Transactions of the Materials Research Society of Japan 28 [2] 453-456 (2003)

Characteristic of DLC films formed by PBII using hydrocarbon gases

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The characteristic of DLC films was different by the plasma conditions for DLC formation as well as by the raw gases in Plasma Based Ion Implantation (PBII). In this study, the hydrocarbons of CH_4 and C_2H_2 were used as a source of carbon. RF-ICP or microwave plasma was ignited, and negative high-voltage pulses were applied, and DLC films were formed on Si wafers and WC substrates. Also, the layer of DLC film by RF and one by microwave were alternately formed and the multi-layers of the DLC films. Raman spectra of these films were measured, and the fractions of four (graphite, disordered graphite, amorphous and C-H chain) components segregated in the spectrum were calculated, these films were examined with a ultra micro hardness and friction testers, and the surfaces were observed by AFM. The characteristics of DLC films with each one layer or multi layers were discussed.
Key words: DLC film, PBII, multi layer, tribology

1. INTRODUCTION

Diamond-like carbon (DLC) films have high potentials for industrial applications, as the coefficient of friction is low, and the surface is smooth. However, the strength of their films, that is, the hardness is insufficient to apply for machining such as drilling and milling. Also, for extending the lives of punches and dies, DLC films needs to improve the hardness. In a case of DLC films of one layer, the hardness come to harder, the stress in the films becomes higher. So, the films are easy to peel off the substrates.

On the other hand, Plasma base ion implantation (PBII) modified the surface properties of materials, which of the original technique was developed by Conrad and co-workers [1]. The more cost-effective technique for engineering parts with a complex shape, and 3-dimensional surface may be to combine PBII and deposition technique. A new coating system was developed which consist fundamentally of plasma-CVD and ion mixing [2] [3].

In this paper, DLC films were formed by the system, which consists of RF and microwave plasma generation, a negative high-voltage pulse power supply for PBII. These films were examined on Raman spectra, hardness, tribological properties and surface smooth. Multi-layers of RF- and MW-DLC films are also produced on Si wafers and WC-Co alloy substrates. The performances of these films were discussed on advancing in the industrial field.

2. EXPERIMENTAL

2.1 Apparatus and film formation

The experimental apparatus consists of vacuum chamber of ϕ 500mm × L800mm with RF and microwave generators and negative high-voltage power supply. The formations of DLC films were used with hydrocarbon gases of CH_4 and/or C_2H_2. DLC films were formed on Si wafers and WC substrates by PBII method. The coating process, which consists of Ar-bombardment, ion-mixing by hydrocarbon gases and DLC formations, were acquired at the previous study [4]. In this study, the first layer of DLC film was formed by RF method with gas pressure 1 Pa, RF-power 50 W, negative pulse voltage −2 kV, duty ratio 0.1%. The second layer was formed by microwave method with MW-power 300W. Multi-layers of the DLC films were formed by RF and microwave methods by turns. The film thickness was near 1.5 μm. The individual coating times were selected at total coating times of 90 minutes. The specific conditions of DLC films were illustrated in table I.

2.2 Measurement

The measurement of the film hardness was carried out with the dynamic ultra-micro hardness tester (Shimadzu, DUH) at a load of 19.6 mN with a triangle indenter and a loading speed of 0.13 mN/s.

Tribological properties were carried out with a ball on disk type apparatus (CSEM, Tribometer). The balls are Al-alloy (A5052) of 6 mm in diameter, and the disks are WC-Co alloys coated with DLC films. Sliding conditions were as follows; applied load 10 N, sliding distance 150 m, room temperature and humidity 35%.

The surface smooth and morphology were observed evaluated by using laser microscope and AFM.

Raman spectra of DLC films were measured at atmospheric room temperature by a back scattering method using the laser Raman spectrophotometer (Dilor, LABRAM-IB). Raman spectra of DLC films generally take the form of an asymmetric broad peak centering around 1500 cm^{-1} and can be divided into several peaks corresponding to the structure of the carbon films. There are two approaches for evaluating them. The first one segregates 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 cm^{-1} and 1500 cm^{-1} assigned to linear C=C bonds with and without hydrogen, respectively [6].

Therefore, the second approach that segregates 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 segregating the Raman spectra. The measured Raman spectra were segregated into four peaks and the structures of DLC films were analyzed.

3. RESULTS AND DISCUSSIONS

3.1 Surface observations and surface roughness

Table I Conditions of DLC film formation. Fig.1 shows a scanning laser microphotograph of multi-layers of DLC film (E). This was formed by that a steel ball of 30 mm in diameter was rolled on DLC films formed on the WC substrate. DLC film of E was produced from the

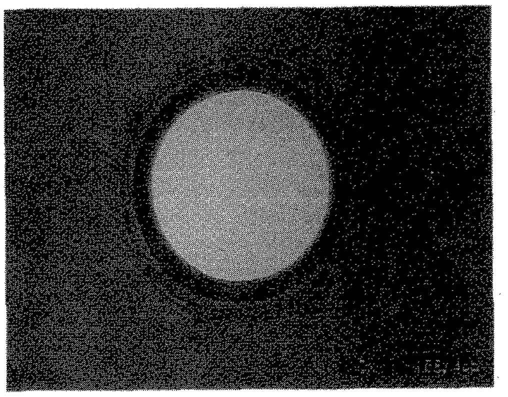

Fig.1 Scanning laser microphotograph of multi-layers of DLC film (E).

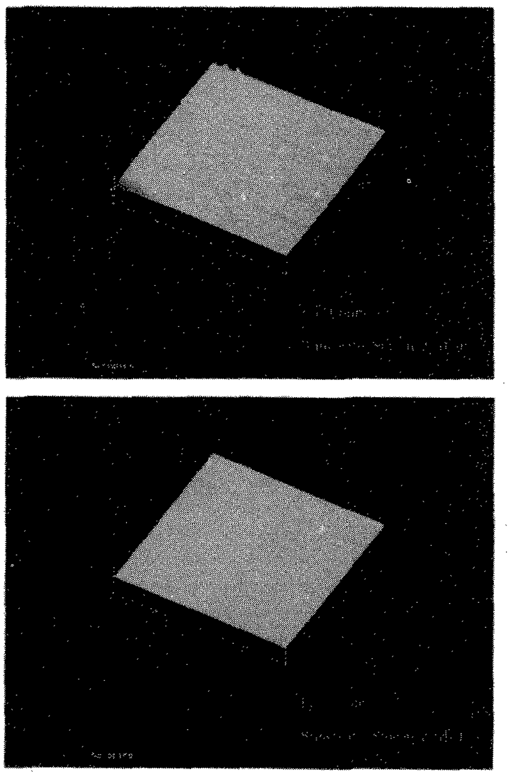

Fig.2 AFM images for RF-DLC film upper and MW-DLC film lower.

Table I Conditions of DLC film formation.

	Type of DLC	Pre-treatment	DLC formation	Total thickness(μm)	Symbol
A	RF-DLC	Ar bombardment	RF:400W, V:-2kV	1.1	○
B	MW-DLC		MW:300W, V:-1kV	1.5	□
C	multi-layers of DLC	Ion mixing with C_2H_2 -8kV, 20min	RF:50W, V:-2kV MW:300W, V:-2kV	1.5	△
D	multi-layers of DLC		RF:50W, V:-2kV MW:300W, V:-2kV	1.5	●
E	multi-layers of DLC		RF:50W, V:-2kV MW:300W, V:-2kV	1.5	■

ion-mixing layer, RF-DLC, MW-DLC, RF-DLC and MW-DLC layers. Four layers were clearly observed in the microphotograph. Fig.2 shows AFM images at the surfaces of RF- and MW-DLC films on Si wafers. The surface roughness of the former is smaller than that of the latter. The surfaces of the films were very smooth and within 2 nm.

3.3 Raman spectra

Raman spectra were measured and analyzed to characterize the structure of the DLC films. Fig.3 shows Raman spectra of RF-DLC and MW-DLC films and Raman spectrum of commercial DLC film segregated into four peaks at 1150, 1360, 1500 and 1590 cm^{-1}[7]. The area fractions were shown in Fig.4. The spectrum of MW-DLC film has the shoulder peak around 1360 cm^{-1}, but that of RF-DLC film was asymmetric broad at the center of 1500 cm^{-1}. So, in MW-DLC films the area fraction contributed to the disordered graphitic structure were rather than that to the graphitic structure.

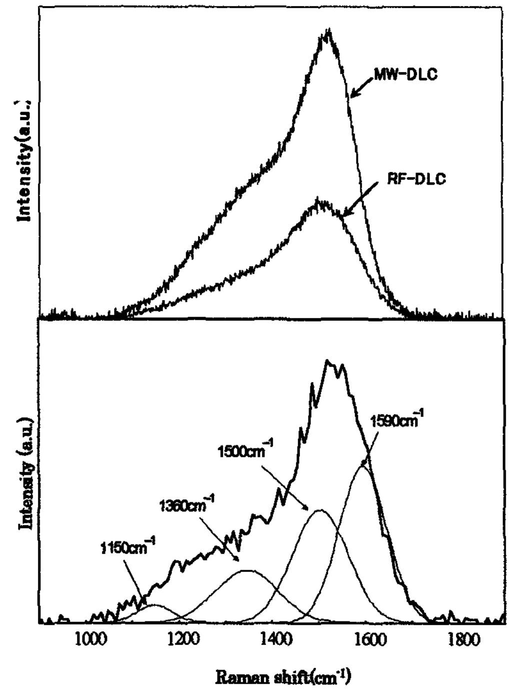

Fig.3 Raman spectra of RF-DLC and MW-DLC films and Raman spectrum of commercial DLC film segregated into four peaks.

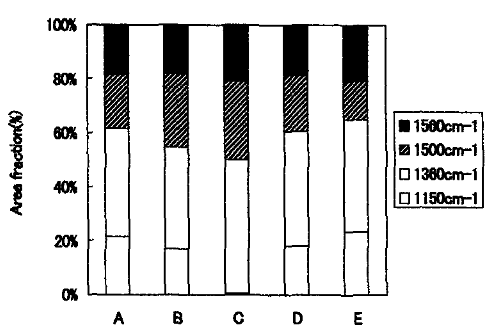

Fig.4 Area fractions of their components segregated into four peaks in every Raman spectrum.

3.4 Mechanical and tribological properties

Fig.5 shows the dynamic hardness of DLC films of A to E measured by an ultra-micro hardness tester. The hardness of the RF-DLC film is the hardest and 2000DH. The other hand, that of MW-DLC film is low and the multi-layers of their DLC films have intermediate values

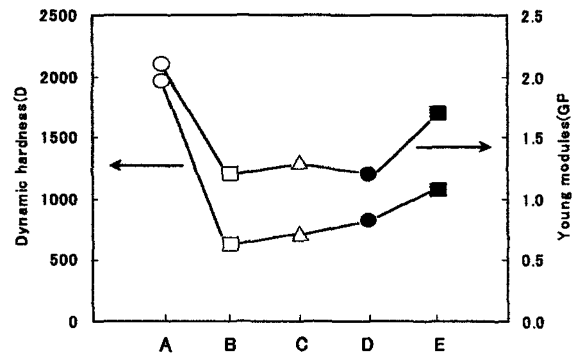

Fig.5 Dynamic hardness and Young modulus of DLC films formed on WC substrates.

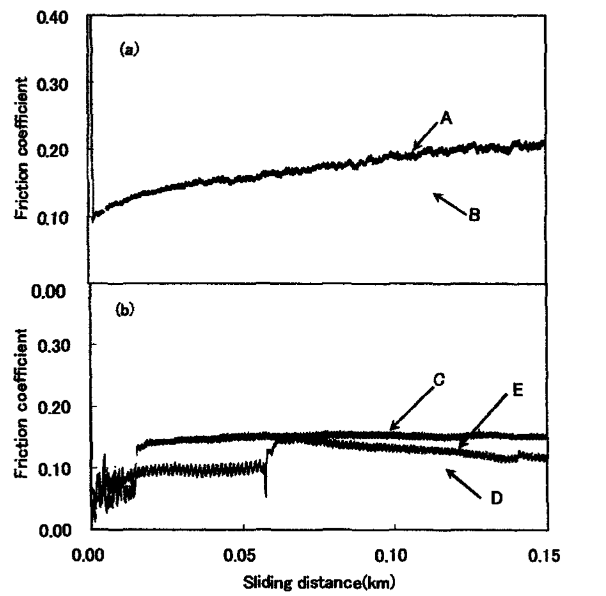

Fig.6 Relationships between friction coefficients and sliding distance by ball on disk tests for DLC films of A to E against Al alloy balls.

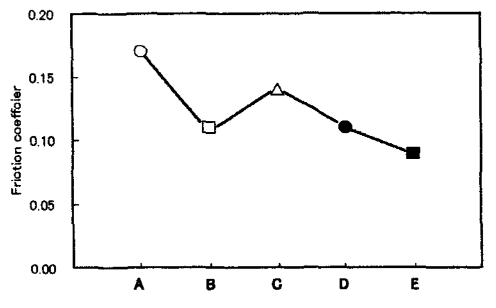

Fig.7 Friction coefficients of DLC films of A to E at the steady state.

to correspond to their thickness. Their hardness evaluated from the depth of indentation with a triangle indenter. In the case of indentation loaded by 19.8 mN, the tip of the indenter come to about 0.1 μ m in depth. Therefore, it was regarded that the hardness of the upper layer may be measured in this case. Their Young modulus, which was calculated from the indentation process, was similar tendency to the hardness.

Fig.6 shows the results of a ball on disk tests for a series of DLC films of A to E. The friction curves at upper were single layer of RF- and MW-DLC and the multi-layers at lower. In single layer, the friction coefficients of RF-DLC film were first lower about 0.1 but become higher with the increase of the sliding distance. However, that of MW-DLC film kept lower about 0.1 and then become higher with the increase of sliding distance reached at about 0.2 same to that in RF-DLC. On the other hand, the friction curves were drawn constant about 0.10 to 0.15 except C, which have a step of 0.10 and 0.15 at sliding distance of about 60 m.

Fig.7 shows the friction coefficients of these films in steady state of sliding. All films exhibited a low value of friction coefficient $\mu < 0.2$. In the case of microwave method, μ is lower than that in the case of RF method. The last layer of the films is RF-DLC or MW-DLC and the tribological properties can control the characteristic of DLC films. Furthermore, the multi-layers of DLC films, which have the different characteristic, are useful for application to the tribological parts needed lower friction coefficient.

4. CONCLUSION

DLC films with one or multi layers were formed on Si wafers and WC substrates by RF and microwave methods. The tribological properties were measured and the characteristics were discussed. The results are as follows.

(1) The surfaces of the films on Si wafer were very smooth and within 2.0 nm.
(2) The friction coefficients of MW-DLC films were very low and rather than those of RF-DLC films.
(3) The hardness of a RF-DLC film was harder than that of a MW-DLC film, and the hardness of the multi-layers was intermediate values of them.
(4) Raman spectra of MW-DLC films have the shoulder peak around 1360 cm^{-1} but those of RF-DLC films have symmetric broad at the center of 1500 cm^{-1}.
(5) The multi-layers of DLC films, which have the different characteristic, are useful for application to the tribological parts needed lower friction coefficient.

5. ACKNOWLEGEMENTS

This research is financially supported by Japan Science and Technology Corporation (JST).

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(Received December 21, 2002; Accepted March 26, 2003)