Tribochemical reaction of hydrogenated diamond-like carbon films: a clue to understand the environmental dependence

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Abstract

Tribological behavior of hydrogenated diamond-like carbon (DLC) films and Si incorporated DLC (Si-DLC) films deposited on Si (100) wafer by r.f.-plasma assisted chemical vapor deposition were investigated by ball-on-disk type tribometry in various environments. The friction tests were performed in ambient air of relative humidity ranging from 0% to 90% or dry oxygen environment. We focused on the tribochemical reactions by analyzing chemical composition, chemical bond structure and agglomerated shape of the debris. High and unstable friction behavior was observed in both humid air and dry oxygen environments. In these environments, Auger spectrum analysis showed that the debris contained large amounts 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. These results show that the humidity dependence of friction coefficient is not an inherent tribological property of DLC films but results from the surface reaction of the steel ball in humid environments. Two possible reasons for the Fe rich debris affecting the friction behavior are presented. Reduced dependence of the friction coefficient on the relative humidity observed for Si-DLC films is discussed in terms of the two possible reasons.

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1. Introduction

The high hardness, chemical stability, and excellent wear resistance combined with low friction coefficient against steel make diamond-like carbon (DLC) film a strong candidate for a wide range of tribological applications. The DLC coating has been applied to the contacting surfaces of machine elements, magnetic storage devices and various tools or dies. Automobile engine components such as tappets or piston rings, bearing elements of spacecrafts, disk and slider surfaces of hard disk drives are such examples, where the low and stable friction, low wear rate, and extreme reliability in a wide range of environments are required. DLC films generally have a friction coefficient in the range of 0.1–0.3 that corresponds to the typical range of values for solid lubricants. By changing the microstructure or chemical composition of the DLC films, much lower friction coefficients in the order of $10^{-3}$ were reported [1–4]. However, studies have shown that the tribological behavior of DLC films is strongly dependent on the test conditions, such as normal load, sliding speed and especially, testing environment [5]. The friction coefficient is less than 0.1 in high vacuum, dry nitrogen or argon environment. However, the friction coefficient increases to 0.6 in highly humid or oxygen atmosphere [6–9]. The humidity dependence of the frictional behavior is opposite to that observed for other hard coatings where the friction coefficient increases in dry air environment.

The environmental dependence of the friction indicates that the tribochemical reaction in the tribo-system is significant to the tribological behavior, even if the DLC film is chemically inert. Many researchers have suggested the mechanisms of the environmental dependence in terms of the tribochemical reactions. Kokaku and Kitoh [10] suggested that an unstable oxide layer on the film surface evolved in humid environment causes a high friction coefficient.
However, Marchon et al. [9,11] and Strom et al. [12] proposed that surface smoothing can be induced by desorption of an oxidized carbon layer in an oxygen environment. Hence, the increased contacting surface area results in higher friction coefficient. In hydrogen-free DLC films, the opposite behavior for the friction coefficient with relative humidity was reported. Ronkainen et al. [13] observed that hydrogen-free DLC coating deposited by vacuum arc discharge exhibited the best wear resistance and friction behavior in water-lubricated conditions. Andersson et al. [14] also reported that friction coefficient of the tetrahedral amorphous carbon (ta-C) film remarkably decreased in a humid environment when similarly coated balls were used as the counterface materials. They discussed the frictional behavior in terms of the passivation of dangling bonds at the surface by environmental gas species, which would reduce the interaction between the film and the sliding ball. It is well known that hydrogen in the film has an important role in tribological behavior, since it passivates the dangling bonds and permits only weak interaction with counterface materials [4,15–17].

Based on their own model of low friction for DLC films [18], Liu et al. [19] suggested that the wear induced graphitization of the surface is suppressed in a humid environment resulting in higher friction coefficient. Voevodin et al. [20] also observed the formation of a graphitic layer after several 1000 cycles on the surface of hydrogen-free DLC films. They discussed the humidity sensitive behavior of DLC films and the increase in the friction coefficient under high vacuum in terms of a graphitic surface layer. It was also reported that the formation of a transfer layer on the counterface is sensitive to the test environment, which significantly affects the frictional behavior [21–24]. Yang et al. [25] focused on the shape of the debris and suggested that the agglomeration of wear debris was enhanced in humid environment, which impedes the sliding. Jiang et al. [26] reported that the lower wear rate in humid environment is presumably due to the formation of low energy surfaces by the adsorption of water at the dangling carbon bonds on the edge-faces of sp² clusters. On the other hand, Tsuchitani et al. [27] reported that the wear rate increases in humid environment. The humidity dependence appeared to be more significant in hydrogenated DLC films than in hydrogen free films [27].

Most of the previous works focus on the chemical reactions between the environmental gas molecules and the DLC film surface. These arguments are based on the experimental observation that a transfer layer build-up occurs on the counterface during the initial running-in period of a few cycles. Afterward, the friction is governed by inter-film sliding between the two carbon faces. Counterface materials were not taken into account in this speculation. However, one should note that the tribological behavior is essentially a three body phenomena composed of the DLC film, the counterface surface and the debris. The debris play an especially significant role in the tribological behavior since the debris is always present between the two sliding surfaces and determines the composition and structure of the transfer layer. The debris results from the mechanical wear or the chemical reactions between the film and the counterface materials in a specific test environment. Consequently, the effect of the counterface materials cannot be excluded in understanding the tribological behavior.

The present work focuses on the effects of the debris and the counterface materials on the humidity dependence of the frictional behavior of hydrogenated DLC (hereafter referred to as DLC) and Si incorporated DLC (hereafter referred to as Si-DLC) films. We show that the enhanced oxidation of a steel ball is closely related to the increased friction coefficient in humid environment. Composition analysis of the debris shows that the increase in friction coefficient in humid environment coincides with the formation of Fe rich oxide debris resulting from wear of the steel ball surface. Accelerated surface oxidation of the steel ball in dry oxygen environment also increases the Fe concentration in the debris and the friction coefficient.

2. Experimental

DLC films were prepared by 13.56 MHz r.f. plasma chemical vapor deposition (r.f.-PACVD) using pure benzene as the precursor gas. A mixture of benzene and diluted silane (SiH₄:H₂ = 10:90) was used for Si-DLC film deposition. The fraction of the diluted silane in the gas mixture was 0.6, where the Si concentration of the deposited film was 2 at.% as measured by Rutherford backscattering spectrometry (RBS). Details of the deposition equipment were previously described [28]. The films were deposited on p-type Si (100) wafers. 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 at about 1.0 μm. Hydrogen concentration of the deposited film was estimated to be about 30 at.% by using both combustion element analysis of carbon, hydrogen and nitrogen and RBS analysis of the silicon to carbon ratio. In the present experimental condition, the hydrogen concentration is independent of the hydrogen fraction in the precursor gas, but depends on the bias voltage and the hydrocarbon pre-
cursor gas [29]. Details of the mechanical properties and atomic bond structure of the film were previously reported [28]. Mechanical properties of the film were characterized by nano indentation. Hardness and plane strain modulus for pure DLC film were 11 and 117 GPa, respectively. Si incorporation slightly increases the hardness of the film to 13 GPa and the elastic modulus to 140 GPa. Improved mechanical properties by Si incorporation were discussed in the previous work [28]. RMS surface roughness measured by an atomic force microscopy was less than 1 nm in both cases.

The friction and wear behaviors were measured with a ball-on-disk tribometer. The tribometer was installed in an environmental chamber where relative humidity and gaseous environment can be controlled. The tribological tests were performed in air environment having a relative humidity ranging from 0% to 90%. During the test, the relative humidity could be controlled to within ±5%, and the temperature inside of 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 6 mm diameter steel bearing ball (AISI 52100) slid over the surface of DLC coated Si wafer at the speed of 20 cm/s with a 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 counterface materials, a 6 mm diameter sapphire hemisphere was also used. The maximum number of the contact cycles 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 which increased from 4.5 × 10⁻¹¹ to 2.9 × 10⁻¹⁰ mm³/cycle as the relative humidity increased from 0% to 90%. However, the morphology of debris covering the wear scar

between 10,000 and 25,000 cycles. The error bar of the measurement represents the range of the friction coefficient variation during this period. In dry air condition, relative humidity of 0%, the friction coefficients were as low as 0.025 in both Si-DLC and pure DLC films. However, the friction coefficient increased with increasing relative humidity, which is well known in hydrogenated DLC films. When the relative humidity was 90%, the friction coefficient of pure DLC film increased to 0.2. Furthermore, unstable fluctuation of the friction coefficient appeared in humid environments as can be judged by the error bar on the data. The friction coefficient of Si-DLC film also increased with relative humidity. However, the humidity dependence of the friction coefficient is much smaller than for pure DLC films: at 90% relative humidity, the friction coefficient of Si-DLC was 0.1 while that of pure DLC was 0.2. This observation agrees very well with the previous reports that the environmental dependence of the friction behavior is suppressed by Si incorporation in the film [30–36].

3.2. Tribochemical reaction in DLC films

In the present work, we focus on the debris to determine the relationship between the tribochemical reactions and the humidity dependence of the friction behavior. Fig. 2(a–c) shows the optical microstructures of the debris accumulated on the steel ball after sliding on DLC films. The circle in the figure indicates the wear scar on the ball. The wear rate of the ball is estimated from the diameter of the wear scar which increased from 4.5 × 10⁻¹¹ to 2.9 × 10⁻¹⁰ mm³/cycle as the relative humidity increased from 0% to 90%. However, the morphology of debris covering the wear scar

3. Results and discussion

3.1. Humidity dependence of the friction coefficient

Fig. 1 shows the average friction coefficient of pure DLC and Si-DLC film against a steel ball in air environment for various relative humidities. After a transient period, the friction coefficient exhibited a steady state behavior. The average friction coefficients were obtained by averaging the frictional coefficient...
surface is similar regardless of the relative humidity. Fig. 2(d) shows the micro-Raman spectra of carbon in the debris for various values of relative humidity. Numbers on the spectra correspond to the values of the percent relative humidity for the experiment. The Raman spectra were essentially the same for all relative humidity values. The spectra have two broad peaks at approximately $1360 \text{ cm}^{-1}$ (D Peak) and approximately $1580 \text{ cm}^{-1}$ (G peak), which is typical of amorphous graphitic material. Material transfer from the DLC film forming a graphitic layer on the ball surface has been considered to significantly affect the frictional behavior [20–23]. However, the humidity dependence of the friction coefficient cannot be understood by the transfer materials because the materials are independent of humidity.

Considerable differences are observed in the morphology and composition of the debris on the wear track. Fig. 3(a–c) shows the SEM microstructures of the debris on the wear track at various relative humidities. It is clear that the debris tend to be larger in the high humidity tests environment. Under dry air conditions, small debris were scattered all around the wear track (Fig. 3(a)). Increasing humidity results in large debris accumulated on the periphery of the wear track as seen in Fig. 3(b) and (c). Large debris seems to be formed by agglomeration of the smaller debris caused by water molecules in the humid environment. However, some debris itself had a large size as can be observed in Fig. 3(c). The larger debris significantly increase the friction 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 small scattered ones [25]. Scanning Auger spectra of the debris are summarized in Fig. 3(d). Prior to the analysis, the specimen surface was sputter cleaned by an Ar ion beam in the analysis chamber to remove the surface contaminants. The spectra were normalized with respect to the oxygen peak and shifted vertically for comparison. Numbers on the spec-
tra are the percent relative humidity for each test. The major composition variable with relative humidity was Fe concentration. In the dry environment, Fe is not observed in the debris; however, the Fe concentration significantly increased with relative humidity. 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 contamination. Comparing this result with the friction behavior in Fig. 1, it is evident that the increase in friction coefficient with humidity is closely related to formation of Fe rich debris.

One can speculate that water molecules enhanced oxidation of the steel ball surface, which accelerated the wear rate of the steel ball. Tribotests in dry oxygen environment could show that the enhanced oxidation of the steel ball eventually increases the friction coefficient by increasing the wear rate of the ball and the Fe concentration in the debris. The frictional behavior against a steel ball in dry oxygen environment is presented in Fig. 4(a). In order to investigate the effect of Fe, the frictional behavior against a sapphire (single crystalline Al₂O₃) ball is also included. In this environment, the friction coefficient for DLC film against the steel ball was very high (maximum 1.0) and unstable. The wear rate of the steel ball (1.8 × 10⁻⁹ mm³/cycle) was approximately two orders of magnitude higher than that in dry air. The Auger spectrum of the debris in Fig. 4(b) shows that a large amount of Fe was incorporated in the debris. However, when using the 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 × 10⁻¹⁰ mm³/cycle, which is similar to that of steel ball in 90% relative humidity but no Fe was incorporated in the debris (Fig. 4(b)).

These results definitely show that the increase in friction coefficient is closely related with Fe incorporation in the debris, and this relationship was maintained regardless of the relative humidity. Even in dry con-

Fig. 3. SEM microstructures of the wear tracks of pure DLC film for relative humidity of (a) 0%; (b) 50%; (c) 90%; (d) auger spectra of the debris from pure DLC film formed by sliding against a steel ball in ambient air of various relative humidities.
ditions, high friction was observed when Fe incorporation in the debris was enhanced by the oxidation of steel ball. In humid environments, surface interaction of the steel ball with water accelerates surface oxidation, resulting in higher a concentration of Fe in the debris. Thus, it can be said that the higher friction coefficient against the steel ball in humid environments is not an inherent tribological property of DLC film, but closely related to formation of the Fe rich debris accompanied by the wear of the steel ball.

Fe rich debris may affect the tribological behavior in two ways. A much higher and unstable friction coefficient was observed in dry oxygen environment than in dry air environment (Figs. 1 and 4). This difference implies that the Fe rich debris caused the higher friction coefficient. In addition, the Fe content in the debris also affects the morphology of the debris on the wear track. Fig. 5 shows the SEM microstructures of the debris in the wear track formed by sliding in a dry oxygen environment. Many of the debris particles for the steel ball (Fig. 5(a)) are much larger than that for sapphire ball (Fig. 5(b)). From this observation, it can be suggested that Fe incorporation in the debris tends to form larger debris.

3.3. Tribocahemical reaction in Si-DLC films

The frictional behavior of Si-DLC films is also dependent on the relative humidity, although the dependence is much smaller than that observed for
DLC films (see Fig. 1). Similarly, in Si-DLC films, the humidity dependence is related to the formation of Fe rich debris. Fig. 6 shows the Auger spectra of the debris on the wear track in Si-DLC films for various values of relative humidity. In dry air, the debris is chemically composed only of C, O and Si. The Si rich carbon hydroxide debris was considered to be the main reason for very low friction coefficient of Si-DLC films in wide range of test condition [33–35]. As the relative humidity increased, Fe concentration in the debris increased, while the Si concentration decreased. The changes in the debris composition are consistent with the wear rate of the steel ball. The wear rate increased from $7.94 \times 10^{-11}$ to $8.34 \times 10^{-10}$ mm$^3$/cycle as the relative humidity increased, similar to that observed for DLC films. The intimate relationship between the Fe concentration in the debris and the friction coefficient between the Si-DLC film and the steel ball is also in good agreement with previous work [37].

Fig. 6. Auger spectra of the debris from Si-DLC film formed by sliding against a steel ball in ambient air of various relative humidities.

Fig. 7. SEM microstructures of the wear tracks of Si-DLC film for relative humidity of (a) 0%; (b) 50%; (c) 90%; (d) raman spectra of the debris from Si-DLC film for various relative humidities.
Fig. 7(a–c) shows the SEM microstructures of the debris in the wear track. In contrast to the case of DLC film (Fig. 3), debris of similar size are scattered around the track regardless of the relative humidity. No significant difference was observed in the transfer layer on the wear scar surface with the relative humidity. Comparing Fig. 6 with Fig. 3(d) further shows that the debris composition for 90% relative humidity is essentially the same as that observed for DLC film. It is thus puzzling that the size of the debris for Si-DLC films was independent of the relative humidity and the Fe concentration in the debris. We observed a considerable difference in the chemical bond structure of carbon in the debris for Si-DLC films depending on the relative humidity. Fig. 7(d) shows the micro-Raman spectra of carbon in the debris for various values of the relative humidity. As the relative humidity increased, the shape of the spectra changed from typical amorphous graphitic material to that of DLC, which has a smeared D-peak shoulder at approximately 1350 cm\(^{-1}\). Wu et al. [31] also reported that the graphitization of wear debris or transfer films do not occur in wear tests in ambient air (R.H. 30–50%), presumably due to the better thermal stability of the Si-DLC. Even if the debris has high Fe concentration, the diamond-like property of the debris seems to suppress formation of large debris in humid environments. In Si-DLC films, therefore, the increase in friction coefficient due to energy dissipation for deforming larger debris is not expected, resulting in the smaller humidity dependence for frictional behavior.

Another contrasting frictional behavior between DLC and Si-DLC film is observed in dry oxygen test environment. While the friction coefficient of pure DLC film against a steel ball was very high, maximum 1.0, and unstable, a low and stable friction coefficient, 0.08, was observed for Si-DLC films. Fig. 8 shows the Auger spectra and the SEM microstructure of the debris on the wear track. In contrast to the case of DLC film where high Fe content is observed in the debris, Fe is not observed in the debris for Si-DLC films (Fig. 8(a)). This result confirms that Fe incorporation in the debris is an important factor in understanding the frictional behavior of DLC materials against steel. Comparing Fig. 8(b) with Fig. 7, it is evident that the quantity of debris was much larger in the oxygen environment than in ambient air, but only small scattered debris particles were observed without agglomeration resulting in very low friction coefficient.

4. Conclusions

The most significant result of the present work is the demonstration that increased friction coefficient for DLC films against steel in humid environment is related to Fe incorporation in the wear debris. This relationship is observed regardless of the test environment, once the oxidation of steel ball surface is enhanced. Therefore, the increased friction caused by humid environments is not due to the reaction of DLC film with environment but results from the oxidation of the steel ball surface. Fe incorporation in the debris seems to affect the frictional behavior in two ways. The Fe rich debris can cause high and unstable friction coefficient. Moreover, the Fe incorporation in the debris can increase the Fe concentration also in the transfer layer. Sliding between Fe rich debris and the transfer layer degrades the lubrication property of the DLC films. The other effect is to enlarge the debris by either agglomeration of the small debris or formation of the large debris. The debris with increased mass requires more dissipation energy to deform during sliding. The humidity dependence of the friction behavior of the Si-DLC film is also related to Fe incorporation. However, the reduced humidity dependence may be due to the suppression of the debris agglomeration related to the diamond-like characteristic of the chemical bonds in the debris.
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