Humidity dependence of the tribological behavior of diamond-like carbon films against steel ball

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Abstract

Diamond-like carbon (DLC) films deposited on Si(100) wafer by r.f.-plasma assisted chemical vapor deposition were friction tested by ball-on-disk type tribometer in various test environments. The friction tests were performed in an ambient air of relative humidity ranging from 0 to 90% or dry oxygen environment. We focused on the tribochemical reactions by analyzing the chemical composition, chemical bond structure and agglomerated shape of the debris. High and unstable frictional behavior was observed in both humid air and dry oxygen environment. In these environments, Auger spectrum analysis showed that the debris contained large amount of Fe. Significant incorporation of Fe in the debris resulted from the wear of the steel ball, which might be enhanced by the surface oxidation of the ball. However, a very low frictional coefficient was observed against the sapphire ball even in dry oxygen environment. These results show that the increased frictional coefficient of the DLC film is closely related with the increased Fe concentration in the debris. Hence, the humidity dependence of the frictional coefficient is not an inherent tribological property of DLC film but results from the surface reaction of the steel ball with humid environment. Two possible reasons for the Fe rich debris to affect the frictional behavior were suggested.

Keywords: Diamond-like carbon; Tribochemical reaction; Humidity dependence; Fe rich oxide debris; Counterface materials

1. Introduction

Because of the superior tribological properties of diamond-like carbon (DLC) films, the DLC film has been applied to the contacting surfaces of machine elements, magnetic storage devices and various tools or dies. Bearing elements of spacecrafts, disk and slider surfaces of hard disk drive are such examples; all of which require a low and stable friction, low wear rate and extreme reliability in a wide range of environment [1]. DLC films generally have the frictional coefficient in the range of 0.1–0.3 that corresponds to the values of typical solid lubricants. By changing the microstructure or chemical composition of the DLC films, much lower frictional coefficient of order $10^{-3}$ was also reported [2–4].

However, one of the technical issues of DLC film is the strong dependence of frictional behavior on tribological test conditions, such as normal load, sliding speed and especially, testing environment [5]. The frictional coefficient is less than 0.1 in high vacuum, dry nitrogen or argon environment. However, the frictional coefficient increases up to 0.6, in highly humid or oxygen atmosphere [6–9]. The humidity dependence of the DLC film is opposite to those observed for other hard coatings, where the frictional coefficient increases in dry air environment. Although the DLC film is chemically inert, the environmental dependence of the friction illustrates the importance of tribochemical reaction in the tribosystem.

A few mechanisms of the increased friction in the humid environment were suggested. Kokaku et al. suggested that the unstable oxide layer on the film surface evolved in humid environment causes the higher frictional coefficient [10]. However, Marchon et al. and Strom et al. proposed that the surface smoothing can be
induced by desorption of the oxidized carbon layer in an oxygen environment [9,11,12]. Hence, the increased contacting surface results in higher frictional coefficient. It was also suggested that hydrogen in the film has an important role in the tribological behavior, since it passivates the dangling bonds and permits only weak interaction with counterface materials [4,13,14]. Yang et al. reported that the agglomeration of wear debris was enhanced in humid environment, which impedes the sliding [15].

In the present work, we showed that the oxidation of steel ball is closely related with the increased frictional coefficient in humid environment. Composition analysis of the debris showed that the increase in the frictional coefficient coincided with the formation of Fe rich oxide debris that results from the wear of the steel ball surface. Accelerated surface oxidation of the steel ball in dry oxygen environment also increased the Fe concentration in the debris and the frictional coefficient.

2. Experimental

Diamond-like carbon (DLC) films were deposited from 13.56 MHz r.f.-plasma decomposition of benzene. Details of the deposition equipment were previously described elsewhere [16]. The films were deposited on p-type Si(100) wafer. Substrates were placed on the water-cooled cathode, where r.f. power was delivered through the impedance matching network. The films were deposited at a bias voltage of \(-400\) V and a deposition pressure of 1.33 Pa. Prior to deposition, the substrate was sputter cleaned by Ar plasma in order to improve adhesion between the film and the substrate. Thickness of the film was fixed to be 1 \(\mu\)m. Surface roughness of the film measured by an atomic force microscope was less than 1 nm in rms value.

The frictional and wear behaviors were measured by using a rotating-type ball-on-disk tribometer. The tribometer was installed in an environmental chamber where relative humidity and gaseous environment can be controlled. The tribological test was performed in air environment of relative humidity ranging from 0 to 90%. During the test, the relative humidity could be controlled within \(\pm 5\)% and the temperature inside the environmental chamber was kept at 20–25 °C. Dry oxygen environment was also used to investigate the tribological behavior in a severe oxidation environment. The steel bearing ball (AISI 52100) of 6 mm in diameter slid over the surface of DLC coated Si wafer at the speed of 20 cm/s and normal load of 4 N. Average Hertzian contact pressure was 0.3 GPa, assuming that the ball is in direct contact with the Si wafer. In order to investigate the effect of the counter face materials, sapphire hemisphere of diameter 6 mm was also used. Maximum number of the contact cycle was 27 000. After the test, the wear rate of the film was calculated from the profiles of the wear track measured by an alpha-step profilometer. Before measuring the profile of the wear track, the samples were cleaned in an ultrasonic cleaner to remove the debris in the track. The wear rate of the ball was obtained from the diameter of the wear scar. Morphologies of the wear track, scar and debris were characterized by an optical microscope or a scan-
ning electron microscope (SEM). Scanning Auger spectroscopy (SAM) and micro Raman spectroscopy were employed to characterize the composition and the chemical structure of debris, respectively.

3. Results and discussion

Fig. 1a shows the frictional behaviors of DLC film against steel ball in air environment for various relative humidities. Numbers on the data are the values of the relative humidity in percentage. It is obvious that the tribological behavior is strongly dependent on the relative humidity. Higher frictional coefficient with an unstable fluctuation was observed in a humid environment. After a transient period, the frictional coefficient exhibited a steady state behavior. The frictional coefficients in Fig. 1b were obtained by averaging the frictional coefficient between 10 000 and 25 000 cycles. In the dry air (relative humidity = 0%), a very low frictional coefficient of 0.025 was observed. However, the frictional coefficient increased with the increasing relative humidity, which is well known in the DLC films [17,18]. When the relative humidity was 90%, the frictional coefficient increased up to 0.2.

Fig. 2a,b and c show the optical microstructures of the debris on the steel ball surface. Circle in the figure indicates wear scar of the ball. Wear rate of the ball estimated from the diameter of the wear scar increased from $4.5 \times 10^{-11}$ to $2.9 \times 10^{-10}$ mm$^3$/cycle as the rela-

Fig. 2. Microstructure of wear scar for relative humidity of (a) 0%, (b) 50%, (c) 90% and (d) Raman spectra of the debris for various relative humidities.
Fig. 3. Optical (a, c, e) and SEM (b, d, f) microstructures of the wear tracts for relative humidity of (a) and (b) 0%, (c) and (d) 50%, (e) and (f) 90%.

tive humidity increased from 0 to 90%. However, the morphology of debris, covering the wear scar surface is similar regardless of the relative humidity. Fig. 2d shows the Raman spectra of carbon in the debris for various values of relative humidity. The Raman spectra were essentially the same for all the relative humidity values. The spectra have two sharp peaks at approximately 1360 cm\(^{-1}\) (D Peak) and approximately 1580 cm\(^{-1}\) (G peak), which is typical of graphite. Materials transfer from DLC film that forms a graphitic layer on the ball surface, has been considered to significantly affect the frictional behavior [19–21]. However, the humidity dependence of the frictional coefficient cannot be understood by the different behavior of materials transfer because the behavior appeared to be independent of the relative humidity.

Fig. 3 shows the optical microstructures of the wear track and SEM microstructures of the debris for various values of the relative humidity. The width of the wear track is proportional to the relative humidity like the diameter of the wear scar. The wear rate of the track increased from \(2.3 \times 10^{-8}\) mm\(^3\)/cycle in dry air to \(6.5 \times 10^{-8}\) mm\(^3\)/cycle in humid air of the relative humidity 50%. However, when the relative humidity was 90%, wear of the track could not be observed at all. The reason for the extreme wear resistance in high humid environment is yet to be resolved. However, an observation of the wear track at higher magnification using SEM illustrated that the swelling of the track surface occurred in the case of 90% relative humidity. The swelling seems to be due to the polymeric characteristics of the present DLC film [22]. Fig. 3 shows that the debris tend to be agglomerated when the relative humidity was high. In the dry air condition, small debris were scattered all around the wear track (Fig. 3a and b). Increasing humidity resulted in the larger debris formation accumulated on the periphery of the wear track as seen in Fig. 3c and d. When the relative humidity was 90%, most of the debris was accumulated near the wear track (see Fig. 3e and f). Water molecules in the humid environment might cause the agglomeration of the debris, forming larger debris. The larger debris can significantly increase the frictional coefficient. Since the debris in the sliding interface should be continuously deformed during sliding, the energy required to deform the agglomerated debris would be higher than that for a small scattered one [15].

Scanning Auger spectra of the debris were summarized in Fig. 4. Prior to the analysis, the specimen surface was sputter cleaned by Ar ion beam in the
Fig. 5. Evolution of the frictional coefficient against steel ball and sapphire ball in dry oxygen environment.

Fig. 6. Auger spectra of the debris formed by sliding against steel ball or sapphire ball in dry oxygen environment.

The spectra were normalized with respect to oxygen peak and shifted vertically for the ease of comparison. Numbers on the spectra are the values of the relative humidity in percentage. The major compositional variation with the relative humidity was Fe concentration. In the dry environment, Fe is hardly observed in the debris. However, the Fe concentration significantly increased as the relative humidity increased. (The origin of the SiKLL peak at 1620 eV is uncertain. However, since the DLC film contains no Si, the peak seems to be due to the wear of the steel ball or contamination from the environment.) Comparing this result with the frictional behavior in Fig. 1, it is evident that the increased frictional coefficient in the humid environment is closely related with the Fe rich debris formation. The role of humidity seems to accelerate the wear rate of steel ball by enhancing oxidation of the surface of steel ball.

Tribotest in dry oxygen environment could show that the enhanced oxidation of the steel ball eventually increases the frictional coefficient by increasing the wear rate of the ball and the Fe concentration in the debris. The frictional behavior against steel ball in dry oxygen environment is presented in Fig. 5. In order to investigate the effect of Fe, the frictional behavior against sapphire (single crystalline Al₂O₃ ball) is also included in Fig. 5. In this environment, the frictional coefficient of DLC film against the steel ball was very high (maximum 1.0) and unstable. Wear rate of the steel ball \(1.8 \times 10^{-9}\) mm³/cycle was approximately two orders of magnitude higher than that in dry air. Auger spectrum of the debris in Fig. 6 shows that large amount of Fe was incorporated in the debris. However, when using sapphire ball, a very low and stable frictional coefficient ranging from 0.02 to 0.07 was observed even in oxygen environment. The wear rate of the sapphire ball was \(2 \times 10^{-10}\) mm³/cycle, which is similar to that of the steel ball in relative humidity of 90%. No Fe was observed in the debris as can be seen in Fig. 6. These results definitely show that the increase in frictional coefficient is caused by Fe incorporation in the debris, and this relationship was maintained regardless of the relative humidity. Even in the dry condition, high friction was observed when Fe incorporation in the debris was enhanced by the oxidation of steel ball. In humid environment, surface interaction of the steel ball with water molecule enhanced the surface oxidation, which results in higher concentration of Fe in the debris. Thus, it can be said that the higher frictional coefficient against the steel ball in humid environment is not an inherent tribological property of DLC film, but closely related with the formation of the Fe rich debris accompanied by the wear of steel ball.

It must be noted that the reason for the increased friction due to the Fe rich debris is yet to be clarified, even if the present work shows their close relationship. The high frictional coefficient can be caused by the Fe rich debris itself. High and unstable frictional behavior observed in dry oxygen environment agrees with this possibility. However, another possibility can be suggested from the microstructure of the debris formed by
sliding in the dry oxygen environment. Fig. 7 shows the microstructure of the debris in the wear track. Regardless of the ball, the small debris were scattered inside and near the wear track. However, the size of the debris for steel ball was much larger than that of the sapphire ball. From this observation, it can be suggested that Fe in the debris tends to enhance their agglomeration. The agglomeration of the debris in humid environment would be much easier when the debris contains large amount of Fe.

4. Conclusion

Environmental dependence of the frictional coefficient of the DLC film against steel ball was investigated in the view point of tribochemical reactions. The increased frictional coefficient of DLC film in humid environment was closely related with the increased Fe concentration in the debris. This relationship could be observed regardless of the test environment, once the oxidation of steel ball surface was enhanced. Therefore, it can be concluded that the increased friction in humid environment is not due to the reaction of DLC film with environment but results from the oxidation of steel ball surface. Fe incorporation in the debris seems to affect the friction in two ways. The Fe rich debris itself degrades the lubricating property of the DLC film. The other effect is to enhance the agglomeration of small debris into larger one that requires larger energy dissipation to be deformed during sliding.

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References