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Surface & Coatings Technology 196 (2005) 226–230

SURFACE & COATINGS TECHNOLOGY

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# Effect of electron temperature on the DLC film properties

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Available online 27 October 2004

**Abstract**

It is well known that diamond-like carbon (DLC) films made by plasma chemical vapor deposition (CVD) have such excellent tribological characteristics that the lifetimes of machine tools and dies are considerably improved when the films are deposited on them. However, the application field has been somewhat restricted since the film-property control has been a little more difficult than other hard coatings like TiN and TiAlN.

In this paper, we try to find out the key factors that control the film properties, from the viewpoint of plasma chemistry. The electron-density distribution in plasma is measured with a Langmuir probe while DLC films are formed on the specimen surfaces of both silicon and tungsten carbide (WC). Hardness and scratch tests are carried out to evaluate the mechanical characteristics of the films. The solid-state structures are investigated by Raman spectroscopy. As a result, it is shown that the electron temperature of plasma strongly affects the film properties such as friction, wear and hardness.


*Keywords:* DLC film; PBII; Hardness; Electron temperature; Hydrogen; TRIM; Amorphous; Plasma source ion implantation

## 1. Introduction

Diamond-like carbon (DLC) films have many useful properties for industrial applications. Especially, the tribological characteristics such as friction and hardness are excellent. However, the films also have some weak points. Since the control of film property has been a little more difficult than other hard coatings like TiN and TiAlN, the application field has been somewhat restricted. Furthermore, the weak points of DLC film such as film peeling and low working temperature restrict the application field. For the application to machine tools and dies, the most necessary characteristics are hardness, critical load and fiction coefficient. Especially, the most important characteristic for industrial applications is the critical load. This characteristic is improved by forming a mixed layer with other element or by adopting a buffer layer.

On the other hand, this characteristic is improved by ion mixing with plasma-based ion implantation (PBII). PBII, the original technique of which was developed by Conrad et al. [1], can modify the surface properties of materials. Combination of PBII with deposition will be a more cost-effective technique for engineering parts having a three-dimensional complex shape. A new coating system was developed, which consists fundamentally of plasma CVD and ion mixing [2,3]. However, this technique is not sufficient for controlling the film properties.

In this paper, we try to find out the key factors of plasma that determine the physical properties of films. The electron density and temperature are measured with a Langmuir double-probe.

## 2. Experimental

### 2.1. Apparatus and conditions for film formation

The experimental apparatus consists of a cylindrical vacuum chamber of 500 mm diameter and 800 mm length,

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doi:10.1016/j.surfcoat.2004.08.081

an RF generator (13.56 MHz, 750 W) for plasma generation and a negative high-voltage pulse power supply (−10 kV) for sample bias as shown in Fig. 1. Plasma generation is pulsed since RF power is modulated by an additional pulse generator. DLC films are formed with hydrocarbon gas of $C_2H_2$. The films are deposited on WC substrate. The coating process that consists of three stages like Ar bombardment (RF80W, high-voltage −2 kV), ion mixing (RF80W, high-voltage −8 kV) by hydrocarbon gases and DLC formations was established at the previous study [4]. In this study, DLC films are formed under the condition of gas pressure of 1 Pa, RF power of 80 W, and −2 kV pulse voltage of 10% duty. Electron density and temperature of plasma are controlled by the repetition frequency of the pulse generator. The repetition frequency of the pulse generator can be changed from 0.1 to 100 kHz and the pulse duty from 20% to 80%. At this time, the impedance matching condition for RF power with the plasma is fixed at the value of 80 W. The specific conditions of DLC films are shown in Table 1. Since the deposition rate changes depending on the condition in this table, the deposition time is chosen so that each film thickness becomes 1 μm.

Table 1
Conditions for DLC film formation by pulsed RF power

| | Electron temperature [eV] | RF power [W] | Pulse signal for RF modulation | Gas pressure [Pa] | Pulse voltage for sample bias | Thickness [μm] |
|---|---|---|---|---|---|---|
| a | 1.07 | 80 | 10 kHz, duty 20% | 1 | −2.0 kV, 2 kHz, duty 10% | ≒1 |
| | 1.69 | | 1 kHz, duty 20% | | | |
| | 2.32 | | 0.1 kHz, duty 20% | | | |
| | 2.39 | | 1 kHz, duty 30% | | | |
| b | 3.31 | 80 | 0.1 kHz, duty 40% | 1 | −2.0 kV, 2 kHz, duty 10% | ≒1 |
| | 3.95 | | 1 kHz, duty 40% | | | |
| | 4.04 | | 1 kHz, duty 70% | | | |
| | 4.17 | | 1 kHz, duty 60% | | | |
| | 4.39 | | 1 kHz, duty 80% | | | |
| | 4.43 | | 1 kHz, duty 50% | | | |

### 2.2. Measurement

The measurement of the film hardness is carried out with the dynamic ultra-micro hardness tester (Shimadzu, DUH) using a load of 9.8 mN on a triangle indenter at a loading speed of 0.355 mN/s.

Measurement of tribological properties is carried out with a ball on disk type apparatus (CSEM, Tribometer). The balls of 6 mm in diameter are made of SUJ2 alloy, and disks are made of WC–Co alloys coated with DLC films. Experimental sliding conditions are as follows: applied load is 10 N, sliding distance 150 m, sliding speed 100 mm/s, room temperature and humidity 35%.

Raman spectra of DLC films are measured at room temperature by a back scattering method using the laser Raman spectrophotometer (Dilor, LABRAM-IB). The spectra generally take the form of an asymmetric broad peak centering around 1500 $cm^{-1}$. They can be divided into several peaks corresponding to the structure of the carbon films. There are two approaches for evaluating them. The first one deconvolutes Raman spectra into a G peak at 1590 $cm^{-1}$ that corresponds to the crystalline graphitic structure and a D peak at 1360 $cm^{-1}$ that corresponds to the disordered graphitic structure [5]. However, it is conceivable that Raman spectra from bombarded polymers similar in shape to those of carbon films cannot be evaluated in detail with this operation, because they include two other peaks at 1150 and 1500 $cm^{-1}$ assigned to be linear C=C bonds with and without hydrogen, respectively [6]. Therefore, the second approach that deconvolutes the Raman spectra into four peaks at 1150, 1360, 1500 and 1585 $cm^{-1}$ was adopted in this paper. The area fractions consist of these components in DLC films can be obtained by deconvoluting the Raman spectra.

The measurement of plasma conditions are carried out with a Langmuir double-probe measurement system (JE Plasma Consult, L2P). Usually, an industrial plasma contains a lot of neutrals besides charged particles like electrons and ions. Conditions of charged particles can be characterized with a current that is flowing between two polarized electrodes inserted into the plasma. From the measured current–voltage characteristic, physical properties of the charged particles in the plasma are obtained. Double probe is especially useful for characterizing electrodeless discharges, in which a reference potential is not well defined. Practically, this probe is very useful

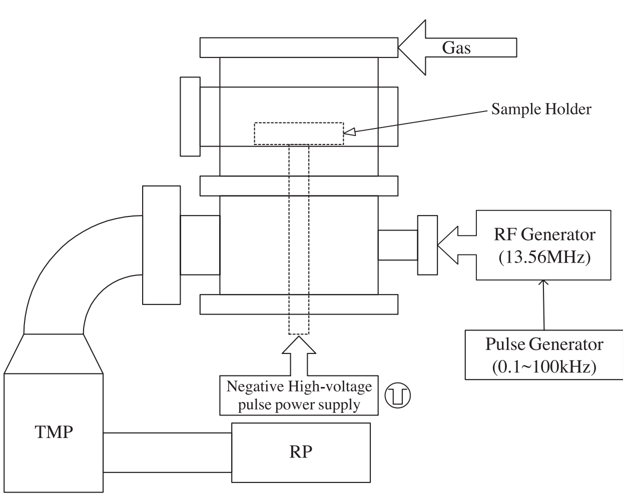

Fig. 1. Schematic drawing of DLC coating chamber.