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Development of ultra-high-speed DLC coating by using microwave-excited high-density plasma
マイクロ波励起・高密度プラズマによる超高速DLC成膜

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We have proposed a novel plasma CVD employing much higher-density plasma (n_e~10^{11}−10^{13} cm^{-3}), which is sustained by microwave propagation along plasma-sheath interface on metal surface. In our previous work, a considerably high deposition rate of 73.2 μm/h, which is about 70 times larger than that of conventional method, was obtained by using the newly proposed method; however, the hardness was not more than 7 GPa. In this work, The hardness of DLC was successfully increased accompanying the increase of substrate current by changing the order of microwave injection and bias application at the start of deposition.

1. Introduction

Recently, with increasing demands for energy saving by friction reduction and lifetime extension by wear reduction in mechanical systems, the application of DLC (Diamond-Like Carbon) to sliding surfaces of mechanical component is spreading gradually and steadily. In this field, higher-speed coating method with an applicability to 3-dimensional shapes is strongly desired in order to expand the application rage of DLC. PECVD (Plasma-Enhanced Chemical Vapor Deposition) is a promising candidate for such demands due to its excellent capability to coat 3-dimensional shapes; however, the typical coating speed with conventional plasma CVDs is not high, ~1 μm/h; in addition, further significant increase of the coating speed is not expected as long as low-density (n_e~10^{8}−10^{10} cm^{-3}) DC or RF plasma is employed. In order to break through the limit, the use of higher-density plasma is considered to be essential. Thus, in order to achieve an ultra-high-speed DLC coating by PECVD, we have proposed the use of a much higher-density plasma (n_e~10^{11}−10^{13} cm^{-3}), which is sustained by microwave propagation along plasma-sheath interface on metal surface [1,2].

In our previous work, a considerably high deposition rate of 73.2 μm/h, which is about 70 times larger than that of conventional method, was obtained by using microwave-excited high-density near plasma [3]; however, the hardness was not more than 7 GPa. In this work, the reason why the hardness of DLC was decreased at such a high deposition rate was investigated in order to know how to suppress the decrease in the hardness of DLC at higher deposition rate.

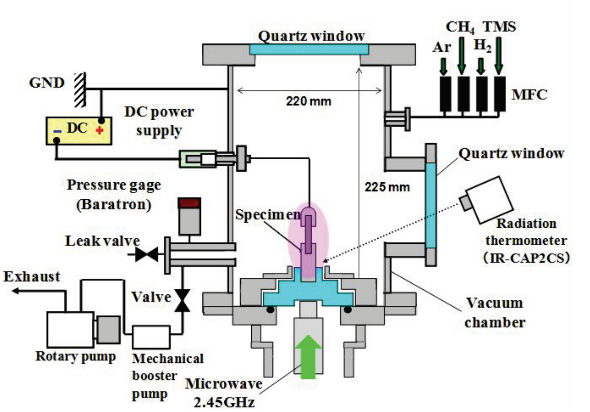

Fig.1 Schematic of DLC coating apparatus with a novel plasma CVD employing high-density near plasma.

2. Experimental setup

Figure 1 shows the experimental apparatus employed for DLC coating. A rotary pump and a mechanical booster pump are connected to the stainless-steel chamber. 2.45-GHz microwaves are injected from a coaxial waveguide connected to the lower flange, propagating into the chamber through a quartz window. A stainless-steel plate (SUS304, JIS) 1 mm in thickness is used as a substrate. The upper end of the substrate is chucked by a stainless-steel jig 10 mm in diameter and 10 mm in length; tungsten wiring is connected to the jig to apply negative voltage provided from a pulsed DC power supply. The lower end of the substrate is chucked by a stainless-steel jig 10 mm in diameter and 20 mm in length; the other end of the jig is inserted into a hole made on the quartz window.

Prior to deposition, the gas pressure is decreased down to 1 Pa. Then, the substrate is cleaned by Ar ion bombardment in Ar. In the coating process after the cleaning, the flow rates of gases, Ar, TMS, and methane were controlled to be 50, 200, and 10 sccm, respectively, at a total gas pressure of 75 Pa. In order to sustain plasma during coating, a pulsed negative voltage of –200 V was applied to the substrate at a pulse frequency of f_{pulse}=500 Hz and duty ratio of D_v %, synchronizing a pulsed injection of 2.45-GHz microwaves at the same pulse frequency and a duty ratio of D_m %.

3. Results and discussion

DLC coating was conducted at a condition: f_{pulse} =500 Hz, D_v=6, 20, 50 %, where D_m was taken to be the half of D_v. Fig. 2 shows the historical changes of substrate current averaged over total bias-on time in one pulse. It can be clearly seen that the substrate current decreased with increase in the duty ratio of microwave from 6 to 50 % (○, Δ, ×, □). In starting the deposition of these 4 DLCs, microwave injection was started prior to bias application; note that the plasma ignites when the microwave injection is started. For duty ratios of 20 and 50 %, DLCs were deposited once more, where bias application was started prior to microwave injection when the plasma was ignited for deposition. It can be clearly seen in Fig. 2 that the substrate current increased by changing the order of microwave injection and bias application at the start of deposition. Considering the initial currents at t=0 for D_v=20 and 50 % were drastically increased, highly insulating films were considered to deposit on the substrate for several second before starting bias application in the first 4 experiments; note that the DLC film typically become highly insulating polymer-like material without substrate bias. Fig. 3 shows the relationship between the hardness of DLC and substrate current averaged over total bias-on time during deposition. The hardness of DLC was increased accompanying the increase of substrate current. Furthermore, it can be clearly shown that starting bias application prior to microwave injection is effective to increase the hardness of DLC by suppressing the decrease in substrate current. The effect of duty ratio on the deposition rate and hardness of DLC are summarized in Figs. 4(a) and 4(b), respectively., indicating that hardness increase is obtained by starting bias application prior to microwave injection, while it leads to the decrease of deposition rate. However, in the case of starting microwave injection prior to bias application, hardness of DLC become much softer than 10 GPa at ultra-high speed over 100 µm/h. Therefore, It is considered that combining ultra-high speed over 100 µm/h and higher hardness over 10 GPa by starting bias application prior to microwave injection, is more suitable for practical use.

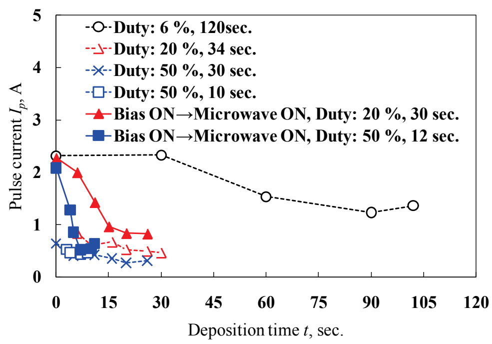

Fig. 2 Historical changes of substrate current in one pulse.

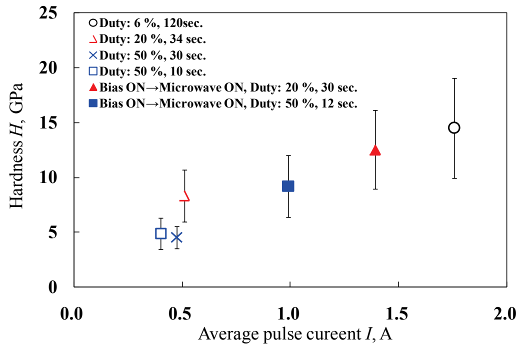

Fig. 3 Relationship between the hardnes of DLC and substrate current averaged over total bias-on time.

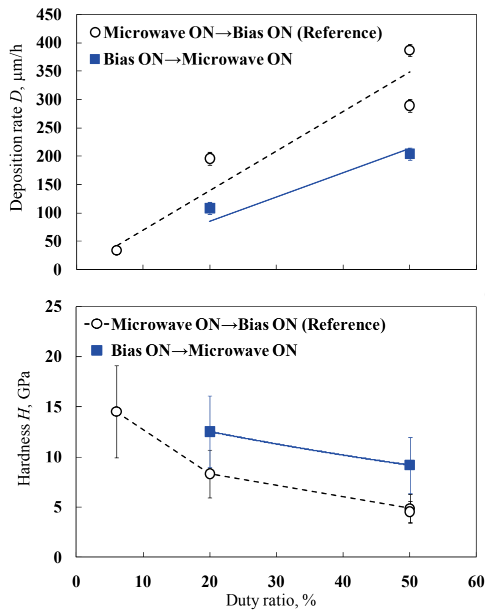

Fig. 4 Effect of duty ratio on the (a) deposition rate and (b) hardness of DLC.

Acknowledgement

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