Friction coefficient of CN_x thin film prepared with various Ar/N_2 ratio against sapphire normal load at (a) 1.96 N and (b) 4.9 N

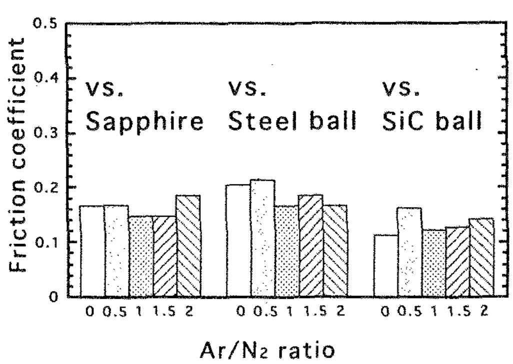

Fig.2 Friction coefficient of CN_x thin film against several materials

investigated as tribological properties in an ambient air. Friction coefficients were examined using reciprocal sliding tribotester. SiC and steel balls of 5 mm in diameter and sapphire pin of 0.5 mm in tip radius were slid against the films at normal load of 1.96 or 4.90 N and a sliding speed of 2 mm/s. Wear resistance was tested by pin-on-disc type tribotester with 498 mN under a sliding speed of 15.7 mm/s against SiC and steel ball. The hardness was measured by the nano-indentation technique with a trigonal diamond

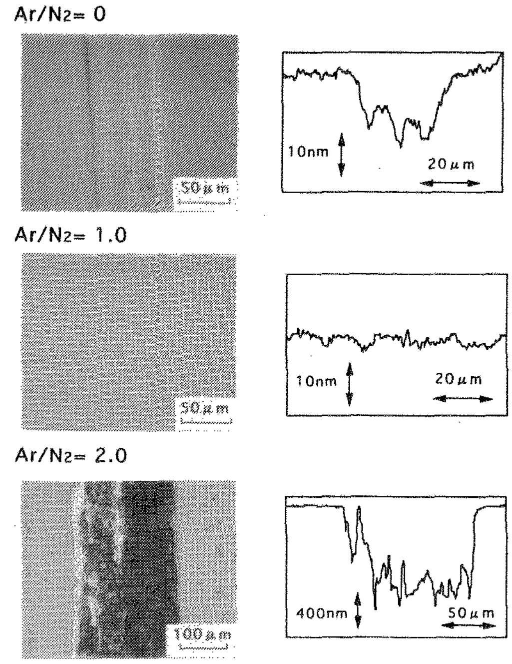

Fig.3 Optical micrographs and cross sectional profiles of wear tracks

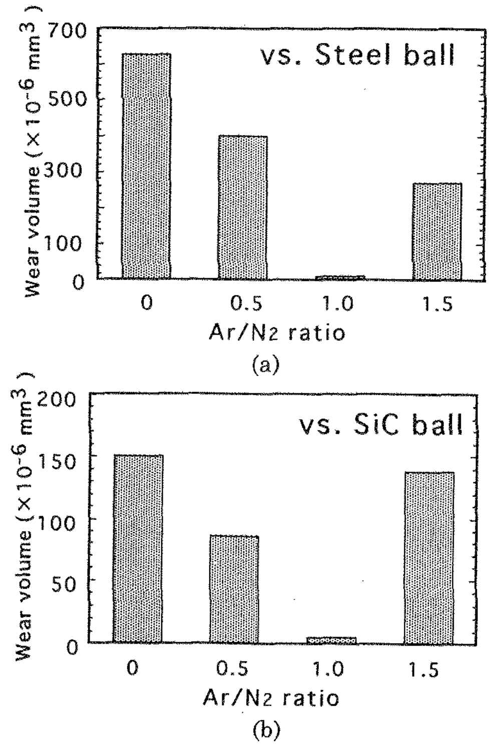

Fig.4 Wear volume of CN_x thin film against (a) steel ball and (b) SiC ball

indenter (Berkovich-type indenter). The atomic content ratio of N/C was estimated by Auger electron spectroscopy (AES). Fourier-transform infrared spectroscopy (FT-IR) was carried out to analyze the chemical bonding state of CN_x thin films. The microstructure of the films was investigated by transmission electron microscopy (TEM) and electron diffraction (TED) patterns.

3. Results and Discussion

First, friction coefficients of CN_x thin films were measured. Fig.1 (a) and (b) show the friction coefficients of the films against sapphire pin. Friction coefficients were about 0.2 irrespective of the Ar/N_2 ratio and normal load. The friction coefficient of the film formed under Ar/N_2 ratio of 2.0 increases to 0.6 due to scratched out of the wear track. Fig.2 shows the effect of three kinds of sliding materials on friction coefficient. Friction coefficients of the films were 0.15-2.0 irrespective of the sliding materials. As a result, there is no remarkable effect of normal load and sliding materials on friction coefficients of CN_x thin films in this study.

Fig.3 shows the optical micrographs of the wear tracks and the profiles of the sections after 7200 cycles against SiC ball by pin-on-disc type tribotester. CN_x thin film formed under Ar/N_2 ratio of 1.0 showed very little wear. In contrast, The film formed under Ar/N_2 ratio of 2.0 was completely scratched out. Fig.4 (a) and (b) show the wear volume of CN_x thin films against SiC ball and steel ball, respectively. Irrespective of sliding materials, the film formed under Ar/N_2 ratio of 1.0 shows only a little wear volume. It can be considered that the Ar addition is a very effective method to improve the wear property of CN_x thin films preparing by ion-beam-assisted deposition.

Fig.5 shows the hardness of CN_x thin films evaluated by nano-indentation technique. The hardness of the films were obviously higher than that formed under Ar/N_2 ratio of 0. The film formed under Ar/N_2 ratio of 1.0 showed the highest hardness of about 20 GPa. This film has also best wear resistance. It is clarified that there is a correlation between wear resistance and hardness of the CN_x thin films in this experiment.

Fig.6 shows the FT-IR transmission spectra of CN_x thin films. The existence of C—N, C=N and C≡N bonds was supported by these spectra. The absorbances of C≡N bond slightly decrease with increase of Ar/N_2 ratio. Hence, it can be considered that increase of Ar/N_2 ratio shift the chemical bond of C≡N bond to C=N or C−N bonds, and the chemical shift corresponds to difference of mechanical properties of CN_x thin films.

Fig.7 shows the typical AES spectrum of CN_x thin film (Ar/N_2 ratio of 1.0) in this study. Carbon and nitrogen content is distributed uniformly to film thickness direction. Atomic content ratio of nitrogen was about 10% irrespective of Ar/N_2 ratio.

To determine the crystallinity of CN_x thin films in this study, XRD analysis was carried out. However, no remarkable peaks were found.

Fig.8 (a) shows the high-resolution TEM and TED images of CN_x thin film formed under Ar/N_2 ratio of 0. No crystallinity and no sharp

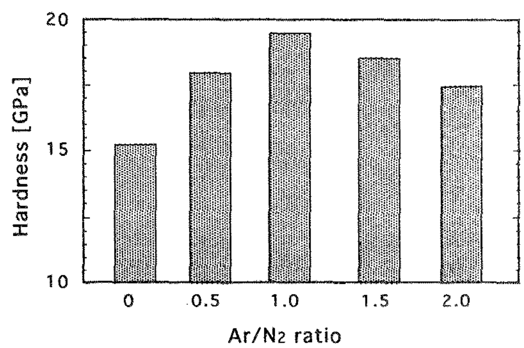

Fig.5 Nano-indentation hardness of CN_x thin films prepared with several Ar/N_2 ratio

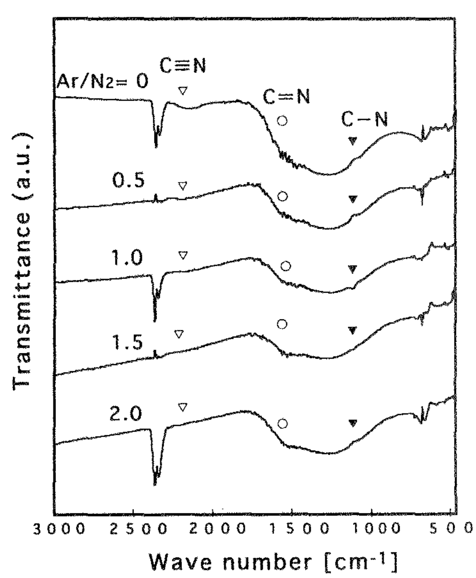

Fig.6 FT-IR transmission spectra of CN_x thin films prepared with several Ar/N_2 ratio

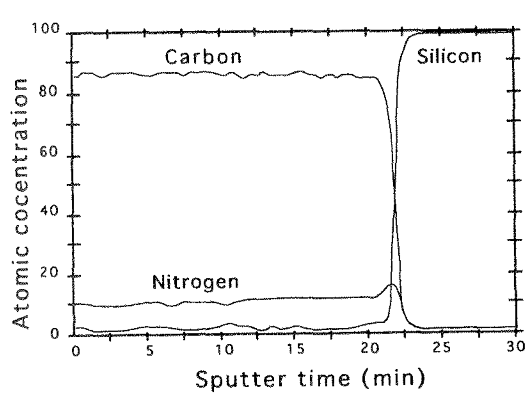

Fig.7 Typical AES spectrum of CN_x thin film (Ar/N_2 ratio of 1.0)

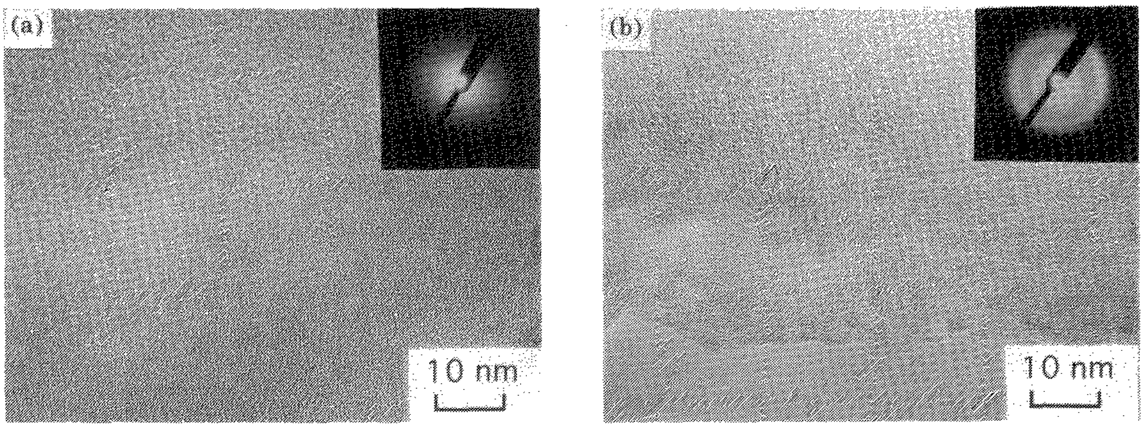

Fig.8 TEM micrographs and TED images of the CN_x thin films prepared with (a) Ar/N_2 ratio of 0 and (b) Ar/N_2 ratio of 1.0

diffraction patterns were found in the film. On the other hand, as shown in Fig.8 (b), the film formed under Ar/N_2 ratio of 1.0 showed quite curved structure. From the TED pattern, the average fringe spacing of the curved structure was estimated to be about 0.34 nm. This spacing suggested a graphite-like[8] layered structure. The CN_x thin film formed under Ar/N_2 ratio of 1.0 was thought to have low crystallinity. Recently, Hayashi *et al.* observed a similar structure in the case of a CN_x thin film prepared by ion-beam-assisted deposition[9]. They reported it has a nanotube-like structure. It can be considered that microstructure of the CN_x thin film changed amorphous to low crystalline structure by Ar ion addition. And it improve the wear resistance and hardness of the CN_x thin film. However, the film formed under Ar/N_2 ratio of 2.0 had a structure similar to the film formed under Ar/N_2 ratio of 1.0. Further study is in progress to clarify the distinct differences of microstructure by cross-sectional TEM observation.

4. Conclusion

CN_x thin films were prepared by ion-beam-assisted deposition on Si (100) substrate with Ar ion addition. Friction coefficients were about 0.2 irrespective of the Ar/N_2 ratio. The film formed under Ar/N_2 ratio of 1.0 showed the most excellent wear resistance and hardness of 20 GPa. The correlation between mechanical properties and microstructures are clarified. FT-IR absorption experiments showed the chemical bonding shift that $C \equiv N$ population slightly decreased with the increase of Ar/N_2 ratio. Microstructure of the film changed amorphous to low crystalline structure by the addition of Ar ion. It can be considered that the microstructural change is the course of improved wear resistance and hardness. The addition of Ar ion is very effective for improvement of wear resistance and hardness when CN_x thin film formed by ion-beam-assisted deposition.

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