Effect of Plasma Treatment on Friction Coefficient of Diamond-like Carbon Films

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In this study, diamond-like carbon (DLC) films are modified using O2 and CF4 plasma. The friction coefficient measured using a ball-on-disk tribometer is greatly reduced using O2 plasma treatment, while CF4 plasma treatment retains the DLC film’s original friction coefficient. In addition, O2 plasma treatment enhances the surface energy of DLC films, making DLC a favorable non-wetting surface. The improved surface energy of O2 treated DLC films results in a greater hydrophilic behavior. O2 plasma treatment also introduces hydroxyl groups on the DLC film surface, increasing the friction coefficient. CF4 plasma treatment introduces fluorinated groups on the DLC film surface, preventing hydrophilicity. The wettability of DLC films is determined by the hydrophilic/hydrophobic state of the film surface.

**Keywords:** Diamond-like Carbon, Plasma Treatment, Surface Modification, Wettability

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1. Introduction

Diamond-like carbon (DLC) films have been extensively studied in the past due to their excellent characteristics, such as chemical inertness, high hardness, low friction coefficients, wear resistance, and biocompatibility. Recent studies have reported that surface-modified DLC films improve biocompatibility, lubricity, stability, and cell adhesion. These characteristics are related to surface roughness, structural bonds, and whether the film is hydrophilic or hydrophobic.

Surface modification of DLC has been performed by dicing with suitable elements and plasma treatment. Owing to the chemically active species in plasma and the ease of processing, plasma treatment is the most widely used method for modifying DLC surfaces. Recently, O2 plasma treatment has become widely used on both experimental and industrial scales; for instance, Santos et al. found that O2 plasma treatment enhances the surface energy of DLC films, which may further improve their surface hardness. In addition, Choi et al. also devoted their enthusiastic attention towards oxygen plasma in DLC films to improve their tribological properties. The improvement of the surface energy and friction coefficient of DLC is a direct consequence of the surface activation processes required for many technological applications, including use as a biomaterial. In this context, O2 and CF4 plasma treatment of DLC film surfaces may provide a new and efficient approach to improve the wetting and tribological properties of the films without the need for complex hybrid system geometry. Thus, further work on this topic should exhibit great promise.

In this study, we have focused on the effect of O2 and CF4 plasma treatment on friction coefficient, and have evaluated the bonding structure and wettability properties of the DLC films.

2. Experimental details

A schematic of the PBII system used for the deposition and plasma treatment of the DLC films has been previously shown in the literature. Si (100) wafers, 0.7 mm thick, were used as substrates. The wafers were sputter-cleaned with Ar for 20 min to remove residual surface contaminants and surface oxides using a negative-pulsed bias voltage of 10 kV. A pulse width of 5 μs, a pulse delay of 25 μs, and a pulse frequency of 1 kHz were utilized during the sputter-cleaned process. Using a negative-pulsed bias voltage of 20 kV, the DLC film interlayer was first deposited with CH4 for 60 min to improve adhesion between the film and the substrate. A pulse width of 5 μs, a pulse delay of 60 μs, and a pulse frequency of 1 kHz were utilized during the creation of the interlayer process. The deposition of the DLC films was performed at a negative-pulsed bias voltage of 5 kV with CH4 for 150 min. A pulse width of 5 μs, a pulse delay of 25 μs, and a pulse frequency of 1 kHz were utilized during the coating process. The deposition pressure was set to 2 Pa, and the total deposited thickness of the films was approximately 450 nm. After deposition, O2 or CF4 plasma was applied in the chamber with various RF powers of 100, 300, and 500 W for 30 min. The plasma treatment pressure was also set to 2 Pa.

The film properties were studied using several characterization techniques. The surface information from a depth close to the film surfaces was carried out with sufficient accuracy by means of fully gas-purging for IR measuring device (JASCO FT/IR-4200), not only a sample room but also a beam splitter room using dry N2, and by using the highly sensitive technique for the film surface called Attenuated total reflectance (ATR). Therefore, the spectrum which does not have influence of the noise by

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moisture was obtained. All the spectra were also detected in the range of 600–4000 cm⁻¹ in transmission mode. The surface morphologies and roughness values of the films were characterized by atomic force microscopy (JSPM-4200 Scanning probe microscope). For each surface, the roughness value was measured five times. The tribological performance was assessed using ball-on-disk friction testing (CSEM; Tribotester). The friction test was performed using a ball indenter, AISI440C (SUS440C, diameter of 6.0 mm), under a normal applied load of 3 N, a rotation radius of 3 mm, a linear speed of 31.4 mm/s, and 6000 frictional rotations. The tests were performed under ambient air at room temperature. The contact angle (θ) was measured under atmospheric conditions at room temperature with a contact angle of 100°C. The films, can be attributed to the O²⁻ atom bonding to hydrogen atoms on the surface during O₂ plasma. It is believed that this is affected primarily due to oxygen content. The ATR-FTIR spectra of the as-deposited DLC film tended to be a hydrophobic surface, indicating the increased of film growth processes, enhancing the increased of film roughness values of the films. The broad band at approximately 2900 cm⁻¹ is observed in O₂ plasma-treated DLC films, and for the O₂ plasma treatment made the hydrophilic surface more hydrophilic and O₂ plasma treatment made the hydrophilic surface more hydrophobic. A broad band is observed at approximately 2900 cm⁻¹ due to the C-H stretching vibration mode. According to Heitz et al., the band at 2860 cm⁻¹ can be assigned to the C-H symmetric vibration mode, whereas the band at 2925 cm⁻¹ can be attributed to the C-H asymmetric vibration mode or to the C-H stretching mode. The C=O peak is also observed at approximately 1600 cm⁻¹. Further, the peaks at approximately 1446 cm⁻¹ correspond to sp² CH₂ deformations, which indicate that the majority of the hydrogen is bonded to amorphous sp² carbon rather than to amorphous sp³ carbon. On the other hand, the broad band at approximately 1300 cm⁻¹, which is observed in CF₄ plasma-treated DLC films, can be attributed to the CF-CH₃ bond, and the CF-CH₃ bond is only observed for the sample etched in CF₄ plasma. It is believed that this is affected mainly due to the CH₃ bond is elongated by the fluorination of the CF stretching. These results indicate that O₂ and CF₄ plasma treatment of DLC films can generate hydroxyl and fluorinated groups, producing hydrophilic and hydrophobic surfaces, respectively.

Further, some of the big absorption peaks in the wavenumber range of 600–1400 cm⁻¹, as shown in Fig. 1, is considered to be absorption originating in the film itself, since the same absorption is observed for as-deposited DLC film.

AFM images of the as-deposited DLC, and O₂ and CF₄ plasma-treated DLC films are shown in Fig. 2. The average surface roughness measured over an area of 1 μm x 1 μm was 0.171 nm for the as-deposited DLC, and for the O₂ plasma-treated DLC were 0.255, 0.225, and 0.2 nm, which are shown in Fig. 2(a)-(d). The O₂ plasma-treated DLC surfaces were rougher than the as-deposited DLC due to the ion-bombardment energy. On the other hand, the CF₄ plasma-treated DLC, the average roughness values were 0.171, 0.154, and 0.133 nm, which are shown in Fig. 2(c)-(g). The CF₄ plasma-treated DLC surfaces were smaller than the as-deposited DLC. This phenomenon may occur due to the continuous film growth processes, enhancing the increased of film thickness, resulting a decreased in the surface roughness.

Contact angle and surface energy measurements have great utility in characterizing the wettability of materials. The contact angle and surface energy results from the as-deposited DLC, and O₂ and CF₄ plasma-treated DLC films are shown in Table 1. The as-deposited DLC film tended to be a hydrophobic surface, with a water contact angle of approximately 75°, while the O₂ plasma-treated DLC films tended to be hydrophilic surfaces, with a water contact angles of approximately 40°—43°. The water contact angles for all the O₂ plasma-treated DLC film surfaces were lower than that of the untreated DLC film surface, indicating that hydrophilic DLC can be obtained by O₂ plasma treatment.

### Table 1: Contact angle and surface energy of the as-deposited DLC compared to O₂ and CF₄ plasma-treated DLC films.

| Sample          | RF Power (W) | Treatment Time (min) | Contact angle (°) | Surface energy (mJ/m²) |
|-----------------|--------------|----------------------|-------------------|------------------------|
|                 |              |                      | Distilled water   | Diiodomethane          | Ethylene glycol       | θ° | θ’’ | θ’’’ | θ’’’’ |
| DLC             |              |                      | 74.8              | 30.3                   | 43.7                   | 40.8 | 3.3 | 2.1  | 46.2  |
| O₂ plasma       | 100          | 30                   | 40.8              | 36.2                   | 20.7                   | 23.3 | 41.7| 22.1 | 87.1  |
| treatment       |              |                      | 43.1              | 35.7                   | 18.8                   | 25.3 | 33.7| 20.1 | 79.1  |
| CF₄ plasma      | 100          | 30                   | 42.3              | 36.0                   | 19.4                   | 25.1 | 34.0| 20.2 | 79.3  |
| treatment       |              |                      | 91.0              | 67.7                   | 62.4                   | 26.7 | 0.7 | 28.4 |
|                 | 300          |                      | 97.4              | 70.0                   | 66.4                   | 25.7 | 0.8 | 26.5 |
|                 | 500          |                      | 97.3              | 70.1                   | 70.2                   | 25.2 | 0.7 | 25.9 |

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Further, the total surface energy also increased (46.2 mN/m to 87.1 mN/m) with O₂ plasma treatment of the DLC film surfaces. According to Yin et al., oxygen plasma produces energetic oxygen species that can bond easily to the DLC film surface. This can increase the concentration of carbon-oxygen structures on the DLC film surface, resulting in increased hydrophilicity and contributing to the adsorption hysteresis related to high surface energy. On the other hand, the CF₄ plasma-treated DLC films were hydrophobic surfaces, with a water contact angle of approximately 91°-97°, and the surface energy values also decreased after CF₄ plasma treatment. The water contact angles for all the CF₄ plasma-treated DLC film surfaces were higher than that of the as-deposited DLC film surface, indicating that hydrophobic DLC can be obtained by CF₄ plasma treatment. Furthermore, the total surface energy ($\gamma_T$) also decreased (46.2 mN/m to 25.9 mN/m) with CF₄ plasma treatment of the DLC film surfaces. The decreasing total surface energy was largely ascribed to the decrease in the polar component (3.3 mN/m to 0 mN/m). It is well known that a decrease in the polar component on a surface favors the reduction of the wettability, resulting in higher contact angles and smaller surface energies.

The friction coefficients of the as-deposited DLC, and O₂ and CF₄ plasma-treated DLC films were measured under ambient air and are shown in Fig. 3(a) for the O₂ plasma-treated DLC, and Fig. 3(b) for the CF₄ plasma-treated DLC. The influence of O₂ and CF₄ plasma treatment on the friction coefficients was examined. As shown in Fig. 3(a), all the films were comparatively stable, with a friction coefficient of approximately 0.1-0.2. However, it is quite obvious that the friction coefficient of the as-deposited DLC was lower than that of the O₂ plasma-treated DLC films. It is well known that the DLC surface is etched by the energetic plasma, and the surface roughness of DLC increases after O₂ plasma treatment. The friction coefficients of the O₂ plasma-treated DLC films were therefore higher than that of the as-deposited DLC. In the case of CF₄ plasma-treated DLC, as shown in Fig. 3(b), all the films were comparatively stable, with a friction coefficient of approximately 0.12. However, the friction coefficients of CF₄ plasma-treated DLC films were not stable in the initial phase (0-2000 cycles). This phenomenon may occur due to the increased cross-links, which can restrict the sliding of the molecular chains, resulting in an increased friction coefficient. Therefore, it was concluded that the CF₄ plasma treatment less influenced the friction coefficient than O₂ plasma treatment on the DLC film surface due to the presence of fluorinated group, which is well known to decrease the friction coefficient.

![Fig. 2](image-url)  
*Fig. 2* AFM images and average roughness (Ra) of the as-deposited DLC, and O₂ and CF₄ plasma-treated DLC films.
4. Conclusion

O$_2$ and CF$_4$ plasma treatment was successfully performed on DLC film surfaces synthesized on Si(100) wafers using the PBIII technique. The films were investigated in terms of their wetting and tribological properties after O$_2$ and CF$_4$ plasma treatment using ATR-FTIR, AFM, ball-on-disk friction testing, and contact angle measurements. The results indicated that hydroxyl group was generated on the O$_2$ plasma-treated DLC film surfaces, with a surface roughness of approximately 0.20-0.25 nm, while fluorinated group was also generated on the surface of the CF$_4$ plasma-treated DLC with surface roughness of approximately 0.16-0.21 nm. The O$_2$ plasma-treated DLC films presented hydrophilic surfaces, while CF$_4$ plasma-treated DLC indicated hydrophobic surfaces, as evidenced by their contact angles and surface energies. Further, the CF$_4$ plasma-treated DLC film surfaces exhibited lower friction coefficients than O$_2$ plasma-treated DLC due to the lower surface roughness and the presence of fluorinated group.

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