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Thermal Stability and Tribological Properties of Si-incorporated DLC Films

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Thermal stability and tribological properties of Si-incorporated diamond-like carbon (Si-DLC) films were investigated. The DLC films were deposited by a bipolar-type plasma based ion implantation and deposition (PBII&D) technique, and the Si contents in the films were varied from 0 to 29 at.%. The deposited DLC films were annealed at 500°C in ambient air. The changes of the structure and mechanical properties of the Si-DLC films with a high Si content (≥ 21 at.%) by the thermal annealing were minimal. The 21 at.% Si-DLC film annealed at 500°C shows low wear as well as low friction, whereas the 29 at.% Si-DLC film exhibited a high friction due to the creation of cracks on the worn surface related to the SiC-like nature. The 11 at.% Si-DLC film annealed at 500°C shows the lowest friction coefficient at the cost of the significant wear in the graphitized film. The formation of a thick silicon oxide layer on the Si-DLC film could be favorable for low friction and wear.

Key words: diamond-like carbon film, silicon incorporation, thermal stability, friction, bipolar-type PBII&D

1. INTRODUCTION

The thermal degradation of the DLC films, i.e., graphitization and hydrogen effusion limits their high temperature application. It has been reported that DLC films maintain stable properties up to about 400°C while the graphitization of the films starts above this temperature [1]. It is required that DLC films should endure up to 500°C under air condition to achieve high temperature applications such as a coating material of mold for magnesium extrusion. Though many studies have been carried out to understand the high temperature behavior of DLC films, most of the studies have dealt with their thermal stability in a vacuum or inert gas conditions [2-4]. In the present study, the thermal and tribological properties of silicon-incorporated DLC (Si-DLC) films in ambient air were investigated. The DLC films were deposited using a bipolar-type plasma based ion implantation and deposition (PBII&D) technique, and the effect of the Si content on the thermal stability of the DLC films was investigated.

2. EXPERIMENTS

A bipolar-type PBII&D system [5] was used for the deposition of the DLC films on steel and Si substrates. The deposition conditions of the DLC films are as follows; precursor gas: a mixture of tetramethylsilane and toluene, positive and negative pulse voltages: +2.0 and -5.0kV, pulse frequency: 4 kHz, pulse duration: 5 μs. The deposition temperature was about 150°C. The deposited DLC films were annealed at 500°C for 30 min in the air. The composition and microstructure of the DLC films were investigated using x-ray photoelectron spectroscopy (XPS, Sigma Probe, Thermo VG) and Raman (in Via, Renishaw) spectroscopy. The hardness of the films was measured by nanoindentation (ENT-2100, Elionix). The friction coefficients were measured by a ball-on-flat type reciprocal friction tester (Type-22, Heidon) in the air. The steel substrates were used for the friction measurements. The applied load, the reciprocal sliding distance, the sliding speed, and diameter of the steel balls were 0.98 N, 8 mm, 0.5 Hz, and 3 mm, respectively. The worn surfaces of the steel balls were

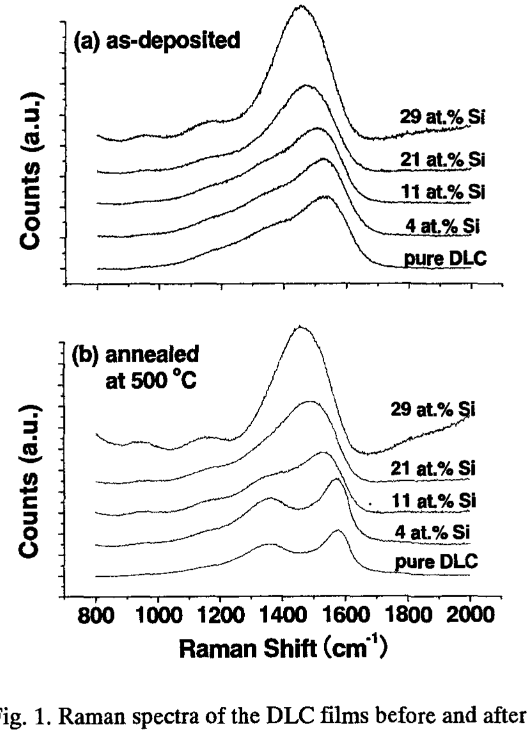

Fig. 1. Raman spectra of the DLC films before and after annealing.

analyzed using electron probe microanalysis (EPMA, JXA-8900, JEOL). The film thickness and wear depth were measured using a microstylus profilometer (ET-350, Kosaka).

3. RESULTS AND DISCUSSION

3.1 Film Structure and Composition

Raman spectra of the DLC films before and after annealing are shown in Fig. 1. The as-deposited DLC film without Si (pure DLC) shows a typical diamond-like structure with peaks centered at 1539 (G band) and 1373 cm^{-1} (D band). With the increasing Si content, the G peak becomes more pronounced relative to the D peak, and the peak for the 29 at.% Si-DLC film can be fitted by a single Gaussian, which has also been reported by Camargo et al [2]. Also, the intensity ratio, I_d/I_g, decreases from 0.81 to 0.15, and the G-peak position is shifted to low wavenumbers from 1539 to 1461 cm^{-1} with the increasing Si content. This behavior is known to be due to the increase in the sp^3 hybridized bonds of carbon [6]. For the annealed DLC films at 500°C, the Raman spectra of the DLC films with a high Si content (= 21 at.%) were not affected by the thermal annealing. On the other hand, the intensity of the D band shoulder becomes more intense for the 11 at.% Si-DLC and the Raman spectra spilt into two discrete peaks for the low Si content (≤ 4 at.%) due to the significant growth of the graphitic islands. Table I shows the hardness changes of the deposited DLC films before and after annealing. The hardness values of the annealed DLC films with low Si contents are drastically reduced compared to those of the as-deposited DLC films due to thermal degradation, whereas the hardness still maintains high values for the DLC films with high Si contents. The slight decrease in the hardness can be attributed to a little formation of silicon oxide on the DLC films during the thermal annealing., but not accompanying critical structural change of the films.

Figure 2 shows the depth profiles of the atomic concentration in the annealed DLC films, which are measured by XPS. As can be seen, the C contents in the Si-DLC surfaces with a higher Si content than 11 at.% are lower than 20 at.%, and the surfaces are covered with SiO_2 layers. The thickness of the silicon oxide is the highest in the 11 at.% Si-DLC sample, (which is qualitatively estimated from the profiles of the O contents with respect to the etching time) though the 21 or 29 at.% Si-DLC films originally contained more Si atoms. The formation of a thicker oxide layer in the 11 at.% Si-DLC film than in the 21 at.% Si-DLC film would be related to the lower thermal stability of the former compared to the latter. In the case of 11 at.% Si-DLC

Table I. The hardness changes of the deposited Si-DLC films before and after annealing. (GPa)

Si content (at.%)	As-deposited	Annealed at 500°C
0	17.0	6.9
4	18.2	6.9
11	16.4	7.5
21	17.9	15.3
29	17.0	15.0

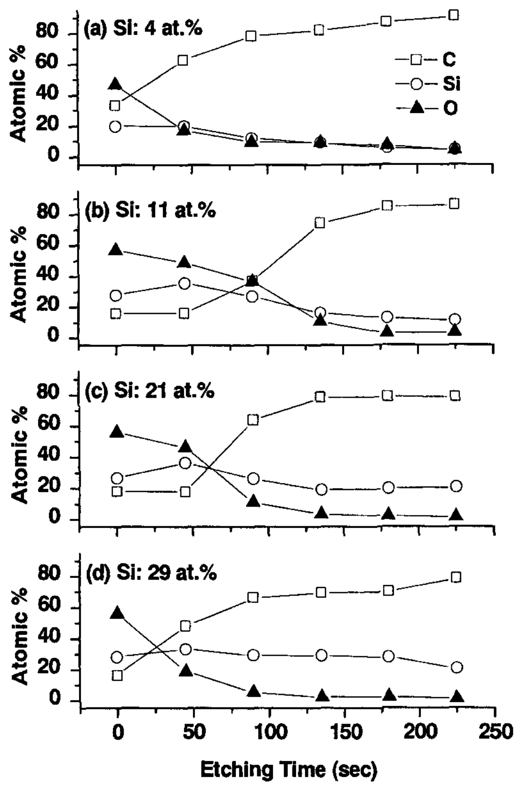

Fig. 2. Depth profiles of the atomic concentration in the annealed DLC films measured by XPS. The etching rate by Ar^+ ion is about 0.05 nm/s.

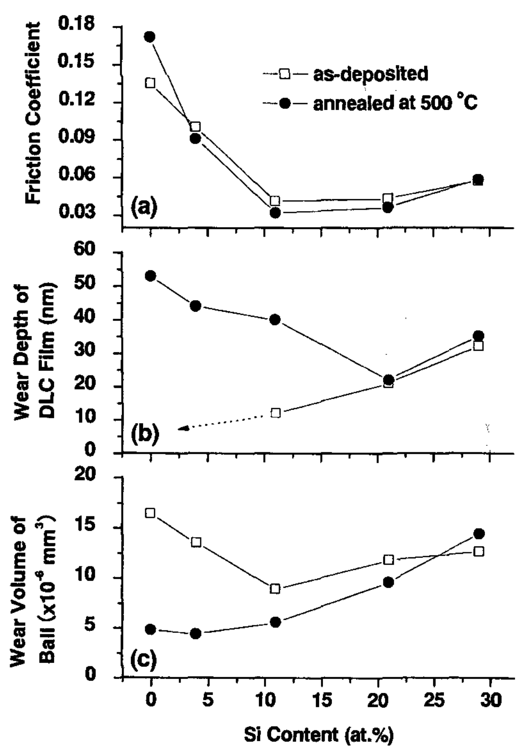

Fig. 3. (a) The friction coefficients, (b) the wear depth of the DLC films, and (c) the wear volume of the steel balls after the friction tests.

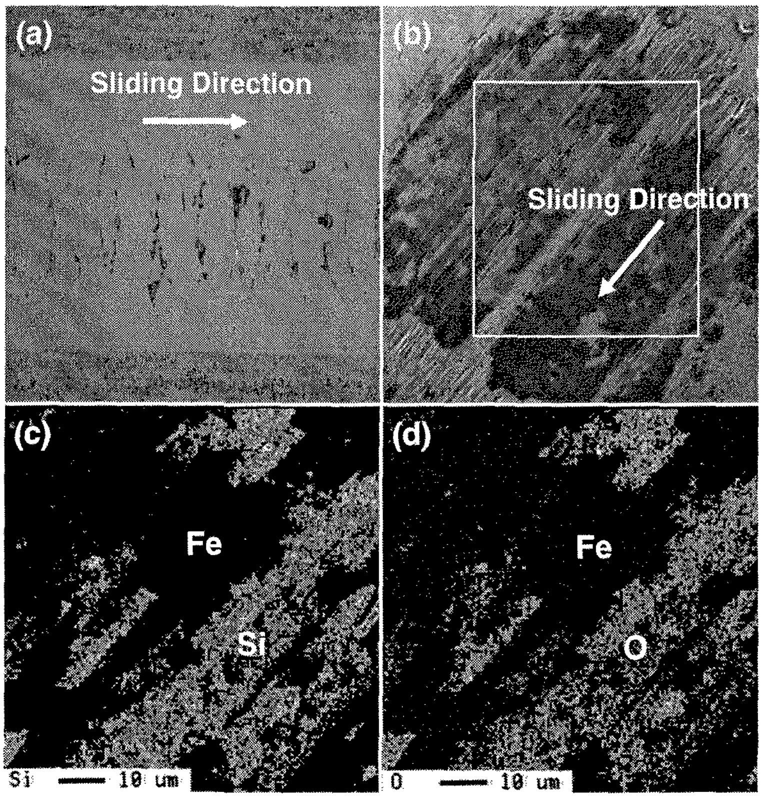

Fig. 4. The worn surfaces of (a) the 500°C-annealed 29 at.% Si-DLC film and (b) the steel ball, and the distribution of (c) Si and (d) O on the worn steel ball surface measured by EPMA. The Si and O mapping were performed in the white rectangular area in figure (b). The dark areas of figures (c) and (d) are Fe-rich regions.

film, more hydrogen and carbon atoms are effused from the surface compared to the 21 at.% Si-DLC film after the thermal annealing in the air, in a result, the remaining larger number of Si atoms in the film can form a thicker silicon oxide layer. With increasing Si content in the film, more silicon bonds to carbon and forms more sp^3-bonded carbon, which stabilizes the structure against thermal annealing. The thickness of the oxide layers in the 4 and 29 at.% Si-DLC films is similar level even though the originally incorporated Si contents are different by about 7 times. This is attributed to the high thermal stability of the DLC film with a high Si content as mentioned above.

3.2 Friction and wear properties

Figure 3 shows (a) the friction coefficients, (b) the wear depth of the DLC films, and (c) the wear volume of the steel balls after the friction tests. The friction coefficient of the pure DLC film (Si-free DLC film) decrease due to the Si incorporation in the film. The low friction of the Si-DLC films is related to the formation of silicon-rich oxide debris and the transferred layers of the silicon oxide on the steel ball surfaces [7,8]. The transferred silicon oxide on the steel ball that slid against the 29 at.% Si-DLC film was detected by electron probe micro-analysis (EPMA) as shown in Fig. 4. The distribution of Si (Fig. 4(c)) on the ball surface corresponds to that of O (Fig. 4(d)), which indicates that the transferred silicon oxide layer is formed on the steel ball surface after the friction test. This silicon oxide layer prevents contact between the steel and DLC surfaces when sliding, resulting in a low friction.

The as-deposited Si-DLC films with the silicon contents of 11 - 21 at.% show reasonably low wear rates in both the film and steel ball as well as very low friction coefficients, which agrees well with the study of Meneve et al. [9]. With a further increase in the Si content to 29 at.%, the film shows an amorphous SiC-like characteristic, that is, some cracks are observed on the film surfaces after the sliding, which results in a high friction as can be seen in Fig. 4. On the other hand, no observable wear could be detected by optical microscopy in the other films.

The friction and wear behaviors of the DLC films could be divided into two regions, the low Si content and high Si content regions, and the boundary of the two regions lies in between 11 and 21 at.% Si. The friction coefficients of the as-deposited DLC films drastically decrease with the increasing Si content up to 11 at.%, and then gradually increase. The annealed DLC films show similar behavior with the as-deposited DLC films, but the friction coefficients of the former are slightly lower than those of the latter. These low friction coefficients of the annealed DLC films are mainly attributed to the low shear strength of the graphitized surfaces. Though the friction coefficients of the as-deposited and annealed DLC films shows similar trends, the wear behavior of the DLC films and steel balls is quite different. So, it is interesting to compare the wear rates before and after annealing in the DLC films and steel balls. At a low Si content, the wear behavior of the DLC films and steel balls is drastically changed by the annealing, that is, the wear of the DLC films is significantly increased due to annealing, whereas the wear of the balls decreased. This is a result of film softening due to the growth of graphitic islands in the annealed DLC films. The difference of the wear amount in the DLC films (or steel balls) before and after annealing gradually decreased with the increasing Si content. The 21 at.% Si-DLC film shows a low wear rate for both the film and steel ball compared to the 29 at.% Si-DLC film. The high friction and large wear in the 29 at.% Si-DLC films are related to the greater SiC-like nature as mentioned above. For the 29 at.% Si-DLC films, cracks were observed as in Fig. 4(a) in both the as-deposited and annealed samples after the friction measurements. The creation of cracks results in a high friction and enhanced wear in both the film and ball compared to the 21 at.% Si-DLC film.

The formation of the thick and stable oxide layer on the 21 at.% Si-DLC films after annealing is probably one of the reasons for the low friction and wear. More silicon oxide debris could be created by a rubbing motion and transferred to the steel ball surface without any abrupt rupture of the silicon oxide layer on the DLC surface. The sliding between the silicon oxide surfaces results in a low friction coefficient [10]. A detailed analysis about the relationship between oxide layer thickness and tribological properties is a subject for our future study.

4. CONCLUSIONS

The silicon-incorporated DLC films were deposited using a bipolar-type plasma based ion implantation and deposition (PBII&D) technique, and the thermal stability and tribological properties of the films with respect to the Si content were investigated. The major results obtained are as follows.

(1) Raman spectral analysis and the hardness measurements revealed that the changes of the structure and mechanical properties of the Si-DLC films with a high Si content ($\geq$ 21 at.%) by the thermal annealing at 500°C in the air were minimal.

(2) The 11 at.% Si-DLC film annealed at 500°C shows the lowest friction coefficient at the cost of the significant wear in the graphitized film. The low friction coefficient is not always corresponding to the low wear of the film. On the other hand, the annealed 21 at.% Si-DLC film shows low wear as well as low friction.

(3) The formation of a thicker silicon oxide layer in the annealed 11 at.% Si-DLC films compared to the annealed 21 or 29 at.% Si-DLC films is attributed to the lower thermal stability of the former than the latter. The formation of a thick silicon oxide layer on the Si-DLC film with a high thermal stability could be favorable for low friction and wear.

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