Synthesis of carbon films using substrate-grounded MVP method

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Diamond is widely used in industry for cutting tools and sliding parts because of its excellent characteristics such as high hardness, low friction, and high wear resistance. Plasma CVD and hot filament CVD (HFCVD) are used to synthesize diamond. HFCVD is used to synthesize diamond films on the three-dimensional metal surface. However, it is difficult to coat films on complex shapes. On the other hand, Microwave-sheath Voltage combination Plasma (MVP) method can synthesize diamond-like carbon films on the three-dimensional shapes. In addition, we demonstrated synthesis of diamond on the plate by MVP method. Therefore, it is expected to deposit diamond films on the three-dimensional surface by MVP method. In this study, the synthesis of carbon films using the substrate-grounded MVP method was investigated. The surface SEM images of the films showed particles at a CH_4 concentration of 1 % and fiber-shaped deposits at a CH_4 concentration of 0.5 %. The Raman spectra showed a D-band around 1350 cm^{-1}, which is due to the disorder and defects characteristic of amorphous carbon, and a G-band around 1580 cm^{-1}, which is due to the graphite structure. The D-band and G-band are loosely connected, suggesting that this is an amorphous carbon similar to diamond. Inconclusion, it was possible to synthesize carbon films with a substrate-grounded MVP.

Keywords: *carbon film, microwave-sheath voltage combination plasma, chemical vapor deposition*

1. Introduction

Diamond has excellent properties such as high hardness, high wear resistance, and low friction[1)]. Diamond coatings offer high wear resistance and a low friction coefficient for mechanical application. Recently, diamond coatings have been used as a cutting tool for carbon-fiber-reinforced plastic[2)]. However, diamond-like carbon coatings have not been applied to molds and friction parts, where they are widely used. Plasma CVD[3)] and hot filament CVD[4)] have been used to synthesize diamond, and hot filament CVD is used to deposit films on three-dimensional shapes. However, it is difficult to handle complex shapes.

On the other hand, Microwave-sheath Voltage combination Plasma (MVP)[5)] is a plasma generation method in which microwaves are propagated along the boundary between the plasma and the ion sheath to generate surface-wave plasma on metal and substrate surfaces. Diamond synthesis by MVP has been investigated, and diamond has been obtained in the intermediate pressure region of about 1 kPa[6)]. However, plasma generation that follows the three-dimensional shapes of MVP is only possible at pressures below 100 Pa, and plasma generation that follows the three-dimensional surface at high pressures has not been confirmed. Therefore, it is necessary to realize plasma generation that follows the three-dimensional shapes at high pressure for a synthesis of diamond on complex shapes. The authors have succeeded in generating plasma at low voltages by using a substrate-grounded MVP method, in which an external electrode is placed and the substrate is grounded[7)]. However, plasma was generated not only on the substrate but also on the microwave leakage prevention jig at the bottom of the jig, because the plasma was spreading to the top and bottom of the substrate and the jig centered on the tip of the quartz tube at the bottom of the substrate. Suppression of plasma generation on the microwave leakage prevention jig is expected to expand the plasma generation area on the base material. In this study, the synthesis of carbon films using the substrate-grounded MVP method was investigated.

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2. Experimental equipment and Conditions

Fig. 1 shows a schematic diagram of the experimental apparatus. The MVP apparatus was used, with the substrate connected to the ground and a positive voltage applied to a microwave leakage prevention jig installed around the quartz tube covering the coaxial. Table 1 shows the experimental conditions. A CH_4-H_2 mixture was used as the source gas, and the CH_4 concentration relative to H_2 was set to 0.5 and 1 %. The films were deposited for 5 hours at a microwave output of 1 kW, chamber pressure of 3 kPa, applied voltage of 350 V, frequency of 1 kHz, and duty ratio of 50 %. The films were observed by scanning electron microscopy (SEM) and qualitatively evaluated by Raman spectroscopy.

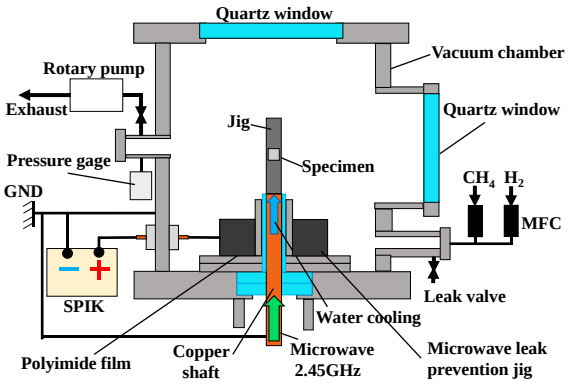

Fig. 1 Schematic diagram of experimental apparatus.

Table 1 Synthesis conditions.

Gas flow rate [SCCM]	H_2	200	
	CH_4	1	2
Pressure, kPa		3	
DC	Peak voltage, V	350	
	Frequency, kHz	1	
	Duty ratio (%)	50	
Microwave	Peak power, W	1000	
	Frequency, kHz	1	
	Duty ratio (%)	50	
Deposition time, min		300	
Substrate temperature,℃		600	634

3. Results and discussion

Fig. 2 shows the surface SEM images. Fiber-shaped deposit was observed in CH_4 0.5%. Particle was observed in CH_4 1%. The grain size of the deposits synthesized by CH_4 concentration of 1 % was about 47 nm.

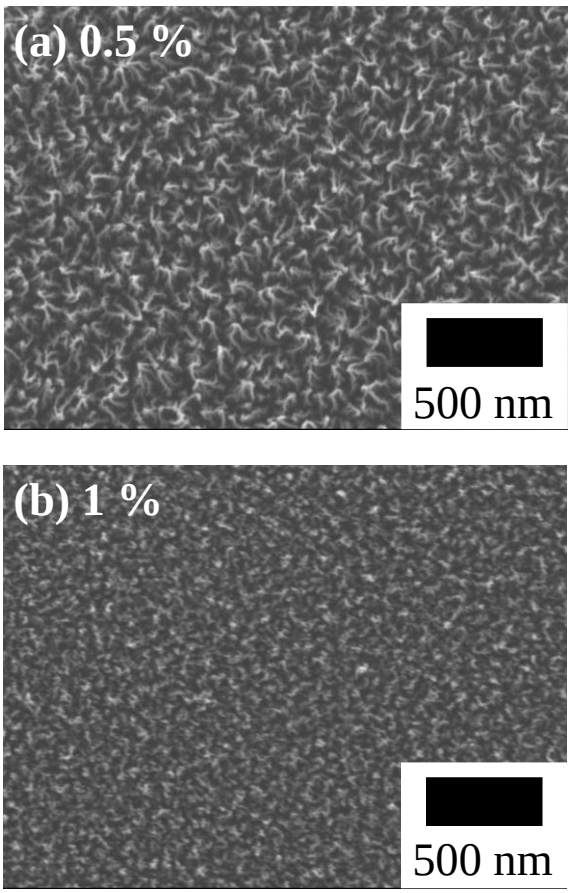

Fig. 2 Surface SEM images of deposits synthesized by each CH_4 concentration.

The Raman spectra of the deposits synthesized under each condition are shown in Fig. 3. In all conditions, a D-band around 1350 cm^{-1}, which is a peak caused by disorder and defects characteristic of amorphous carbon, and a G-band around 1580 cm^{-1}, which is caused by the graphite setup, were observed. Table 2 shows the I_D/I_G, G peak position, and FWHM(G) of carbon films deposited under each condition. I_D/I_G was 0.65 at a CH_4 concentration of 0.5 % and 0.63 at a CH_4 concentration of 1 %. The G peak position was 1590 cm^{-1} at 0.5 % CH_4 concentration and 1583 cm^{-1} at 1 % CH_4 concentration. As the CH_4 concentration increased, the G peak shifted to the low wavenumber side, and the value of I_D/I_G became smaller. This suggests that the proportion of sp^3 binding is increasing.

Table 2 ID/IG ratio, G peak position, and FWHM(G) of the carbon films deposited by each CH_4 concentration.

CH_4 concentration (%)	0.5	1
I_D	938.439	414.045
I_G	1451.55	654.138
I_D/I_G ratio	0.65	0.63
G peak position, cm^{-1}	1590	1583
FWHM(G), cm^{-1}	390	390

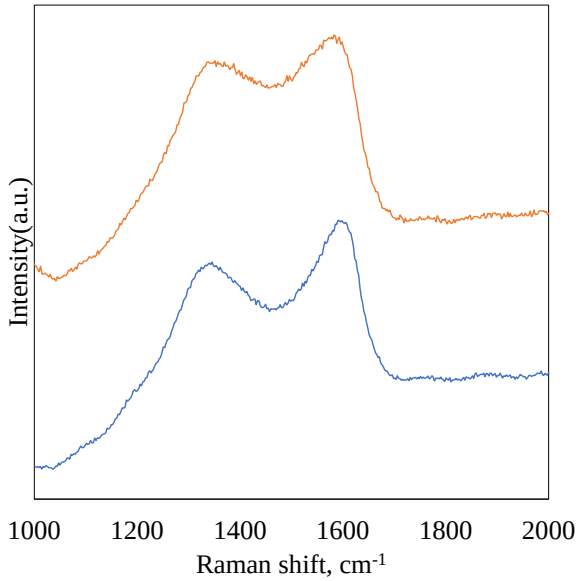

Fig. 3 Raman spectra of deposits synthesized by each CH_4 concentration.

4. Conclusions

We investigated to synthesis of carbon films using substrate-grounded MVP method in this study. It was possible to fabricate carbon films on a bar-shaped specimen table using a substrate-grounded MVP. The results of Raman spectra indicate that the deposited films are amorphous carbon.

References

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