Effects of Substrate Temperature on Film Hardness and Hydrogen Content in Diamond-like Carbon Films Prepared with a Repetitive Nanosecond Pulsed Glow Hydrogen/Methane Discharge Plasma

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A repetitive nanosecond pulsed glow hydrogen/methane discharge plasma generated at 1.2 kPa gas pressure led to diamond-like carbon films with high hardness and a high-speed deposition rate of 0.13 μm/min. Film hardness showed strong substrate temperature dependence, reaching up to 15 GPa. Raman spectroscopy revealed that hydrogen content in the films decreased with increasing substrate temperature. The mechanisms of the changes in film hardness and hydrogen content are considered to be the substrate temperature dependence of the hydrogen abstraction reaction and etching by irradiation with hydrogen radicals.

Keywords: diamond-like carbon, nanosecond pulsed glow discharge, Raman spectroscopy

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Diamond-like carbon (DLC) films have attracted broad interest in various industrial fields owing to their excellent material properties [1]. Increasing the deposition rate and reducing the cost of deposition is necessary to enable DLC films to be widely used in industry. High-speed DLC film deposition experiments using nanosecond pulsed plasmas at sub-atmospheric/ atmospheric pressures have been conducted [2], but uniform deposition was difficult to achieve because of the use of streamer discharges. We have recently performed a high-speed DLC deposition experiment using a repetitive nanosecond pulsed glow helium (He)/methane (CH_4) discharge [3]. Although using He, which is expensive, as a dilution gas can obtain a stable glow discharge, an alternative gas would reduce costs. In this study, we prepared DLC film by generating a repetitive nanosecond pulsed glow discharge plasma using hydrogen (H_2) instead of He. In particular, the effect of substrate temperature on DLC film properties was investigated.

Details of the experimental setup can be found in [3]. In the present study, a mixture of H_2 and CH_4 with a gas pressure of 1.2 kPa was used for 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 pulsed voltage with a frequency of 30 kHz and pulse width of 300 ns between the electrodes. The peak values of the voltage and current were 1.5 kV and 1.9 A, respectively. Figure 1 shows the plasma emission spectrum at 1 mm from the high-voltage electrode. The CH emission related to DLC deposition and hydrogen atom emission (H_α) are observed. An optical image of a typical plasma discharge captured using a digital camera is also shown in the inset of Fig. 1, which exhibits a uniform discharge plasma generated through the whole electrode area.

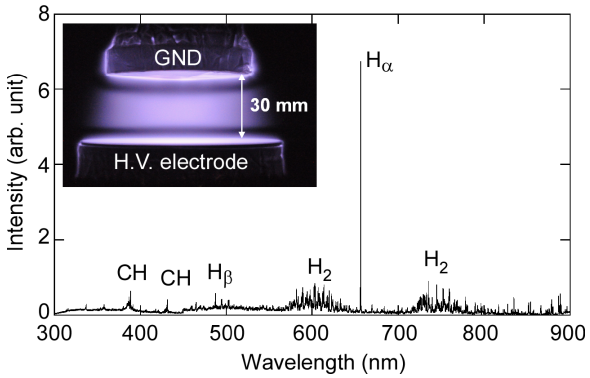

Fig. 1 Time-integrated emission spectrum of the pulsed glow H_2/CH_4 discharge at 1 mm from the high voltage electrode.

For DLC film deposition experiments, silicon (Si) wafers ($25 \times 25 \times 0.6\,mm^3$) were used as substrates. The substrates were pretreated in acetone wash with an ultrasonic vibrator and then installed on the water-cooled high-voltage electrode. After argon 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 5 min. The substrate temperature, T_s, was determined by the balance between plasma irradiation heating and water cooling of the electrode. In this study, T_s was measured with irreversible temperature indicators attached to the high-voltage electrode on which the substrate was in-

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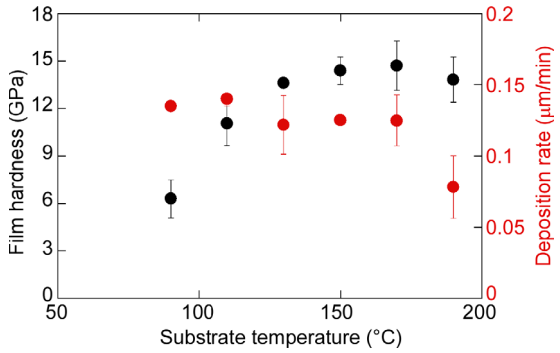

Fig. 2 Film hardness and deposition rate of DLC films as a function of substrate temperature.

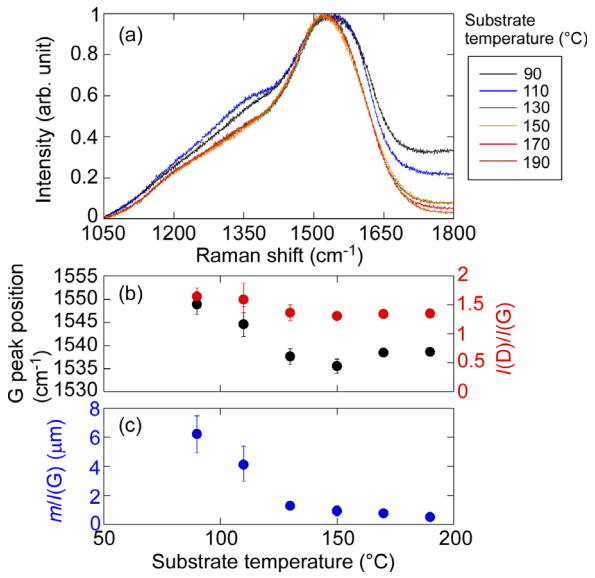

Fig. 3 (a) Raman spectra, (b) G peak position and $I(D)/I(G)$ and (c) $m/I(G)$, as functions of substrate temperature.

stalled, and it was controlled by inserting metal spacers as thermal insulation between the substrate and water-cooled electrode. The measurement resolution was 15°C. Moreover, the gap length was adjusted to be 30 mm even after the metal spacers were inserted. The film hardness was measured using a nanoindentor. The microstructure of the deposited DLC film was evaluated employing Raman spectroscopy using an incident laser wavelength of 532 nm.

Figure 2 shows the film hardness and deposition rate of the DLC films as a function of T_s. The displacement depth was approximately 200 nm in the nanoindentor measurement. As T_s increased from 90°C to 170°C, film hardness increased; however, it decreased slightly at 190°C. Such a substrate temperature effect was not observed in the deposition experiment with the He/CH_4 plasma. Furthermore, the maximum hardness was 15 GPa, which was higher than 13 GPa obtained in our previous study [3]. The deposition rate of the DLC film, approximately 0.13 μm/min, was approximately six times higher than that of a conventional low-gas pressure plasma chemical vapor deposition experiment [4]. Moreover, it was also found that the deposition rate shows a slight decreasing trend with increasing T_s, especially at 190°C.

Figure 3 (a) shows the Raman spectra of the DLC films. The broad peaks can be deconvoluted into two Gaussian components centered at approximately 1550 cm^{-1} (G band) and 1350 cm^{-1} (D band), indicating the typical Raman spectra characteristics of a DLC film. The Raman spectra were characterized using the G peak position and the D band and G band area ratio, $I(D)/I(G)$, as shown in Fig. 3 (b). The relationships among G peak position, $I(D)/I(G)$, and the sp^3 fraction of a DLC film have been investigated [5]. Applying those relationships to the present study, the sp^3 fraction was identified as approximately 35% at T_s of 150 °C. It is also well known that hydrogen content of a DLC film correlates with the slope of the photoluminescence background of the Raman spectrum [6]. The $m/I(G)$, or the ratio of the slope of the fitted linear background from 1050 to 1800 cm^{-1}, m, to the G peak intensity, $I(G)$, increases exponentially with hydrogen content. As shown in Fig. 3 (c), as T_s increases, $m/I(G)$ decreases, indicating decreasing hydrogen content in the film.

It has been reported that varying the substrate temperature from 50°C to 200°C results in very large changes in deposition rate and film structure [7, 8]. The main mechanism is the etching and hydrogen abstraction effects in the film caused by hydrogen radical irradiation, which are accelerated as substrate temperature increases. The dependence also varies with ion irradiation conditions. As the hydrogen content in the DLC film decreases, the film density sharply increases [9], which in turn causes an increase in film hardness [10]. As shown in Fig. 1, the substrate is irradiated with hydrogen atom radicals during film deposition, which is thought to cause the hydrogen abstraction and etching effects. Consequently, the increase in the film hardness at high T_s is ascribed to the decreased hydrogen content in the films. Conversely, it is known that graphitization occurs at more than 200°C [11]. The slight decrease in film hardness at 190°C shown in Fig. 2 may be attributed to graphitization because a significant decrease in film hardness was observed when T_s was raised above 200°C by increasing the repetition frequency of the pulsed voltage.

In this study, preparation of DLC films with a deposition rate of 0.13 μm/min and the film hardness of 15 GPa was successfully conducted using repetitive nanosecond pulsed glow H_2/CH_4 discharge plasma. The DLC film hardness could be increased by hydrogen radical irradiation under controlled substrate temperatures.

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[1] C. Zou *et al.*, Jpn. J. Appl. Phys. **55**, 115501 (2016).
[2] N. Ohtake *et al.*, Jpn. J. Appl. Phys. **43**, L1406 (2004).
[3] Y. Kikuchi *et al.*, Jpn. J. Appl. Phys. **56**, 100306 (2017).
[4] Y. Oka *et al.*, IEEE Trans. Plasma Sci. **34**, 1183 (2006).
[5] A.C. Ferrari *et al.*, Phys. Rev. B **61**, 14095 (2000).
[6] C. Cashiraghi *et al.*, Diam. Relat. Mater. **14**, 1098 (2005).
[7] A. von Keudell *et al.*, Diam. Relat. Mater. **11**, 969 (2002).
[8] M. Shinohara and H. Fujiyama, J. Plasma Fusion Res. **83**, 935 (2007) (in Japanese).
[9] X. Dong *et al.*, Jpn. J. Appl. Phys. **55**, 01AA11 (2016).
[10] T. Ishikawa and J. Choi, Diam. Relat. Mater. **89**, 94 (2018).
[11] H. Li *et al.*, Thin Solid Films **515**, 2153 (2006).