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Study on hybrid nano-diamond films formed by plasma chemical vapor deposition (CVD)

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Abstract

Diamond-like carbon (DLC) films made by plasma chemical vapor deposition (CVD) have many useful properties for tribological characteristics. Especially, friction coefficient is very low. However, the films have weak points i.e., very low heatproof temperature of less than 300 °C and low hardness insufficient for industrial applications like machine tools. On the other hand, it is well known that diamond films made by plasma CVD have excellent hardness. But, they also have inferior properties for industrial applications, such as higher surface roughness and lower critical load than DLC films. In this study, we developed hybrid nano-diamond (HND) films that are formed by alternately depositing DLC films and diamond films in a same chamber. The HND films have sufficiently high hardness as well as excellent tribological characteristics due to the multi-layer structure of DLC and diamond. The process of forming HND films are discussed.

Keywords: DLC; PBII; Hardness; Nano; Diamond; Electron temperature; Hybrid

1. Introduction

Diamond-like carbon (DLC) films made by plasma chemical vapor deposition (CVD) have many useful tribological properties. Especially, friction coefficient is very low. However, they also have some weak points that a heatproof temperature is less than 300 °C and that the hardness of DLC films is not sufficient for industrial applications like machine tools.

On the other hand, it is well known that diamond films made by plasma CVD have excellent hardness. However, they also have inferior properties for industrial applications, such as higher surface roughness and lower critical load than DLC films.

In this study, we developed new multi-layered carbonaceous films, i.e., HND films that are made by alternately depositing DLC and diamond in a same chamber. The hybrid nano-diamond (HND) films have high hardness as well as excellent tribological characteristics because of the multi-layer structure of the DLC and the diamond as shown in Fig. 1. Both the DLC films and the nano-diamond (ND) films are formed by plasma based ion implantation (PBII) using radio frequency (RF) plasma that is ignited in pulses with inductively coupled RF power of 13.56 MHz. The processing temperature is less than 300 °C, that is, less than the heatproof temperature of DLC film. The ND density on the DLC film is controlled by adjusting the plasma parameters.

We found out that the electron temperature can be controlled by changing both or either of the pulse repetition frequency and the pulse duty of RF power, and that the hardness of DLC films can be controlled with the electron temperature [1]. In this paper, we discuss both the ND film formation and the HND films from the view point that the hardness is changed by the electron-temperature control.

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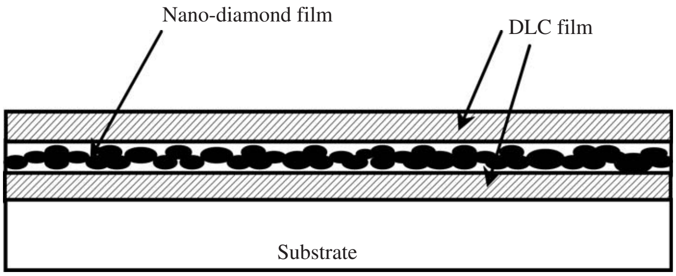

Fig. 1. Cross section of a HND film.

2. Experimental

2.1. Apparatus

The experimental apparatus consists of a cylindrical vacuum chamber of 500 mm in diameter and 800 mm in length, an RF generator (13.56 MHz, 750 W), a microwave generator for plasma generation (2.45 GHz, 3000 W) and a negative high-voltage pulse power supply (−10 kV, 2 kHz, duty10%) for sample bias as shown in Fig. 2. Plasma generation is pulsed by modulating RF power with an additional 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%.

2.2. Conditions for film formation

HND films are formed with hydrocarbon gas of C_2H_2 diluted with hydrogen gas. A HND film consists of three layers; the first layer is formed with DLC, the second is formed with ND, and the third is formed with DLC of less thickness than the first layer. In this study, the DLC layer in the HND film are formed under the condition of C_2H_2 gas pressure of 1 Pa, RF power of 80 W, and −2 kV pulse voltage of 10% duty. The ND layer in the HND film is formed under the conditions of C_2H_2 and H_2 mixture-gas pressure of 1 Pa and the same RF power and pulse bias voltage as DLC formation.

The HND film is deposited on Si and WC–Co substrate. The coating process consists of four stages, i.e., substrate cleaning by hydrogen gas (Microwave power 1000 W), Ar ion bombardment (RF 80 W, high voltage −2 kV), ion mixing by hydrocarbon gases (RF 80 W, high voltage −8 kV) and HND formation. Ar ion bombardment process is for cleaning carbonaceous compound and oxide on substrate. Ion mixing process is for improving adhesion. The most important technique in this process is controlling the electron temperature of plasma by adjusting the repetition frequency of the pulsed RF power. In this experiment, the impedance matching condition for RF power with the plasma is fixed at the value of 80 W RF power. Since the deposition rate changes depending on the condition, the deposition time is chosen so that first layer (DLC) thickness becomes 0.15 μm, second layer (ND) thickness 0.06 μm, third layer (DLC) thickness 0.04 μm.

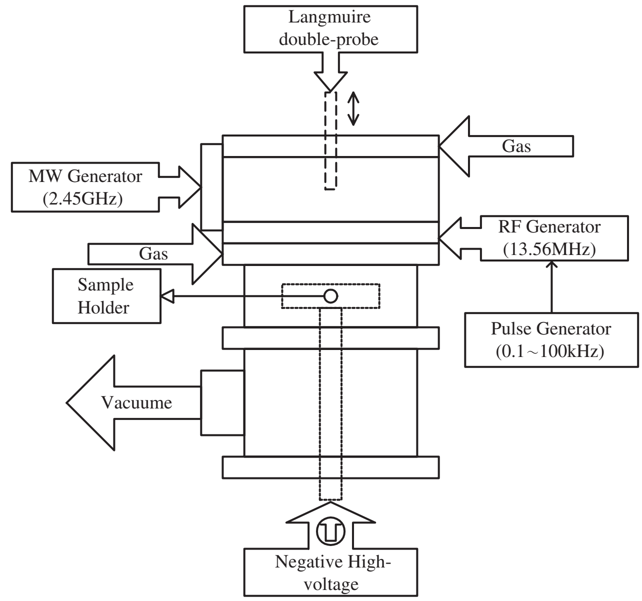

Fig. 2. Schematic drawing of HND coating chamber.

3. Measurements

The film hardness is measured with the dynamic ultra-micro-hardness tester (Shimazu, DUH) using a load of 9.8 mN on a triangle indenter at a loading speed of 0.355 mN/s. Tribological properties are measured 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 HND films. Experimental sliding conditions are as follows; applied load is 10 N, sliding distance 150 m, sliding speed 100 mm/s, room temperature 20 °C and humidity 35%.

Raman spectra of DLC films are measured at room temperature by a back scattering method using laser Raman spectrophotometer (JOBIN YVON, LabRAM). X-ray diffraction (XRD) pattern is measured by the X-ray diffractometer (Hi-star, AXSburuker).

The measurement of plasma conditions are carried out with a Langmuir double-probe measurement system (JE Plasma Consult GMbH, L2P).

4. Result and discussion

4.1. Formation of DLC films

The DLC film formation on a Si specimen is carried out with C_2H_2 gas. The DLC film formed on Si is a typical DLC Raman spectrum that has G peak at 1590/cm corresponding to the crystalline graphitic structure and D peak at 1360/cm corresponding to the disordered graphitic structure [2]. Fig. 3 shows the relationship between electron temperature and hardness of DLC films. The electron temperature can be controlled by changing both or either of the pulse repetition frequency and the pulse duty of RF