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Effects of Si Content in DLC Films on Their Friction and Wear Properties

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Diamond-like carbon (DLC) has been well known as a very hard and very low friction materials. The most critical issue of DLC film formation is to improve their adhesion. To improve the adhesion, we have studied the effects of Si content on friction and wear properties of DLC films made by our bipolar pulse PBII system. The content of Si was changed by the flow rates of tetramethylsilane (TMS). Friction coefficient (FC) was measured with SUJ2 balls of 3 mm diameter. Si concentration in the film is almost linearly corresponded to the TMS flow rate. Hardness was gradually decreased with the increase of TMS flow up to 1.0 sccm, and it decreased drastically for high flow rate or high Si content. Internal stress of the films decreased with the increase of TMS flow. Without Si doping, FC was the largest. With the increase of Si content, the FC decreased. The DLC of 1.0 sccm shows the largest critical load and the lowest FC in scratch test. We can conclude that 2 % of Si doping is very suitable for improving the adhesion of film and reduction of internal stress with maintaining the surface hardness of DLC film.

Key words: PBII, DLC, Si, Friction, Wear

1. INTRODUCTION

Diamond-like carbon (DLC) films have been interested in because their excellent mechanical properties of high hardness, low friction coefficient and high wear resistance. There have been many successes in practical usage of DLC films in low-stress contact, but there are few successes in mechanical industries. The most critical issues on commercialization of DLC films in mechanical industries are DLC film formation on complicated shaped materials and durability of DLC films or to improve adhesion strength and to reduce internal stress of films, besides the cost.

On the formation of DLC films on the complicated shaped materials, we have invented a new system of plasma based ion implantation (PBII) technique, which can apply bipolar (plus and minus) pulsed high voltage to target materials, and have been demonstrated the formation of DLC films not only on the outer wall of stainless pipes but also on the inner wall [1,2]. Our system is very suitable for the DLC coatings on the complicated shaped materials, because the target material itself is used as an electrode for plasma formation and any external plasma sources are not necessary.

To improve the adhesion strength and to reduce the internal stress of DLC films, other elements doping to DLC films prepared by plasma-enhanced chemical vapor deposition (PECVD) has been studied, especially on Ti, W and Si [3]. Recently, many researchers have reported that Si doping can improve adhesion strength and reduce the internal stress [3-5]. In this paper, we have studied the effects of Si content on friction and wear properties of DLC films made by our bipolar pulse PBII system.

2. EXPERIMENTAL

Outline of our PBII system using bipolar pulses has been described in our previous papers [1,2]. In this study, we have used a new system, which has a chamber of 600 mm in diameter and 600 mm in deep with very large peak current (up to 50 A) pulse power supplies.

As a precursor gas, toluene ($C_6H_5CH_3$) was used for DLC coating. The content of Si in DLC films was changed by the flow rates of tetramethylsilane (TMS: $(CH_3)_4Si$) as 0, 0.5, 1.0, 2.0 and 3.5 sccm. Flow rate of toluene gas was set at constant of 2.5 sccm, and the total gas pressure in DLC coating process was also set at constant of 0.27 Pa.

Mirror polished stainless steel (SUS304) sheets (10 mm X 25 mm X 1 mm) were used as substrates. Si (100) wafers and glassy carbon sheets were also used as substrates for analyses of film thickness, internal stress and composition of films. DLC coating process consists of: (1) Ar plasma sputter cleaning at -2 kV, (2) carbon ion implantation at -20 kV using CH_4 plasma, then (3) DLC deposition with –5 kV pulses under toluene and TMS plasma. Process times of (1), (2) and (3) were 30 min, 30 min and 2 h, respectively.

Silicon, carbon and hydrogen contents in the DLC films on glassy carbon substrates were measured by XPS (VG, Sigma Probe, UK), and RBS and ERD using 2.8 MeV He^+ ion beam from a tandem type accelerator (NEC, 5SDH-2, USA) with 70° incidence to the surface normal, respectively. Film thickness and internal stress of DLC films were evaluated from step height at the film edge and curvature of DLC coated Si (100) substrate using a stylus profiler (Kosaka, ET-350, Japan), respectively. Hardness of the films was also measured with a dynamic- indentation tester (Akashi, MZT-5, Japan) with a Berkovich indenter at the maximum load of 2.5 mN.

Friction forth or coefficient (FC) was measured by a reciprocating friction tester (Heidon, Type 22) with a steel (SUJ2) ball of 3 mm diameter. The length of

Table I Thickness* and composition** of each DLC film

Flow Rate (sccm)	0.0	0.5	1.0	2.0	3.5
Thickness (nm)	416	543	740	476	557
H Content (%)	20.9	21.5	21.0	20.7	20.8
C Content (%)	79.1	77.8	77.0	75.4	71.0
Si Content (%)	0.0	0.7	2.0	3.8	8.2

*Measured by a stylus profiler

**Estimated from XPS, and RBS and ERD results neglecting any other elements, such as oxygen

sliding was 2 mm, the speed was 10 mm/s, and the load was 4.9 N. The load of 4.9 N is relatively high for usual friction test by our tester, because we want to evaluate the adhesion strength of the films as well. The time of sliding was for 40 min, or it is about 3160 reciprocations. Total sliding distance is about 6.3 m. The tests were carried out at room temperature and about 35 % of relative humidity. Scratch test was also performed with the same friction tester with a diamond stylus of 50 µm in radius. Maximum load was 4.9 N and the length of scratch was 10 mm.

3. RESULTS AND DISCUSSION

Table I shows thickness of the DLC films which was measured with a stylus profiler. The thickness is in the range of 410 to 740 nm. Composition of each DLC film estimated from XPS, and RBS and ERD measurements, was also shown in Table I. In this estimation, we neglect any other elements except for H, C and Si, such as oxygen. For 0.5 sccm of TMS flow, the Si concentration is 0.7 %, and 2.0 % for 1.0 sccm. Then, Si concentration increased to 3.8 % and 8.2 % for 2.0 and 3.5 sccm, respectively. It is very clear that Si concentration in the film is almost linearly corresponded to the flow rate.

There is another very interesting result in Table I. The hydrogen contents in the films are almost the same , about 20 %, regardless of the TMS flow or Si content. So, the summation of C and Si contents is also constant.

Hardness of DLC films evaluated from dynamic indentation test and internal stress of the films from the curvatures of Si wafer samples are shown in Table II. It must be noted that the maximum penetration depths of the Berkovich indenter are about 80 to 90 nm they are larger than the one-tenth of the film thicknesses (410-740 nm). So, the hardness we measured is affected by the softer substrate and became smaller than the intrinsic value of each DLC film.

The hardness was gradually decreased with the increase of TMS flow up to 1.0 sccm, and it decreased drastically for 2.0 and 3.5 sccm. It can be said that too much Si doping is not good in order to maintain the high hardness of un-doped DLC film. The tendency of hardness decrease with the increase of Si concentration is the same as Si-DLC films prepared by PECVD [3, 5].

On the other hand, the internal stress (compressive) of the films (Table II) decreased with the increase of TMS flow. The change between 0.0 (no TMS flow) and 0.5 sccm is very drastic (0.18 GPa). Wu et al. [3] also showed the rapid decrease of internal stress at small Si content. Si doping into DLC film is a very useful technique for reducing internal stress of the film formed with PBII.

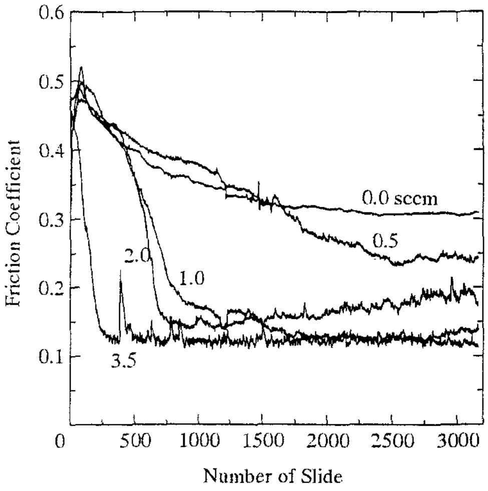

Fig. 1 Results of friction measurement for each DLC film

Time evolutions of friction coefficient (FC) are shown in Fig. 1. Without TMS flow (0.0 sccm), FC was the largest almost all over the period. The final value of FC is 0.31. For 0.5 sccm, FC became smaller than that of 0.0 sccm after about 1700 times reciprocation and the final value is 0.24.

For 1.0 and 2.0 sccm, it shows a rapid decrease of FC at about 700 cycles and the final values are 0.14 and 0.18, respectively. For 3.5 sccm, it decreased drastically at the initial stage and keep almost same value of 0.12.

Wear rates of SUJ2 balls were calculated from the size of scare on the balls and results are shown in Fig. 2. The width of sliding trace on DLC film is also shown. Both of wear rate and width of trace are the largest for 0.0 sccm and the smallest for 0.5 sccm. For 1.0 sccm, those values are the same or little bit larger than those of 0.5 sccm. For 2.0 sccm, both of them tend to be larger. For 3.5 sccm, the wear rate is relatively small but the width of trace is larger.

To observe the surfaces of DLC films and balls by an optical microscope, DLC film partly came off for 0.0 and 2.0 sccm. A lot of debris on the counter ball is

Table II Hardness and internal stress of each DLC film

Flow Rate (sccm)	0.0	0.5	1.0	2.0	3.5
Hardness (GPa)	16.3	15.6	15.1	12.1	11.6
Internal Stress (GPa)	1.05	0.825	0.814	0.773	0.639

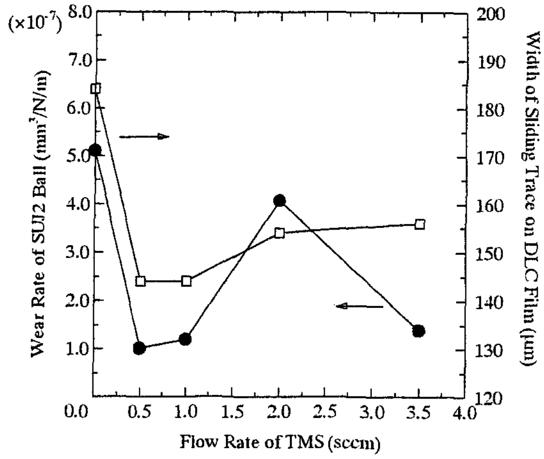

Fig. 2 Wear rate of SUJ2 ball and width of sliding trace on DLC film

observed for 0.0, 2.0 and 3.5 sccm, and it is observed even on the DLC films for 2.0 and 3.5 sccm. The apparent increase of debris on DLC film and ball for 2.0 and 3.5 sccm must be caused by this decrease of the hardness.

The results of scratch test are shown in Figs. 3 and 4. For 0.0 sccm, it shows very large vibration of friction force from the load of about 0.8 N (critical load) and the amplitude of vibration is increased with the load. FC is larger than 0.25 for almost all loads and it occasionally exceeds 0.5. For 0.5 sccm, the vibration started at about 1.0 N and FC dose not exceed 0.3 except for larger load than 4.0 N.

For 1.0 and 2.0 sccm, the slope of friction force is little bit smaller than others and the critical loads are about 2.3 N and 1.5 N, respectively. FC of 1.0 sccm is the smallest and less than 0.2 in the range from 0.4 to 2.2 N. For 3.5 sccm, the critical load is about 1.0 N and FC is larger than 0.25 almost all load.

From the result of friction test and scratch test, there is an optimum condition of TMS flow rate or Si concentration in DLC film, which is around 1.0 sccm or 2.0 %.

As mentioned above, apparent thicknesses of DLC films were different with TMS flow rates. Especially, the thickness of 1.0 sccm is about 1.8 times larger than that of 0.0 sccm. There are two reasons of this difference; one is the difference of the film density, and the other is the difference of number of elements in the films. To see it clear, number density of C in each film was calculated by using the areal number density of C estimated from RBS and ERD measurement and the apparent thickness of the each film. The results are shown in Table III.

Areal number density shows that the DLC films of 0.0, 2.0 and 3.5 sccm consist of almost same number of C atoms. On the other hand, the DLC film of 0.5 sccm consists of 15 % less C atoms and the DLC film of 1.0 sccm consists of 30 % more to compare 0.0 sccm. From this result, it can be said that the increase of film thickness partly owes to the difference in number of atoms in the film for 1.0 sccm. However, for 0.5 sccm, the increase of thickness cannot be explained by the difference of number of atoms.

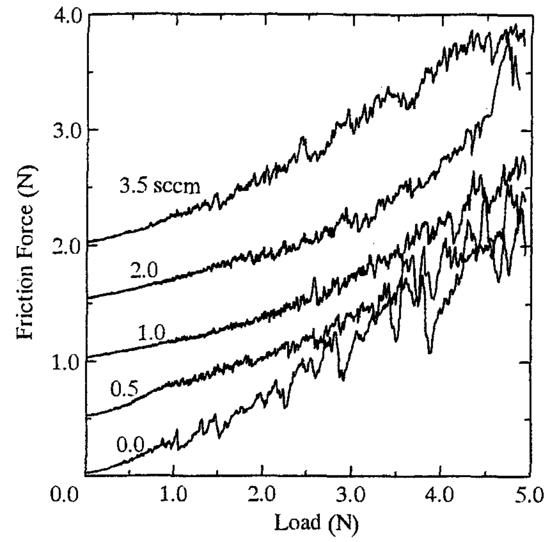

Fig. 3 Results of scratch test
Origins of ordinate shift 0.5 N by 0.5 N.

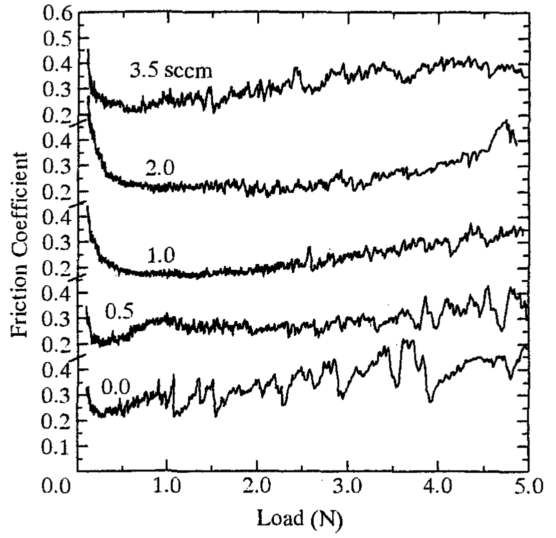

Fig. 4 Friction coefficient of DLC films in scratch test

To see the number density of C, those for 0.5 and 1.0 sccm are considerably smaller than others. It shows the densities of these DLC films are smaller than others. So, the increase of the film thickness owed to the decrease of film density. This decrease of the film

Table III Estimated* areal number density and number density of C for each DLC films

Flow Rate (sccm)	0.0	0.5	1.0	2.0	3.5
Thickness (nm)	416	543	740	476	557
Areal Number Density of C ($\times10^{18}$ /cm^2)	7.0	5.9	9.0	7.1	7.4
Number Density of C ($\times10^{23}$ /cm^3)	1.7	1.1	1.2	1.5	1.3

*Evaluated from RBS and ERD measurements density might be related to the structure change of DLC films. Some authors [4, 5] pointed out that an increase of Si contents in DLC films lead to an increase of sp^3 fraction of C · bonding from Raman spectroscopy. Recently, we have also started Raman spectroscopy and EELS measurements, and found that the sp^3 fraction might be higher for the films of 0.5 and 1.0 sccm (not shown). We are now analyzing these data. The detail will be presented elsewhere.

4. CONCLUSION

We have studied the effects of Si content on friction and wear properties of DLC films made by our bipolar pulse PBII system with changing the flow rates of TMS. Si concentration in the film is almost linearly corresponded to the TMS flow rate. Hardness was gradually decreased with the increase of TMS flow up to 1.0 sccm, and it decreased drastically for high flow rate or high Si content. Internal stress of the films decreased with the increase of TMS flow. Without Si doping, FC was the largest. With the increase of Si content, the FC decreased. The DLC of 1.0 sccm shows the largest critical load and the lowest FC in scratch test. We can conclude that the TMS flow rate of 1.0 sccm or 2 % of Si doping is very suitable for improving the adhesion of film and reduction of internal stress with maintaining the surface hardness of DLC film.

5. ACKNOWLEGEMENT

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