Source gas depletion in narrow metal tube during internal DLC coating with microwave-excited high-density near plasma

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1. Introduction

Recently, internal coating of DLC (Diamond-Like Carbon) for small mechanical elements is strongly desired from industries. Thus, we proposed a new method of plasma generation along 3-dimensional metal surface by using microwave propagation along plasma-sheath interface [1,2]; "Microwave-sheath Voltage combination Plasma (MVP)" method. It was demonstrated by the MVP method that plasma column is steadily sustained inside a narrow metal tube whose inner diameter is in the range of millimeter and the length is more than 10 times of it [3]. In our previous work, DLC film was deposited on the inner surface of a stainless-steel tube 4.4 mm in inner diameter and 50 mm in length by MVP method. However, as the axial distribution of the film thickness obtained was considerably non-uniform, we further improved the uniformity by employing the method proposed by Segner; the characteristic of their method is to repeat the depletion and refill of source gases in a coated tube during plasma-on time T_{on} and plasma-off time T_{off} , respectively, by pulsed plasma generation inside the tube [4]. In our experiment, uniform distribution was achieved by taking T_{off}=96. 8 and T_{on}=3.2 ms [5]. However, source gas depletion itself has never been directly measured, although researchers employing the same method claimed that it surely occurs [4,6,7]. For further optimization of coating result, it is considered essential to correctly understand how the source gas depletion occurs in a metal tube during DLC coating. Thus in this work, we tried to visualize the source gas depletion in our newly proposed method, or internal DLC coating with MVP method.

2. Experimental Setup

2.1 DLC coating equipment

Figure 1(a) is the schematic of the PECVD (Plasma-enhanced chemical vapor deposition) apparatus with a stainless-steel chamber 225 mm in inner diameter and 220 mm in height, presently employed for the internal DLC coating with MVP method. As shown in Fig. 1(b), a set of a 1/4 inch stainless-steel tube (SUS316, JIS) and a steel plate (SCM420, JIS) of 1 mm thickness and 5.2 mm width is employed as a tube shape-simulated substrate to be coated. The length of the substrate is taken to be 50 mm. The tube is cut along the axial direction so that the width of the rest part is 5 mm in the cross section perpendicular to the tube axis. The cut cross-section of a tube is covered by the steel plate. The lower part of the tube shape-simulated substrate is chucked by a stainless-steel holder (SUS304, JIS) so that the substrate stably stands on a microwave injection window made of quartz. Note that the tube shape-simulated substrate is electrically insulated from the chamber by the quartz window and the holder have 4 halls 4 mm in diameter through which gases diffuse into the tube. Here, the center of the bottom end of the substrate is defined as the origin of cylindrical coordinate, or $(r,z)=(0,0)$ for the following explanations.

A coaxial cable for guiding 2.45-GHz microwaves is connected to the bottom flange where the microwaves are introduced into the chamber via the microwave injection window. Microwaves introduced into the chamber propagate as surface waves into the tube shape-simulated substrate along the interface between plasma column and ion sheath bounded by the inner surface of the substrate. The substrate is connected to a high-voltage DC power supply with tungsten wire 0.5 mm in diameter in order to apply a negative voltage against the grounded chamber. The temperature of the substrate is monitored through a quartz window by a radiation thermometer (IR-CAP2CS, CHINO)

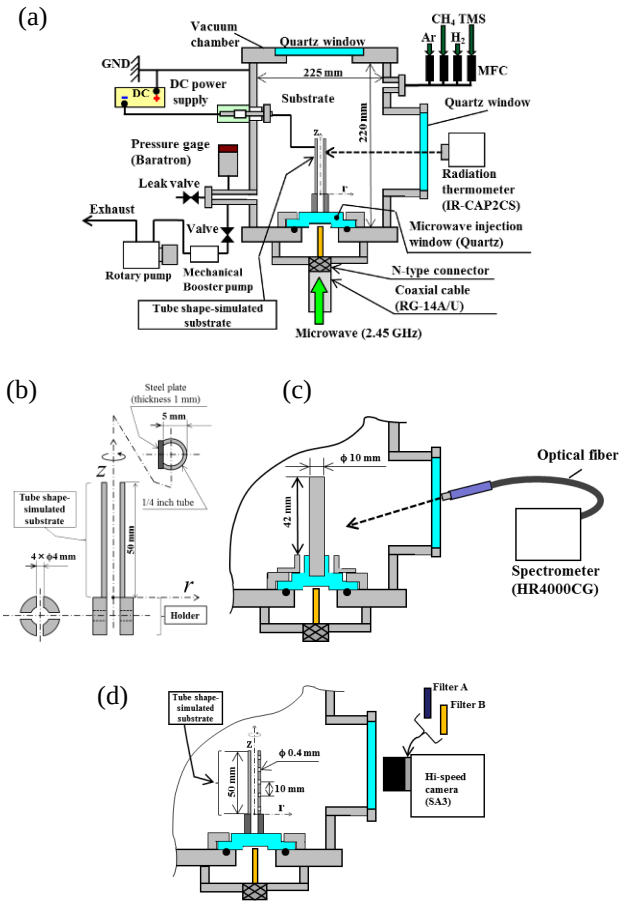

Figure 1. (a) Schematic of the plasma CVD apparatus for internal DLC coating of narrow metal tube. (b) Enlarged view of a tube shape-simulated substrate and substrate holder. (c) Enlarged view of a microwave launcher and metal rod. This configuration is employed for optical emission spectroscopy by using spectrometer. (d) Enlarged view of a microwave launcher and metal tube with small holes 0.4 mm in diameter fabricated at every 10 mm on the side wall of the tube. This configuration is employed for high-speed camera observations.

using infrared light 2 μm in wavelength. The chamber is evacuated by a set of mechanical booster pump and rotary pump.

2.2 Configuration for optical emission spectroscopy

Figure 1(c) is the enlarged view around the lower part of the chamber, that configuration is arranged for optical emission spectroscopy of microwave-excited high-density plasma generated along the outer surface of a stainless-steel rod 10 mm in diameter and 55 mm in length. In this configuration, microwaves propagate as surface waves along the interface between plasma column and ion sheath bounded by the outer surface of the rod [8-10]. The optical emission from the plasma is measured through the side quartz window by a compact spectrometer. (HR4000CG, Oceanoptics)

2.3 Configuration for high-speed camera imaging

Figure 1(d) is the enlarged view around the lower part of the chamber, that configuration is arranged for high-speed camera imaging of microwave-excited high-density plasma generated inside the tube shape-simulated substrate. In this experiment, small hall 0.4 mm in diameter is fabricated on the tube wall every 10 mm along the axis from z=5 to 45 mm so that the inner plasma can be monitored by observing the leakage light through the halls.

3. Results and discussion

3.1 Selection of bandpass filter for high-speed camera imaging

It was considered that we can more directly understand the source gas behavior in a metal tube during internal DLC coating by monitoring the plasma condition. For this purpose, we planned to directly measure the optical emission from the plasma generated inside the tube during DLC coating. Here, we assumed that C_2 dimer would be a good indicator of the source gas (CH_4) existence in the plasma, because C_2 is formed through the dissociation of CH_4.

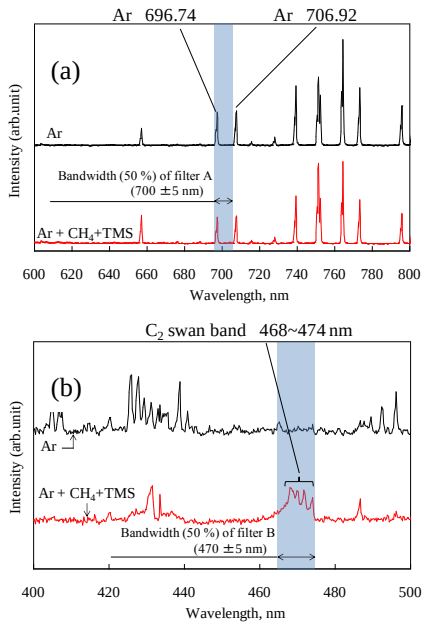

Figure 2. Optical emission spectra of argon plasma and argon/methane/TMS plasma (a) from 600 to 800 nm and (b) from 400 to 500 nm, measured by using spectrometer.

Optical emission spectroscopy was conducted by using the apparatus shown in Fig. 1(c) in order to select bandpass filters used in high-speed camera observation. First, Ar plasma was generated along the outer surface of a stainless-steel rod (SUS304, JIS) 10 mm in diameter 55 mm in length at a total gas pressure of 80 Pa where the flow rate of Ar is controlled to be 14 sccm. Here, a pulsed negative voltage of –200 V was applied to the rod at a pulse frequency of f_{pulse}=10 Hz and duty ratio of D_v=3.2 %, synchronizing a pulsed injection of 2.45-GHz microwaves with a peak power of 1000 W at the same pulse frequency and duty ratio of D_m=4 %. Note that T_{on}=3.2 ms and T_{off}=96.8 ms in this condition. After the measurement of Ar plasma, DLC coating was conducted under the same condition except the gas composition where the flow rates of Ar, methane, and TMS gases are controlled to be 14, 2, and 0.2 sccm, respectively. Then the measurement of plasma during DLC coating was also conducted. Figure 2(a) shows the spectra, where Ar atom lines of 696.74, 706.92 nm appear [11], obtained for Ar plasma and coating plasma. It was confirmed that these two peaks are not disturbed by the emission from other species regardless of source gas (CH_4 and TMS) inclusion in plasma; in addition, there are no peaks comparable to these two peaks from 695 to 705 nm. Therefore, it was considered that high speed camera image with a bandpass filter of 695-705 nm will be the image of Ar atom emission. As shown in Fig. 2(b), C_2 Swan band, 468~474 nm [12], was confirmed from Ar, methane, and TMS plasma. Therefore, it was considered that high speed camera image with a bandpass filter of 465-475 nm will be the image of C_2 dimer emission. Thus, we selected 465-475 nm and 695-705 nm bandpass filters for C_2 dimer and Ar atom emission images, respectively.

3.2 Observation of source gas depletion with high-speed camera

High-speed camera imaging of the plasma during internal DLC coating was conducted by using the configuration shown in Fig. 1(d). In the coating process, the flow rates of gases, Ar, methane, and TMS were controlled to be 14, 2, and 0.2 sccm, respectively, at a total gas pressure of 80 Pa. In order to sustain plasma during coating, a pulsed negative voltage of V_{tube}=–200 V was applied to the pipe at a pulse frequency of f_{pulse} Hz and duty ratio of D_v %, synchronizing a pulsed injection of 2.45-GHz microwaves with a peak power of 1000 W at the same pulse frequency and duty ratio of D_m %. DLC coating was conducted for 2 hours under the condition: f_{pulse}=10 Hz, D_v=3.2 and D_m=4 %, where T_{on}=3.2 ms and T_{off}=96.8 ms.

Figures 3(a) and 3(b) show time-resolved images of emission from Ar atom and C_2 dimer, respectively. The images were taken from the start to end of DC voltage application at an interval of 0.2 ms with an exposure time of 0.2 ms by using the high-speed camera. Figures 4(a) and 4(b) show the historical shots of the brightness values for Ar atom and C_2 dimer, respectively. It was indicated that the brightness of Ar atom, which is not consumed for film formation, was approximately constant during plasma-on time. On the other hand, the brightness of C_2 dimer was decreased until T_{on}=1.6 ms, and then converged in a constant value.

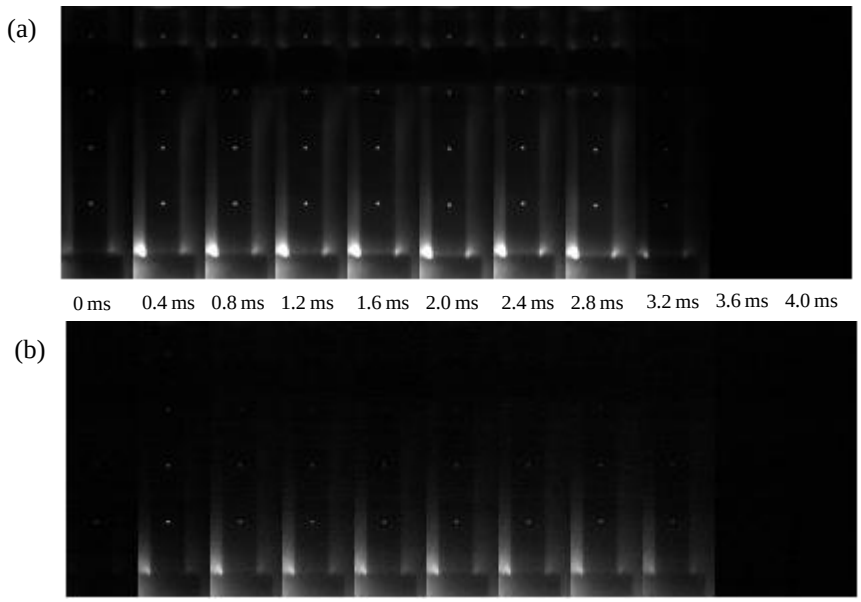

Figure 3. Time-resolved images of argon/methane/TMS plasma during internal DLC coating, taken by using high-speed camera with (a) 695-705 nm (for Ar atom) and (b) 465-475 nm (for C_2 dimer) bandpass filters.

In typical low pressure plasmas, emission intensity I_M from an excited species M is expressed by the following formula.

$$I_M \propto k_M(T_e)\cdot n_e \cdot n_M , \qquad (1)$$

where k_M is the rate constant of excitation from ground state to an upper state due to electron collision which is the function of electron temperature T_e, n_e is the electron density, and n_M is the number density of species M. Thus in our case, it is assumed that the emission intensity of Ar and C_2 are written in the same formulas, respectively.

$$I_{Ar} \propto k_{Ar}(T_e)\cdot n_e \cdot n_{Ar} , \qquad (2)$$

$$I_{C_2} \propto k_{C_2}(T_e)\cdot n_e \cdot n_{C_2} , \qquad (3)$$

Considering Ar is not consumed during deposition, n_{Ar} can be assumed to be constant. Here, the brightness of Ar atom was approximately constant during plasma-on time as shown in Fig. 4(a), and thus $k_{Ar}(T_e)n_e$ was considered to be constant during plasma-on time. We can expect from the constant $k_{Ar}(T_e)n_e$ that T_e and n_e were constant during plasma-on time. If T_e and n_e are constant, I_{C_2} is proportional to n_{C_2} from Eq. (3). Thus, the brightness of C_2 dimer is considered to indicate the number density of C_2 dimer during the period where Ar emission is constant. Based on these interpretations, the decrease in the brightness of C_2 dimer from 0.2 to 1.6 ms in Fig. 4(b) is ascribed to the consumption of CH_4 gas which is considered to be a main source of C_2 dimer formation. In the same figure, the plateau of C_2 dimer is observed from 1.6 to 3.0 ms, being ascribed to C_2 dimer provided through the sputtering of DLC film by Ar ion after the depletion of source gas.

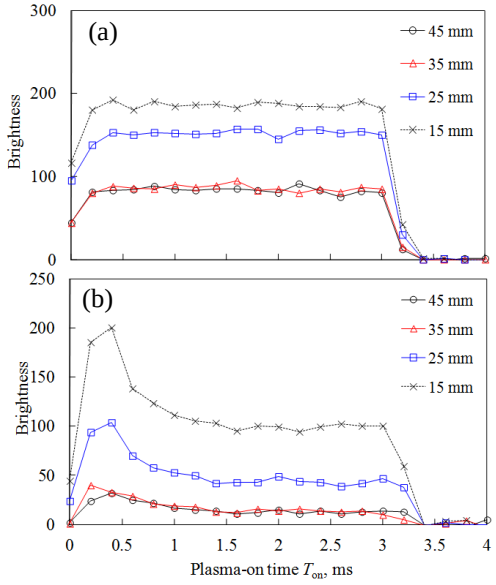

Figure 4. Historical shots of the brightness of (a) Ar atom emission (696, 706 nm) and (b) C_2 dimer emission (468-474 nm), obtained at z=15, 25, 35, and 45 mm for a pulse frequency of f_{pulse}= 10 Hz (plasma-off time: T_{off}=98.8 ms, plasma-on time: T_{on}=3.2 ms).

In order to confirm the C_2 dimer formation from DLC film by Ar ion sputtering, optical emission spectroscopy was conducted for Ar plasma generated along the outer surface of the DLC-coated rod; the condition of plasma generation was the same as the last experiment except the change in gas composition from Ar, methane, and TMS to pure Ar. As shown in Fig. 5, C_2 Swan band, 468~474 nm was observed in the Ar plasma. This result implied that the constant brightness of C_2 dimer during T_{on}=1.6-3.0 ms in Fig. 4(b) was brought about by the C_2 dimer provided through the sputtering of DLC film by Ar ion after the depletion of source gases.

3.3 Effect of plasma-on time on the thickness of DLC film

Internal DLC coating to 1/4 inch stainless-steel tubes (SUS304, JIS) 50 mm in length were conducted by using the apparatus and substrate shown in Figs. 1(a) and 1(b), respectively. In the coating process, the flow rates of gases, Ar, methane, and TMS were controlled to be 14, 2, and 0.2 sccm, respectively, at a total gas pressure of 80 Pa. In order to sustain plasma during coating, a pulsed negative voltage of V_{tube}=–200 V was applied to the pipe at a pulse frequency of f_{pulse}=10 Hz, synchronizing a pulsed injection of 2.45-GHz microwaves with a peak power of 1000 W at the same pulse frequency. If the plasma-on time T_{on} is enough duration in which source gases are depleted at any position, and the resultant plasma-off time T_{off} is enough duration in which source gases are uniformly distributed along the axis, it is expected that uniform distribution of film thickness in

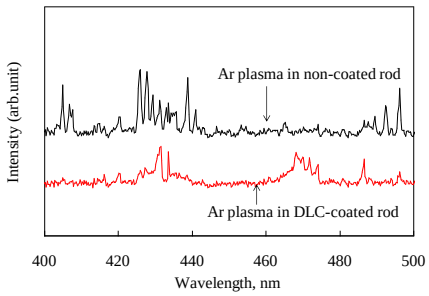

Figure 5. Optical emission spectra of Ar plasma generated in a non-coated rod and DLC-coated rod, measured from 400 to 500 nm by using spectrometer.

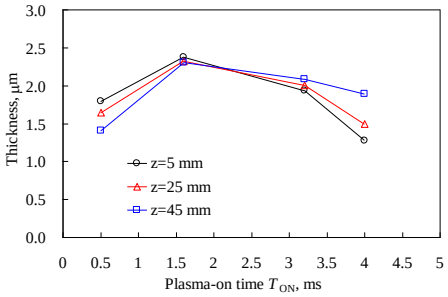

Figure 6. Axial distribution in the thickness of DLC film measured at z=5, 25, and 45 mm on the DLC-coated plate, obtained for different plasma-on time T_{on}=0.5, 1.6, 3.2, and 4.0 ms.

the axial direction and the highest deposition rate are obtained under this condition. Figure 6 shows the distribution in the thickness of DLC film measured at z=5, 25, and 45 mm on the DLC-coated plate, obtained for different plasma-on time T_{on}=0.5, 1.6, 3.2, and 4.0 ms. Note that the film thickness value of DLC were obtained by measuring the step height at the interface between DLC coated and uncoated surfaces on the steel plate by using stylus type surface roughness tester. As shown in the figure, the axial distribution of film thickness was the most uniform in the case of T_{on}=1.6 ms, or the depletion time experimentally identified. What is the reason for the non-uniform distributions of film thickness in the cases of T_{on}=0.5, 3.2, and 4.0 ms ? In a microwave-excited high-density plasma column, plasma electron density typically decreases with the distance from the microwave injection point, because more power is deposited at a position closer to the microwave injection point [8-10]. Therefore, it is considered that consumption speed of source gases became lower with axial position. In the case of the T_{on}=0.5 ms, it is considered that the source gas was exhausted during plasma-on time not at any position due to short plasma-on time. As a result, the film thickness was considered to have a negative slope with axial position as shown in Fig. 6. On the contrary, In case of T_{on}=3.2 and 4.0 ms, it is considered that the source gas was exhausted during plasma-on time at any position due to long plasma-on time. Thus, it is considered that the sputtering of DLC film by Ar ion after the depletion of source gas is occurred. In addition, it is considered that the time of sputtering is shorter and the sputtering speed of DLC film became lower with axial position due to negative slope of plasma electron density. As a result, in case of T_{on}=3.2 and 4.0 ms, the distribution of film thickness has a positive slope with axial position as shown in Fig. 6. From this result, it is considered that T_{on}=1.6 ms is enough duration in which source gases are depleted at any position.

4. Conclusion

In this work, we tried to visualize the source gas depletion in our newly proposed method of internal DLC coating employing microwaves. High-speed camera observations were conducted to the plasmas generated inside the 1/4 inch stainless-steel tube for internal DLC coating at a plasma–on time T_{on}=3.2 ms. The emission from 695 to 705 nm including only Ar atom emission which is not consumed for film formation, was approximately constant during plasma-on time. On the other hand, the emission from 465 to 475 nm including only C_2 dimer emission was decreased and then converged in a constant value in 1.6 ms after plasma ignition. As the decrease in the C_2 dimer emission is ascribed to the consumption of CH_4 gas, the source gas depletion time was identified to be 1.6 ms. Then, DLC coatings were conducted again at T_{on}=0.5, 1.6, 3.2, and 4.0 ms under the same condition. The deposition rate and axial uniformity of DLC film were the highest and the most uniform, respectively, in the case of T_{on}=1.6 ms.

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