

TRIBOCHEMICAL REACTIONS OF Si INCORPORATED DIAMOND-LIKE CARBON FILMS DURING THE INITIAL TRANSIENT PERIOD

MYOUNG-GEUN KIM, KWANG-RYEOL LEE and KWANG YONG EUN *

*Thin Film Technology Research Center, Korea Institute of Science and Technology, P. O. Box 131, Cheongryang, Seoul, 130-650, Korea

ABSTRACT

Tribochemical reactions between Si incorporated diamond-like carbon (Si-DLC) films and steel ball were investigated during initial stage of tribo-test. The films were deposited by r.f. PACVD using mixtures of diluted silane ($\text{SiH}_4:\text{H}_2=10:90$) and benzene gases. Si concentration in the film was varied from 0 to 10 at.% by adjusting the diluted silane fraction in the reaction gases. A rotating type ball-on-disk wear rig was employed for the tribo-test in ambient atmosphere. When the Si concentration was less than 5 at.%, initial transient period of high friction coefficient was commonly observed. After the transient period, the friction coefficient becomes lower with increasing contact cycles. The initial transient period becomes shorter and the starting and maximum friction coefficients in transient period decreased with increasing Si concentration. Composition of the debris on the wear scar surface was analyzed by Auger spectroscopy at various stages in the initial transient period. We observed that when the friction coefficient increased in earlier stage of the transient period, iron and oxygen was observed in the debris. However, decrease in the friction coefficient in the later stage of the transient period was associated with the formation of silicon rich oxide debris. This result supports the friction mechanism of Si-DLC films that the formation of Si rich oxide debris results in low friction coefficient in ambient atmosphere.

INTRODUCTION

Although diamond-like carbon (DLC) films generally show excellent tribological performances of low friction and high wear resistance, the friction behavior is strongly dependent on the test environment such as humidity [1]. In ambient atmosphere, the friction coefficient between steel ball and the film is relatively high ranging from 0.1 to 0.4, while the coefficient is as low as 0.02 in dry atmosphere or in high vacuum [2, 3, 4, 5]. Many attempts were performed to reduce the environmental dependence by adding third elements such as Si, N or various transition metals. Remarkable successes were recently reported that Si incorporation to DLC films reduces the environmental dependence of the tribological behaviors and results in extremely low friction coefficient of less than 0.05 against steel ball [6, 7, 8, 9].

A number of mechanisms of the low friction coefficient between Si incorporated DLC (Si-DLC) films and steel ball in humid air was also suggested. Oguri *et al* studied the tribological behaviors of the Si-DLC films of Si concentrations ranging from 10 to 40 at.% [6]. They showed by EPMA analysis that silicon rich oxide debris were formed at the sliding surface in humid air [6]. Hence, the Si oxide debris were suggested to play an important role for the low friction behaviors in humid environment. By employing micro FTIR to analyse the chemical state of the debris, they further suggested that sliding between Si-DLC and silica sol layer results in the extremely low friction in humid air [10]. In dry condition, the materials transfer was suggested as the low friction mechanism.

Sugimoto *et al* investigated the tribological behaviors of 5 - 50 at.% Si DLC films prepared by electron cyclotron resonance (ECR) plasma [8, 11]. They reported the friction coefficient of 0.007 between Si-DLC films and steel ball in high vacuum [8]. It was suggested that the low

friction coefficient is attributed to hydrocarbons transferred from the film to the ball surface and oriented along the sliding direction. They further investigated the microtribological behaviors in ambient air of controlled relative humidity [12]. When the normal load is in the order of μN , low friction coefficient of less than 0.1 could not be observed. However, they observed that the reduced surface energy by CF_4 plasma fluorination improved the friction behaviors and wear resistance of the Si-DLC films [12].

Hioki *et al* prepared Si incorporated carbonaceous films by combining vapor deposition of silicon oil and simultaneous ion irradiation [7]. They also reported the low friction coefficient against hardened steel pin of about 0.05 in both air and nitrogen gas of relative humidities ranging from 20 to 70 %. The moisture insensitivity was suggested to arise from the fact that the films contains organic siloxane polymers of large hydrophobicity [7]. EPMA analysis of the wear scar showed that the material transfer occurs from the films to the pin.

Tribological behaviors between steel ball and the Si-DLC films of Si concentrations less than 10 at.% were reported by the present authors [13]. We showed that the average friction coefficients monotonically decreased from 0.21 to 0.06 when the Si concentration in the film increased from 0 to 9.5 at.%. We also found that the major decrease in the friction coefficient appeared in the range of Si concentrations from 0 to 3.2 at.%. By analysing the compositions of the debris on the wear track, we could show that the low and stable friction coefficient is associated with the formation of the Si rich oxide debris. This result is consistent with a low friction mechanism suggested by Oguri *et al* [6, 10].

When the Si concentration was less than 5 at.%, an initial transient period of high friction coefficient was observed during the tribo-test. In the present paper, we reported the tribochemical reactions occurred during the initial transient period. We could find an intimate relationship between the low friction coefficient and the Si rich oxide debris formation by analysing the debris compositions at various stages in the transient period. This result can be thus considered as another evidence to clarify the role of silicon rich oxide debris for the low friction behaviors of Si-DLC films in humid environment.

EXPERIMENTAL METHOD

Si-DLC films were deposited on p type Si (100) wafer by radio frequency plasma assisted chemical vapor deposition (r.f.-PACVD) method. Details of the deposition equipment were described in the previous paper [14]. The films were deposited at a bias voltage of -400 V and a deposition pressure 1.33 Pa . Mixtures of benzene and diluted silane ($\text{SiH}_4:\text{H}_2=10:90$) were used as the reaction gases. Deposition rates decreased from 4.8 to $0.6\ \mu\text{m}/\text{h}$ with increasing volume fraction of the diluted silane from 0 to 90 %, which would results from increasing hydrogen fraction in the reaction gas. The deposition time was thus adjusted to obtain $1\ \mu\text{m}$ thick films in all diluted silane fractions. The composition of the films was measured by Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) analysis using a collimated $^4\text{He}^{++}$ beam of 2.2 MeV .

The silicon concentration in the films gradually increased to 2 at.% with increasing the diluted silane fraction up to 60%. Further increasing the diluted silane fraction significantly increased the Si concentration to 9.5 at.% at the diluted silane fraction of 90%. Total hydrogen concentrations slightly decreased from 18 to 15 at.% with increasing diluted silane fraction. Details of the atomic bond structure and the mechanical properties of the Si-DLC films were previously reported [14]. By using the diluted silane as the silicon source gas, we could systematically control the film compositions when the Si concentration is very low. It was thus possible to investigate the tribological properties of Si-DLC films of low Si concentrations.

Friction and wear behaviors were measured with a rotating type ball on-disk tribometer in ambient air. The temperature and the relative humidity were in the range from 25 to 30°C and

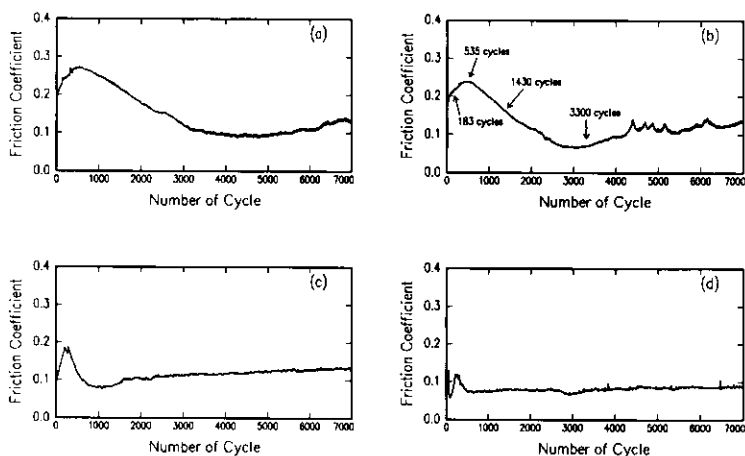


Fig. 1. Evolutions of friction coefficient during the initial transient period for various Si concentrations (a) 0.1 at.% of Si (b) 0.5 at.% of Si (c) 2.0 at.% of Si (d) 5.0 at.% of Si

from 50 to 60%, respectively. The samples were placed on a specimen holder which is installed on a rotating axis of AC servo motor. The steel ball (AISI 52100, 6 mm diameter) slides over the surface at the normal load of 5.9 N (Average initial Hertzian pressure was 0.54 GPa, assuming that the ball is in direct contact with the Si wafer.) and the sliding speed 20 cm/s. The tangential force was measured by a load cell of 9.8 N full scale. Auger spectroscopy was employed to analyze the compositions of the debris on the wear scar surface. The morphologies of the wear track and the scar surface were observed by SEM and optical microscope.

RESULTS AND DISCUSSION

Fig. 1 shows typical evolutions of the friction coefficient during the initial transient period for various Si concentrations. During the transient period, the friction coefficient increased to a maximum value and then decreased to a lower stable value with increasing contact cycles. As can be seen in Fig. 1, the transient behavior was dependent on the composition of the Si-DLC film. With increasing Si concentration, the transient period became shorter and eventually disappeared when the Si concentration was larger than 5 at.%. Both the starting and maximum friction coefficients also decreased as the Si concentration increased.

In order to investigate the tribochemical reactions during the initial transient period, we performed four experiments that stopped at 183, 535, 1430 and 3300 cycles, respectively. For this series of experiments, we used 0.5 at.% Si-DLC films where the initial transient period could be clearly observed (see Fig. 1 (b)). Fig. 1 (b) shows that the friction coefficient increased to a maximum value of 0.24 at about 500 contact cycles, and stabilized to lower value of 0.12 after about 3000 cycles. As indicated by arrows in Fig. 1 (b), each experiment was thus to investigate the debris formation behavior in the initial increasing stage, maximum stage, decreasing stage and stabilized stage of the friction coefficient, respectively. Fig. 2 shows the microstructures of the wear scars and the evolutions of the friction coefficient of each experiment. In the initial stage

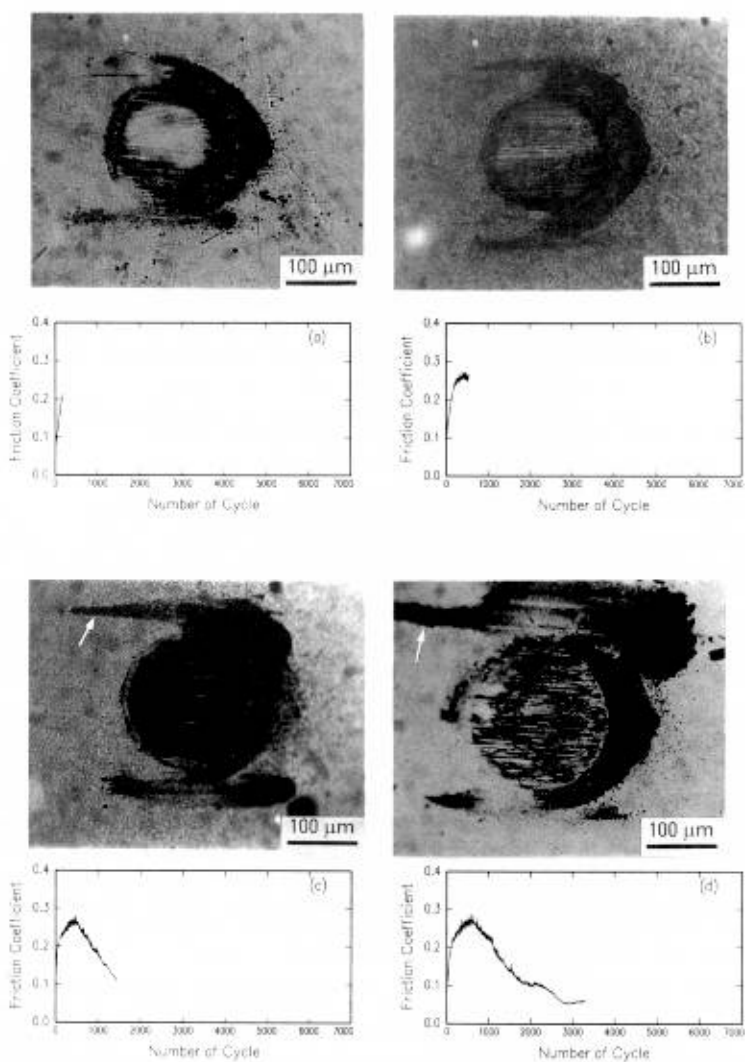


Fig. 2. Microstructures of wear scars and the evolutions of the friction coefficient
 (a) 183 cycles (b) 535 cycles (c) 1430 cycles (d) 3300 cycles

of the tribo-test, the debris were accumulated in front of the wear scar (Fig. 2 (a) and (b)). As the tribo-test continued, the debris lines were formed along the boundary of the wear track as indicated by arrows in Fig. 2 (c) and (d). In the present work, the compositions of the debris accumulated in front of the wear scars were compared by an Auger spectroscopy.

Fig. 3 shows the Auger spectra of the debris. In order to compare the compositions between the samples, the spectra were normalized to the oxygen signal at 510 eV and translated upward for the ease of comparison. All spectra were obtained after sputter cleaning the specimen surfaces in analysis chamber. In the initial increasing and maximum stage, iron, oxygen and a little carbon could be observed in the debris. This result shows that in the initial stage, wear of ball dominate to form Fe oxide type debris. Hence, the differences in the starting and maximum friction coefficient with Si concentration can be explained in terms of the factors which influence the ball wear behavior. One of the factors would be the roughness of the film surface. Fig. 4 shows the variation of rms roughness of the film surface with Si concentration. Although large uncertainties were encountered in the roughness measurement, the rms roughness decreased with increasing Si concentration. It can be thus said that the decrease in the starting and maximum friction coefficients with Si concentration is due to the decrease in the roughness of the film surface.

As the tribo-test continued beyond the maximum stage, Si and C concentrations in the debris increased, whereas the Fe concentration decreased (Fig. 3 (c)). This behavior becomes more significant in the stabilized stage as can be seen in Fig. 3 (d). This result showed that in the decreasing stage, the film wear start to occur to form the Si rich oxide debris. The Si rich oxide debris seem to suppress the effect of Fe oxide debris that increase the friction coefficient. It is thus clear that the Si rich oxide debris play a key role for low and stable friction behaviors of Si-DLC films in ambient atmosphere. Shorter transient period with increasing Si concentration could be also explained in terms of these tribochemical reactions. As the Si concentration increased, the initial ball wear was suppressed due to the smoother surface. On the other hand, the film wear rate becomes higher as the Si concentration increased [13]. Hence, the initial transient period was significantly reduced when the Si concentration was high, because of the dominant effect of the Si rich oxide debris formation.

CONCLUSIONS

When the Si concentration in Si-DLC films was less than 5 at.%, initial transient period appeared in the early stage of the tribo-test. We observed that the transient behavior is related with the changes in debris compositions from Fe oxide type debris to Si oxide type one. This result support the friction mechanism of Si-DLC films that the Si rich oxide debris formation plays a key role for low and stable friction behaviors in ambient atmosphere [6, 10]. The changes in the transient period, starting friction coefficient and maximum friction coefficient with Si concentration could be also explained by the changes in the debris compositions and the surface roughness.

ACKNOWLEDGEMENT

This work was financially supported by the Ministry of Commerce and Industry of Korea and Daewoo Heavy Industry Co. Partial support from the Korea Science and Engineering Foundation through the Center of Interface Science and Engineering of Materials at Korea Advanced Institute of Science and Technology is gratefully acknowledged.

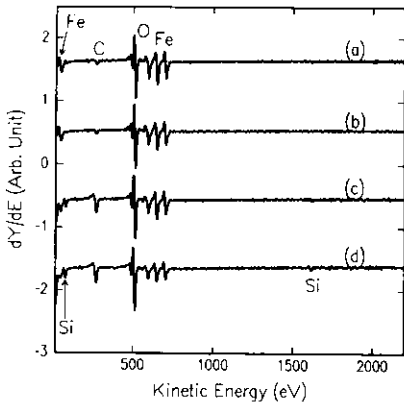


Fig. 3. Auger spectra of the debris on the wear scar for various contact cycles.

- (a) 183 cycles (b) 535 cycles
(c) 1430 cycles (d) 3300 cycles

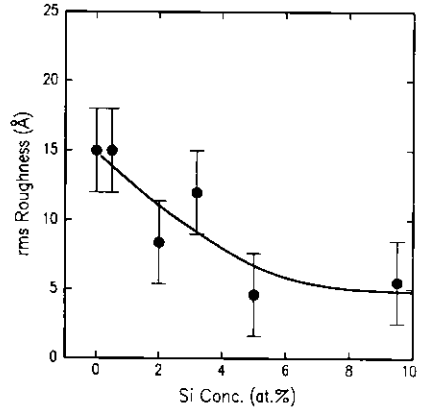


Fig. 4. Dependence of the surface roughness on the Si concentration of the Si-DLC film.

REFERENCES

1. A. Grill, *Wear*, **168**, 143 (1993).
2. K. Enke, *Thin Solid Films*, **80** (1981) 227.
3. R. Menning, H. J. Tolle and P. E. Wierenga, *Thin Solid Films*, **143** (1986) 31.
4. A. K. Gangopadhyay, W. C. Vassell, M. A. Tamor and P. A. Willermet, *Trans. ASME*, **116** (1994) 454.
5. B. Marchon, N. Heiman and M. R. Khan, *IEEE Trans. Magn.*, **26** (1990) 168.
6. K. Oguri and T. Arai, *Surf. Coat. Technol.*, **47**, 710 (1991).
7. T. Hioki, Y. Itoh, A. Itoh, S. Hibi and J. Kawamoto, *Surf. Coat. Technol.*, **46**, 233 (1991).
8. I. Sugimoto and S. Miyake, *Appl. Phys. Lett.*, **56**, 1868 (1990).
9. J. Meneve, E. Dekempeneer and J. Smeets, *Diamond Films and Technology*, **4**, 23 (1994).
10. K. Oguri and T. Arai, *J. Mater. Res.*, **7**, 1313 (1992).
11. S. Miyake, R. Kaneko, Y. Kikuya and I. Sugimoto, *Trans. ASME J. Tribology*, **113**, 384 (1991).
12. S. Miyake, T. Miyamoto and R. Kaneko, *Wear*, **168**, 155 (1993).
13. M.-G. Kim, K.-R. Lee and K. Y. Eun, Submitted to *Thin Solid Films* (1997).
14. K.-R. Lee, M.-G. Kim, S.-J. Cho, K. Y. Eun and T.-Y. Seong, *Thin Solid Films.*, in press (1997).