Low-Temperature Deposition of Diamond-like Carbon Films Using a Repetitive Nanosecond Pulsed Glow Discharge Plasma Operated in Burst Mode

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A diamond-like carbon film with a film hardness of 12 GPa was prepared at a low substrate temperature of 60°C using a repetitive nanosecond pulsed glow hydrogen/methane discharge plasma operated in burst mode under a gas pressure of 1.2 kPa. As the peak electrical power of the pulsed discharge increased, the hydrogen content in the films estimated by Raman spectroscopy decreased and the film hardness increased. The ion irradiation to the substrate is considered to be the main factor determining the film properties, since the hydrogen abstraction reaction and the etching of graphite components by hydrogen radical irradiation are weakened in the low-temperature deposition.

Keywords: diamond-like carbon, nanosecond pulsed glow discharge, burst operation

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Diamond-like carbon (DLC) films have been used in various industrial applications owing to their excellent material properties [1]. DLC coating on low-melting point materials such as plastics and rubbers has been performed by low-temperature deposition below 100°C using low-gas-pressure plasma devices [2, 3]. If high-speed deposition of DLC at low temperatures becomes possible, it is expected to contribute to the expansion of DLC applications. In our previous study [4], a DLC film was successfully prepared at a deposition rate of 0.13 μm/min and the film hardness of 15 GPa using a repetitive nanosecond pulsed glow hydrogen (H_2)/methane (CH_4) discharge plasma at a gas pressure of 1.2 kPa, where the substrate temperature during the deposition was 170°C. Under such a high substrate temperature, the film hardness can be expected to increase due to the hydrogen abstraction reaction and the etching effect of graphite components by hydrogen radical irradiation [5]. In this study, DLC deposition was performed by maintaining a low substrate temperature of 60°C using a repetitive nanosecond pulsed glow discharge plasma operated in burst mode.

Details of the experimental setup can be found in our previous paper [6]. A mixture of H_2 and CH_4 with a gas pressure of 1.2 kPa was used as the process gas. The gas flow rates of H_2 and CH_4 were 1 and 0.6 L/min, respectively. A pulsed glow discharge plasma was generated by applying a repetitive bipolar nanosecond pulse voltage between a pair of parallel-plate stainless steel electrodes. The gap distance between the electrodes was 30 mm. Figure 1 shows the typical waveforms of the discharge voltage and current. The repetition frequency of the pulsed voltage is defined as f_{pulse} and the burst frequency as f_{burst}. For all f_{pulse} and f_{burst} conditions, the voltage pulse width (FWHM) was 300 ns and the burst pulse width was 40 μs. As shown in Fig. 1 (a), the peak value of the first voltage of the pulse train is higher than the others. Figure 1 (b) shows the waveforms for one cycle of voltage and current. The pulsed voltage is higher due to the decay of the afterglow caused by the pause in the pulsed voltage application,

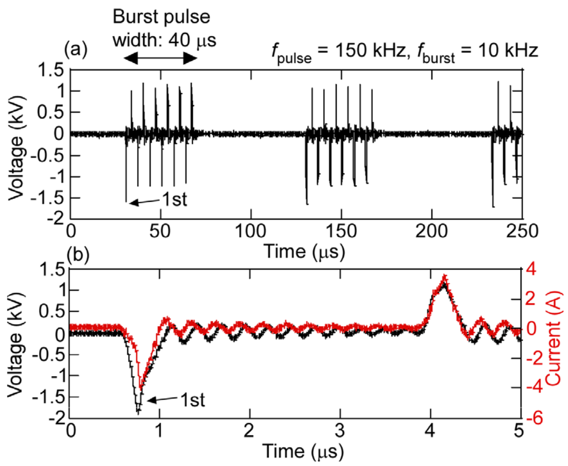

Fig. 1 Waveforms of (a) the pulsed voltage train and (b) the pulsed voltage and current. The repetition frequency of the pulsed voltage is 150 kHz and the burst frequency is 10 kHz.

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which reduces the preionization effect. After the second pulse, the peak voltage value is slightly lower than that of the first pulse due to the effect of the previous pulsed discharge, and the voltage value is affected by both f_{pulse} and f_{burst}. Therefore, the voltage, current, and electrical power of the pulsed discharge vary depending on f_{pulse} and f_{burst}. Their effects on DLC deposition will be discussed below.

For DLC film deposition experiments, silicon (Si) wafers ($25 \times 25 \times 0.6\,\mathrm{mm}^3$) were used as substrates. The Si substrate was placed on the bottom electrode with a 70-mm diameter. After Ar and H_2 mixed-gas discharge plasma irradiation at a gas pressure of 100 Pa for 20 min, the substrate was exposed to the repetitive nanosecond pulsed glow discharge plasma with a H_2/CH_4 gas mixture for 20 min. The substrate temperature T_s during the deposition was determined by the balance between plasma irradiation heating and water cooling of the electrode. Here T_s is considered to be almost the same temperature as that of the electrode surface, which is also irradiated with the same plasma. Because low-temperature Si is transparent in the infrared wavelength, T_s was determined by the electrode surface temperature near the Si substrate measured using a radiation pyrometer. In this study, T_s was maintained at 60°C by adjusting f_{burst}, and the film hardness was measured using a nanoindentor. The hydrogen content of a DLC film was evaluated by Raman spectroscopy using an incident laser wavelength of 532 nm. The analysis method is detailed in [7].

Figure 2 (a) shows the film hardness and hydrogen content of the DLC films as a function of f_{pulse}. Here, f_{burst} was adjusted such that T_s was 60°C, as shown in Fig. 2 (b). The displacement depth was set to approximately 200 nm in the nanoindentor measurement. The results show that the maximum film hardness of 12 GPa is obtained, although it is slightly lower than the film hardness of 15 GPa at T_s of 170°C [4]. Furthermore, the film hardness varies from 6 to 12 GPa depending on f_{pulse}. There is also a correlation between the film hardness and the hydrogen content of the DLC films, indicating that the film hardness increases with the lower hydrogen content. Figures 2 (c) and (d) show the pulsed voltage, current, and peak discharge power obtained from the second shot of the pulse train. This result shows that there is a strong correlation between the peak discharge power and film hardness.

The mechanism of the changes in the film properties can be considered as follows. In our previous study [4], the hydrogen content was high and the film hardness was low at $T_s < 100$°C. The effects of hydrogen abstraction reaction and etching of graphite components by hydrogen radical irradiation have shown strong dependences on substrate temperature, and the effects are weakened at lower substrate temperatures [5]. Therefore, in this study, the effects of the hydrogen radical irradiation on the DLC film properties are considered to be very small at T_s of 60°C. In contrast, it is known that ion irradiation conditions such as ion bombardment energy and ion flux are important to

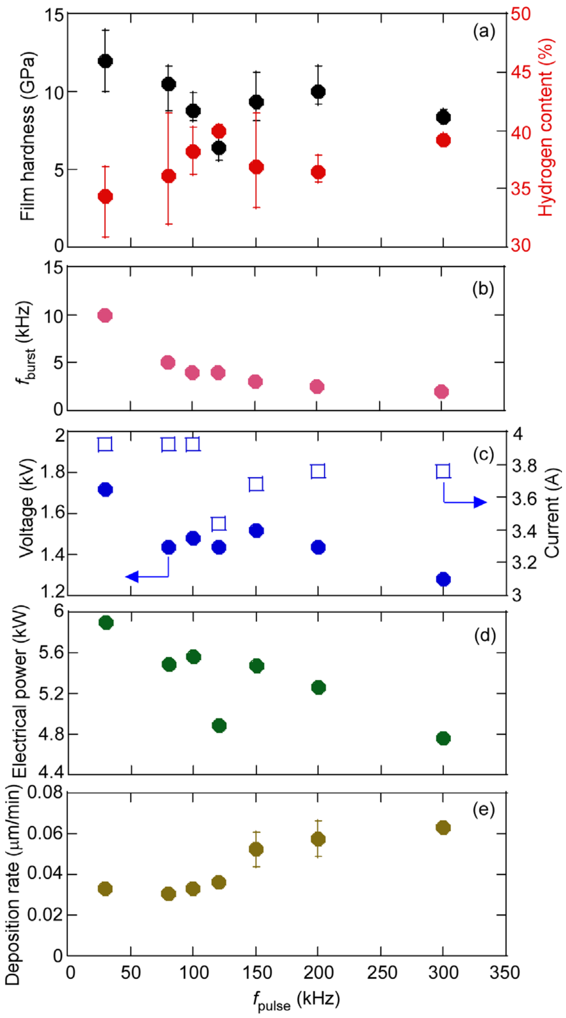

Fig. 2 (a) Film hardness and hydrogen content of DLC films, (b) burst frequency, (c) discharge voltage and current, (d) peak electrical discharge power, and (e) deposition rate as a function of the repetition frequency of the pulsed voltage. The substrate temperature was 60°C.

obtain DLC films with high hardness [8, 9]. Since the film hardness is correlated with the peak discharge power, as shown in Fig. 2, the film hardness in this experiment is considered to be mainly determined by the ion irradiation to the substrate.

As shown in Fig. 2 (e), the deposition rate increases with f_{pulse}. Even in the low-temperature deposition using the burst operation, the deposition rate was several times higher than that of a conventional low-gas-pressure plasma deposition experiment [10]. Therefore, increasing the peak discharge power at high f_{pulse} is key to obtaining a hard DLC film at a high deposition rate.

In this study, DLC deposition experiments were conducted at T_s of 60°C by operating a repetitive nanosecond pulsed glow H_2/CH_4 discharge plasma in burst mode. As a result, a DLC film with a hardness of 12 GPa was successfully deposited even under the low-temperature condition.

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