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Abstract

In recent years, hydrogenated diamond-like carbon (DLC) films have attracted great interest because of their unique tribological properties. Earlier work showed that the friction coefficient of the diamond-like carbon (DLC) films varies between 0.001 and 0.6, depending on the synthesis method, counter-face materials and testing conditions.

In this project, we investigated the effect of relative humidity on the friction properties of two kinds of hydrogenated diamond-like carbon films: one contained sulfur, and another was sulfur-free. Both kinds of hydrogenated carbon films were grown by magnetron sputtering of graphite in an argon-hydrogen plasma or argon-hydrogen-hydrogen sulfuride plasma. Both plasma contained about 13% hydrogen gas. The influence of sulfur content and substrate bias on the friction properties and the surface topography of the films was also investigated.

Introduction

Friction

Friction is the resistance between two surfaces that are in contact with each other. Friction = $\mu N$, where $N$: Normal force, $\mu$:Coefficient of friction

Coefficient of friction depends on the surface roughness, molecular forces between the two surfaces, such as covalent force, van der Waals forces and electrostatic attraction, and environment, such as relative humidity.

Diamond-like Carbon film

Diamond-like carbon (DLC) films are amorphous carbon films. They exhibit unique mechanical and tribological properties, such as being extremely hard, chemical stable and providing some of the lowest known friction coefficient on a sliding surface. These properties make them suitable for a number of applications such as protective coatings for mechanical elements, magnetic recording media and heads in computer data storage systems.

Hydrogen plays an important role in the frictional properties of the DLC films. Firstly, hydrogen added to the DLC film can pair with the covalent or free $\sigma$-bond of carbon atoms, so that the free $\sigma$-bond is eliminated. Secondly, it can prevent $\text{C}=$ $\text{C}$ double bonding, in turn, the $\pi$-$\pi^*$ interactions. Finally, by adding hydrogen, a hydrocarbon top-coats surface is formed. The force between the $\text{C}=$ $\text{H}$ bonds is only weak van der Waals interactions, so superlow friction coefficient achieves.
Various physical and chemical methods have been employed to synthesize DLC films, such as sputtering, pulsed laser deposition, plasma-enhanced chemical vapor deposition (PECVD) and filtered vacuum arc. In this project, Magnetron sputtering was used.

**Expected effect of sulfur on friction**

When friction test is performed at ambient relative humidity, the capillary force will be dominant. Adding sulfur to the DLC films should reduce the environmental effect. Because sulfur has low surface energy, sulfur will most likely go on the film surface. And as sulfur is highly electronegative, the dipoled water molecules on the film surface will be aligned, with the positive pole towards the films surface. As like charge repel, the water molecules will repel each other and the water content on the film reduces. Thus, friction coefficient at ambient relative humidity reduces.

**Sputtering**

Sputtering is a vacuum process used to deposit thin films on substrates. It is performed by applying a high voltage across a low-pressure gas, usually argon at about 5 millitorr. A plasma, which consists of equal number of electrons and gas ions in a high-energy state and emits a colorful halo of light, is created in the sputtering process.

During sputtering, energized plasma ions strike a target--the desired coating material, and cause atoms from that target to be ejected and travel to, and bond with, the substrate. The energy of neutrals (reflected atoms and sputtered atoms) carry to the growing film depends strongly on system pressure. Plasma ions also strike the film surface. These arrive with energies that largely depend on the potential gradient across the anode plasma sheath and gas pressure. A negative bias voltage placed on the substrate can substantially increase the energy of bombarding ions.

**Magnetron sputtering**

Magnetron sputtering is the most widely used variant of DC sputtering. This technology uses powerful magnets to confine the plasma to the region closest to the target plate. That makes the electron/gas molecule collision process much more efficient. Thus, a higher deposition rate is provided by magnetron sputtering than simple DC sputtering. A schematic diagram of a magnetron sputtering is shown in figure 1.
**Atomic Force Microscopy (AFM)**

Atomic force microscopy (AFM) also called Scanning Force Microscopy (SFM). There are three primary modes of AFM: Contact Mode AFM, Non-Contact Mode AFM and Tapping Mode AFM. Contact Mode AFM was used in this research.

**Contact Mode AFM**

Contact mode AFM operates by scanning a tip attached to the end of a cantilever across the sample surface while monitoring the change in cantilever deflection with a split photodiode detector. The tip contacts the surface through the adsorbed fluid layer on the sample surface. A feedback loop maintains a constant deflection between the cantilever and the sample by vertically moving the scanner at each \((x, y)\) data point to maintain a "setpoint" deflection. By maintaining a constant cantilever deflection, the force between the tip and the sample remains constant. The distance the scanner moves vertically at each \((x, y)\) data point is stored by the computer to form the topographic image of the sample surface. Fig. 2 is the schematic diagram of the contact mode AFM.

![Fig. 2 schematic diagram of the contact mode AFM](image)

**Friction Test**

Friction tests can be performed on a wide variety of materials including fluid lubricants, greases, cutting fluids, metals, composites, ceramics, polymers, and coatings. Several configurations are available for friction tests, such as Pin on Disk, and Cylinder on Flat contact area configurations.
pin-on-disk tribometry

In pin-on-disk tribometry, a flat, a pin or a sphere is loaded onto the test sample with a precisely known weight. The pin is mounted on a stiff lever, designed as a frictionless force transducer. The deflection of the highly stiff elastic arm, without parasitic friction, insures a nearly fixed contact point and thus a stable position in the friction track. The friction coefficient is determined during the test by measuring the deflection of the elastic arm. Furthermore, the control of the test parameters such as speed, frequency, contact pressure and varying time, and the environmental parameters, temperature, humidity and lubrication allow a close reproduction to the real life conditions.

Experimental details

The hydrogenated diamond-like carbon films were deposited on Si(100) wafer by magnetron sputtering with target power of 100W, target voltage of 244V, substrate bias of -25V, -50V, -75V, -100V respectively, and total pressure of 6mTorr. The sputter gas for sulfur free hydrogenated diamond-like carbon films was argon-hydrogen plasma containing 13% hydrogen gas. The sputter gas for sulfur added hydrogenated diamond-like carbon films was argon-hydrogen-hydrogen sulfide plasma containing 13% hydrogen gas and 0.09% hydrogen sulfide. And one more sulfur added hydrogenated diamond-like carbon films was made under plasma containing 0.18% hydrogen sulfide at substrate bias of -50V.

The topography of the samples were measured by contact mode AFM with scanning range equaled to 5µm x 5µm. The root-mean-squares of the roughness were calculated by the computer. The friction coefficients of the samples were obtained by using pin-on-disk sliding tester. The sliding velocity was set to be 200rev/ min and the load was 10N. The friction coefficients were measured at both ambient relative humidity(RH) and < 1% RH. A bare steel ball was used to slide on the DLC films <1%RH was achieved by filling the chamber with dry air. After the RH meter reached 0%RH, wait for 1hour.
**Results and Discussion**

**Appearances of the sample**

The films made under -25V, -50V and -75V substrate bias were firmly attached with non-uniform color in which the darkness, from black, deep purple, green to light orange, was proportional to the distance from the target. The phenomenon could be accounted for the change of the film thickness which was because of higher deposition rate at the region near the target.

The films grown under -100V substrate bias were delaminate. See fig.4. The reason was that the negative bias voltage placed on the substrate could substantially increase the energy on the bombarding ions, the bombardment between the plasma and the films became more vigorous as the substrate bias increased to -100V. Thus, higher stress was induced in the films under -100V substrate bias.

\[
\text{Elastic-strain energy per unit volume} = \frac{\sigma \varepsilon}{2}
\]

\[
= \frac{\sigma^2}{2E}
\]

where \(\sigma\) is the stress, \(\varepsilon\) is the strain, \(E\) is the Young’s Modulus

\[
\therefore \text{The elastic-strain energy per unit volume in the film made under -100V substrate bias was higher than others, and the total energy/area} = \frac{\sigma^2 t}{2E}, \text{where} \ t \ \text{is the thickness of the film. As the film grew thicker, the elastic-strain energy per area in the film increased. When the elastic-strain energy stored in the film is larger than the surface energy, the film will be delaminate. See fig.5}
\]

![Fig.4 Schematic diagram of delaminate](image-url)
Fig. 5 Energy vs thickness

**Topography images for the samples**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Substrate bias: -25V</th>
<th>-50V</th>
<th>-75V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur free hydrogenate diamond – like carbon (CHx)</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Hydrogenate diamond – like carbon with 0.09% Sulfur containing (CHx+S)</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Roughness of the samples:

Voltage effect on roughness:

The roughness root-mean-square values of the samples were more or less the same. See fig. 6 which shows the average of the roughness “root-mean-square” values vs the substrate bias voltages

The effects of the substrate bias on the roughness of the films were negligible.

The topography of the films were depended on the growth mode of the film and the energy of the bombarding ions. The growth modes of these films were layer mode. That is the films grew layer by layer and would be very smooth. From the graph, we could see that the roughness was only about 0.15nm.
The defect densities usually increase as the ions energy rises, thus, the film may be rougher under high substrate bias. However, when the energetic ions cause atoms in the film to resputter. The less tightly bound atoms at atomic projections and regions of high curvature that are particularly vulnerable to resputtering under angular impact. Therefore, the films will become smoother. The topography of the films will finally depend on the combination of all these effects.

**friction test**

Fig. 7 shows the typical graph for friction coefficient vs time. The flat part of the graph indicates the value of the kinetic friction coefficient of the sample.

![Fig. 7](image)

**Relative humidity effect and voltage effect on friction coefficient**

Fig. 8 shows the average values of the friction coefficient for sulfur free hydrogenated diamond-like carbon films vs substrate bias at both ambient RH and <1%RH.
Fig. 8 shows the average values of the friction coefficient for sulfur contained hydrogenated diamond-like carbon films vs substrate bias at both ambient RH and <1% RH.

Fig. 9 shows the average values of the friction coefficient for sulfur contained hydrogenated diamond-like carbon films vs substrate bias at both ambient RH and <1% RH.
From fig.8 and fig.9, it could be concluded that the voltage did not have significant effect on the friction coefficient of the films too. After adding the error bar to the results, the friction coefficients of the films were overlapped.

On the other hand, it is obvious that the friction coefficients of the films were higher when measuring at ambient RH, which was about 1. but at <1% RH, the friction coefficient was only about 0.1. The reason was that in dry test environments, the force between the two counter-faces was mainly weak van der Waals forces. But in wet test environment, there was strong capillary force between the counter-faces. Therefore, the friction coefficients of the films were higher when measuring at ambient RH.

**Sulfur effect on friction coefficient**

Fig.10 shows the average values of the friction coefficient for the two sulfur contained hydrogenated diamond-like carbon films made under -50V substrate bias vs substrate bias at both ambient RH and <1%RH.

The effects of sulfur on the friction coefficient were not significant at both ambient RH and <1% RH. The reason of losing the expected sulfur effect is that a bare steel ball was used in the friction tests, although sulfur had an effect on reducing the water content on the films, the counter-face: steel ball did not have this effect; the water content on the films could not be reduced effectively. Thus, capillary force was still dominant in the measurements.
**Conclusion**

The coefficient of friction of the hydrogenated diamond-like carbon film containing 13% hydrogen content made by magnetron sputtering could be as low as 0.01 at <1% relative humidity. The voltage did not have significant effect on the roughness and friction coefficients of the films. The coefficients of friction of the films measured at ambient RH were much higher than that measured at <1% RH. The sulfur effect on the friction coefficient was not significant because the counter-face material used in the friction test was not sulfur added hydrogenated DLC film, but steel ball, which was containing high water content. According to my partner’s result, using sulfur added hydrogenated DLC film as the counter-face, the coefficient of friction of the films could be reduced at ambient RH.

**Acknowledgement**

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**Reference**

6. Milton Ohring, Materials Science of Thin Film