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ORIGINAL PAPER

Tribological Performance of Alternating-Layered Si-DLC/DLC Films Under Humid Conditions

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Abstract The tribological behavior of alternating-layered diamond-like carbon (DLC) films was examined under a variety of humid conditions. Alternating deposited layers with Si-incorporated DLC (Si-DLC) and DLC films were prepared using a hybrid coating system. The residual stress of the alternating-layered films was reduced while the hardness was relatively less dependent on the number of alternating-layered sets. A ball-on-disk type tribological test was carried out under the following humid conditions: dry, 50% and 90% relative humidity. The friction coefficient for higher number of alternating-layered sets decreased with increasing humidity conditions but there was no dependency on the wear rate.

Keywords Diamond-like carbon · Si-DLC · Alternating-layered · Friction · Humidity

1 Introduction

Diamond-like carbon (DLC) films have attracted considerable research interest on account of their widespread applications, such as protective coatings for optical windows, magnetic storage disks, car parts, biomedical coatings, micro-electromechanical devices, and micro-actuators [1–5]. Although DLC films are strong candidates for low friction and good wear resistant coatings, there are some drawbacks, such as the high residual compressive stress and fragility in humid environments [6]. Recently, several methods for incorporating metals or Si into DLC films [7–9] or alternating-layered coatings of metal–DLC/DLC systems had been developed to improve the stability under environmental conditions [10, 11]. Okuri and Arai reported that Si-DLC films could reduce the friction coefficient to approximately 0.05 regardless of the test conditions [8] but they showed poorer wear resistance than DLC films due to the reduced hardness. Dress et al. reported that the properties of DLC films could be enhanced by alternating-layered coatings, such as Si-DLC/DLC, with a low residual compressive stress level and high wear resistance [10]. However, there are few reports on the tribological behavior of alternating-layered Si-DLC/DLC coatings under a range of environments [11, 12].

In this study, the tribological behavior of alternating-layered Si-DLC/DLC films was examined under a range of humidity conditions by varying the number of multi-layer sets. The hardness was evaluated by nano-indentation and the residual compressive stress was calculated from the radius of curvature measured using a two-beam laser method. The friction coefficient and wear volume of each set of films were measured using a wear test under a variety of humid conditions. The wear scar of the balls was analyzed by optical microscopy.

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2 Experimental Details

2.1 Si-DLC/DLC Films Preparation

DLC, Si-DLC, and alternating-layered sets of Si-DLC/DLC films were deposited on p-type (100) Si wafers

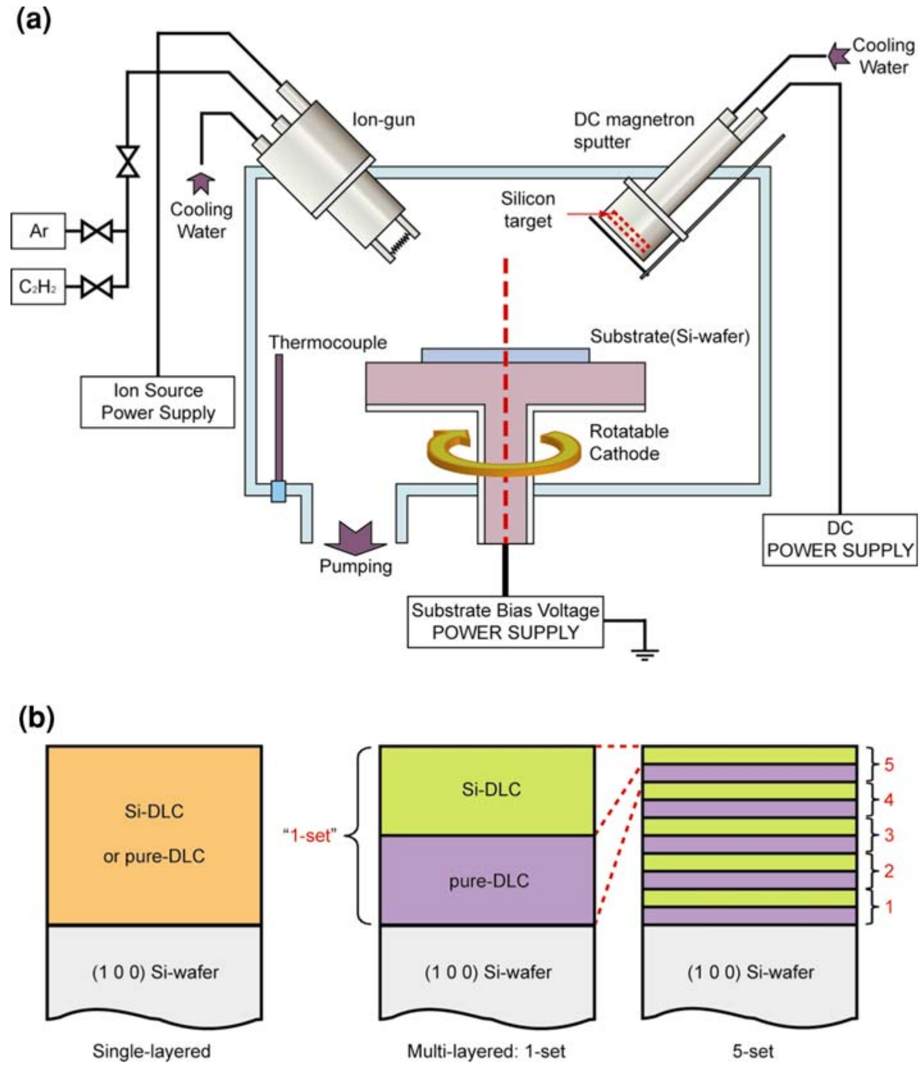

Fig. 1 **a** Schematic diagram of the hybrid coating system and **b** schematic structure of the deposited alternating-layered Si-DLC/DLC films

using a hybrid coating system (Fig. 1a), which was equipped with an ion gun for DLC film deposition and a DC magnetron sputter gun for incorporating Si atoms into the DLC matrix. The Si substrates were cleaned ultrasonically with acetone and blown with N_2 gas. After introducing the Si substrates, the chamber was heated to 120 °C to evaporate the water molecules in the chamber, and then evacuated to $<2.7 \times 10^{-4}$ Pa. Subsequently, the substrates were cleaned again by argon ion bombardment with a substrate bias at −600 V for 30 min to remove the surface native oxide, which improved the interfacial adhesion between the Si substrate and buffer layer of the amorphous SiC layer (or a-Si:C) at bias of −200 V for 5 min and a working pressure of 0.4 Pa before depositing various sets of Si-DLC/DLC films. The DLC Films were prepared using mixed gases of acetylene (C_2H_2) and argon without a bias voltage. The anode current, voltage, and working pressure of the ion gun were 2.0 A, 110 V, and 0.66 Pa, respectively. The silicon source for the synthesis of Si-DLC films was sputtered by magnetron sputtering during the DLC deposition process with Ar gas. In this process, the supplied power of the sputter gun was 20 W. Si-DLC/DLC alternating-layered films were deposited with alternate sequences of pure DLC and Si-DLC films, as shown in Fig. 1b. The number of alternating layers of the Si-DLC/DLC films was varied from 1 to 10, in which the thickness of each layer was varied by controlling the deposition time. The total thickness of the films was 500 nm (see Fig. 1b).

The hardness of the films was assessed by nano-indentation (MZT-4, AKASHI Co.), and the residual stresses were determined by measuring the radii of curvature of the Si strips, 100 μm in thickness, using Stoney's equation [13]. Rutherford back scattering spectroscopy (RBS) (MEV Ion Beamaccelerator System, National Electrostatic Corp.) with a collimated 2 MeV $^4He^{2+}$ ion beam was used to confirm the composition of the 10-set Si-DLC/DLC alternating-layered films.

2.2 Wear Test Under Various Humid Conditions

The tribological properties, such as the friction coefficient and wear behavior of the samples, were assessed using a ball-on-disk type tribo-meter under a normal load at 2 N and a rotational speed of 10 cm s^{-1} under a variety of relative humidity (RH) conditions: dry air with less than 10% RH and a humid air with 50% and 90% RH. The sample was adhered to a flat SUS-steel plate and rotated against a stationary ruby ball of 3 mm in diameter. The friction coefficient between the film and ball was obtained automatically using a PC interface system. The wear rates of the films were calculated by measuring the worn-out volume in the wear track. The wear behavior in the wear scar of the ball surface was observed by laser microscopy.

3 Results and Discussion

3.1 Multi-Layered Films Characterization

Figure 2 shows the results of RBS analysis for the alternating Si-DLC/DLC layer with the 10-set case. The results confirmed that the Si-DLC/DLC multi-layer contained 0.5 at.% Si, which is similar to the amount of Si at.% for the different number of sets of alternating layers and Si-DLC films. Figure 3 shows the micro-hardness and residual stress of the DLC, Si-DLC, and alternating-layered Si-DLC/DLC films. The hardness value (~30 GPa) of the Si-DLC film was slightly lower than that of the DLC film

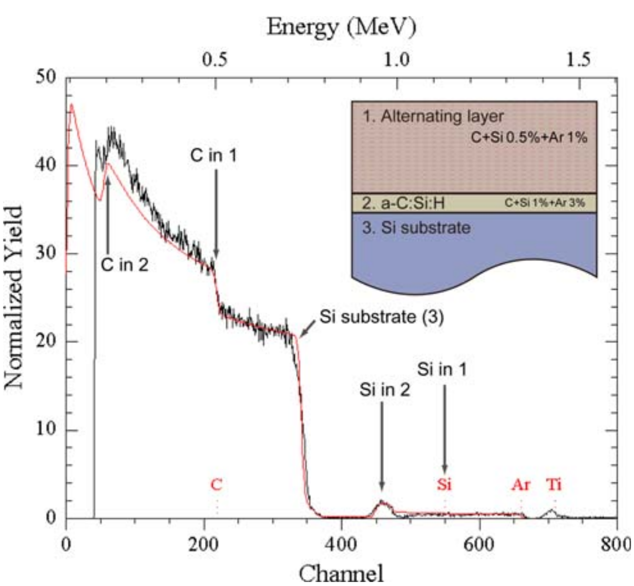

Fig. 2 Silicon concentration in a 10-set of Si-DLC/DLC film by Rutherford backscattering spectroscopy (RBS). Inserted numbers of 1, 2, and 3 indicate each alternating-layer, a buffer of SiC and Si substrate, respectively. The *red solid line* is a PUMP simulation

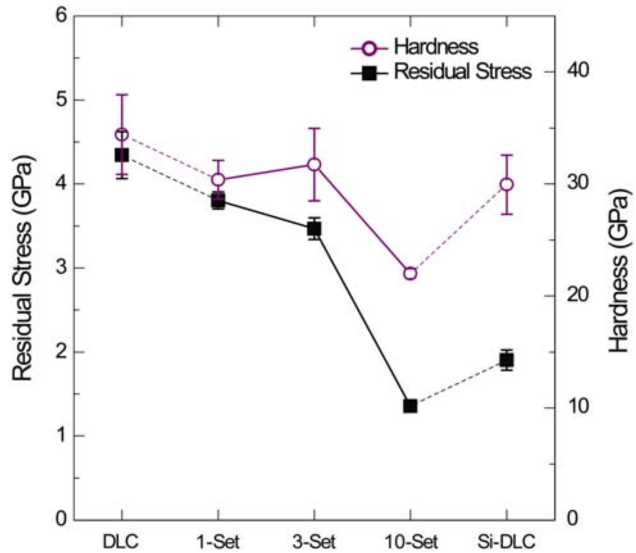

Fig. 3 Residual stress and micro-hardness of DLC, Si-DLC, and Si-DLC/DLC alternating-layered films

(~35 GPa). However, the residual stress (~2.0 GPa) of the Si-DLC decreased dramatically in comparison to that of the DLC film (~4.3 GPa). This can be explained by the carbon networks being weakened slightly by the incorporation of Si, which would play a role in stress absorption [14]. However, further studies will be needed to clarify this because the 10-set of alternating-layered Si-DLC/DLC film showed a significantly lower stress level than the Si-DLC film.

3.2 Tribological Behaviors in Various Environment

Figure 4 presents the frictional behavior and change in the mean friction coefficients for DLC, Si-DLC, and alternating-layered films under dry and humid air conditions. In dry air conditions, the friction coefficient was very low (<0.05) regardless of the number of sets (Fig. 4a, d). However, the friction coefficients for all samples increased significantly at 50% and 85% RH (Fig. 4b, c). Moreover, the frictional behavior of the DLC film was unstable at a relative humidity of 50% (Fig. 4b) compared to that obtained under the dry air condition. The friction coefficient of a single set of DLC and Si-DLC increased from ~0.05 in dry air to almost 0.2 in humid air, indicating that the friction coefficient of single-layered films strongly depends on humidity, which is similar to the previous results in that Si-DLC with a higher Si content between 5 and 10 at.% showed a low dependency on humidity [6, 15, 16]. While the friction coefficient of the alternating-layered films was lower than those of single-layered films under humid air conditions, it decreased with increasing set of alternating-layered films under humid air conditions (Fig. 4d).

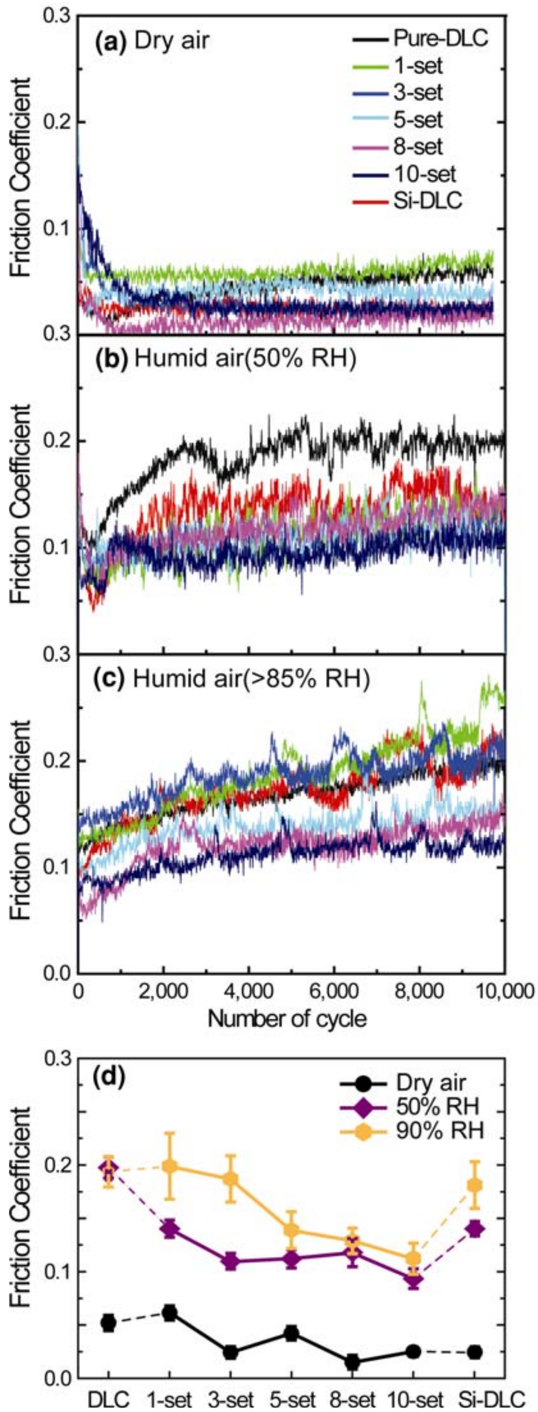

Fig. 4 Frictional behavior of DLC, Si-DLC, and Si-DLC/DLC alternating-layered films as a function of **a** dry air, humid air with **b** 50% RH and **c** 90% RH, and **d** change in the mean friction coefficients under various humidity conditions

The dependency of the wear rates on humidity was also examined by exploring the worn-out volume of the wear track formed on the films after the wear test. Figure 5 shows that the wear rates of the pure DLC film decreased linearly with increasing humidity, while the Si-DLC film

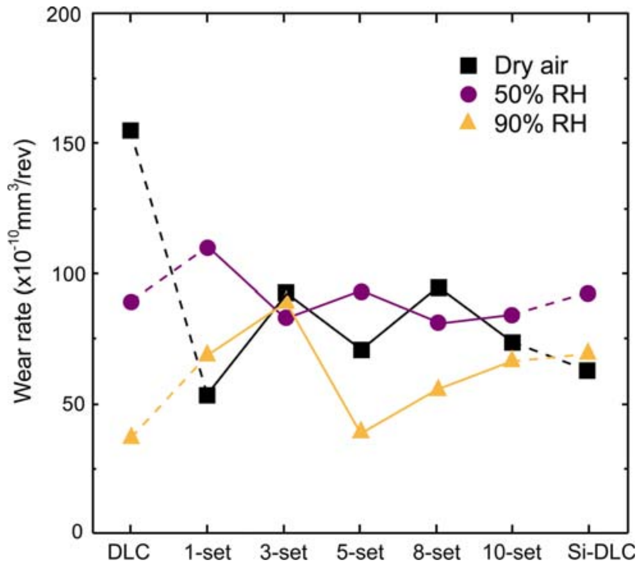

Fig. 5 Change in the wear rates for DLC, Si-DLC, and Si-DLC/DLC alternating-layered films under various humidity conditions

showed less dependency on moisture and was less worn out at lower humidity than DLC. In the case of alternating-layered films, the dependence of the wear resistance on humidity was minimized by increasing the set number of alternating layers, even though the trend in wear resistance was irregular with increasing relative humidity. In particular, the films with 3- and 10-set alternating layers showed almost no dependency on humidity.

The tribological behavior, such as the friction coefficient and wear resistance, would be affected by the hardness, surface roughness, and chemical reaction at the interface of both materials, which are sliding in contact with each other. The hardness of the films would play an important role in reducing the friction coefficient in dry air, as shown in Figs. 3 and 4d. However, under humid conditions, the chemical reaction between the film surface and ball surface should be considered to be a main parameter that governs the tribological behavior [17]. Figure 6 shows optical images of the wear scar for DLC films and 10-set alternating-layered films under three humid conditions, dry, 50% and 90% RH. Here, the black arrows indicate the sliding direction of the ball. In dry air, the wear scar of DLC film (Fig. 6a) and alternating-layered film (Fig. 6d) showed a similar surface morphology. However, a lump of wear debris that accumulated in the head of the wear scar of the DLC film (Fig. 6b) and alternating-layered film (Fig. 6e) was observed at 50% RH. With further increase in humidity with 90% (Fig. 6c), the debris on a pure DLC film was agglomerated easily due to moisture, which affected the tribological behavior with the change in RH. In particular, at 90% RH, agglomerated debris with a gel-type appearance was observed in front of the wear scar of the

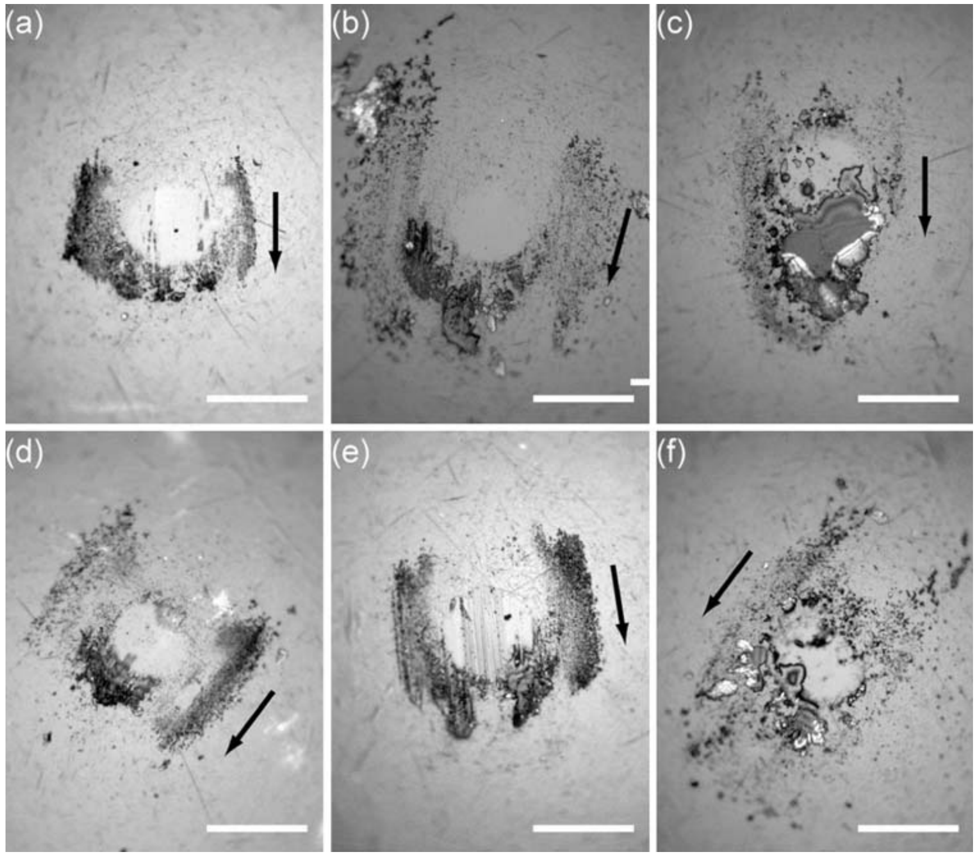

Fig. 6 Optical images of the wear scar on counter balls; the pure DLC films (**a–c**) and 10-set of Si-DLC/DLC alternating-layered films (**d–f**) with (**a**); **d** at dry air; **b**, **e** at 50% RH; and **c**, **f** at 90% RH. Bars = 10 μm

ball against the pure-DLC, as shown in Fig. 6c. On the other hand, the wear debris around the wear scar of the alternating-layered film showed less agglomeration than that of the DLC film (see Fig. 6c, f).

4 Conclusions

This study examined the mechanical properties and tribological behavior of 0.5 at.% Si-incorporated Si-DLC/DLC films as a function of the number of alternating layers under three humidity conditions (dry air, 50% and 90% RH). The high hardness and wear resistance of pure DLC under dry conditions and the ability of Si-DLC to reduce the residual stress were combined by depositing alternating-layered Si-DLC/DLC. The hardness and residual stress were strongly dependent on the number of alternating layers of Si-DLC/DLC set while the tribological behavior improved for the alternating-layer films but the number of alternating layers had no significant effects. Although the friction coefficients of all cases increased with increasing relative humidity, the alternating-layered films showed a relatively lower friction coefficient than that of the single-layered DLC or Si-DLC films. The wear rate of the pure DLC film depends largely on the humidity while the Si-DLC and Si-DLC/DLC alternating layers were less affected by humidity.

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