Diamond-like carbon film preparation using a high-repetition nanosecond pulsed Ar/CH_4 glow discharge plasma

M. Kawaguchi , J. Tamakoshi and Y. Kikuchi

Graduate School of Engineering, University of Hyogo, Hyogo, Japan

Abstract: Diamond-like carbon (DLC) films were prepared using high-repetition nanosecond pulsed Ar/CH_4 glow discharge plasmas at gas pressures from 0.36 kPa to 1.2 kPa. As the gas pressure was decreased, the hydrogen content in the DLC films decreased and the film hardness increased, reaching approximately 12 GPa. By adjusting the gas pressure, the dilution gas can be replaced from expensive He to Ar, and the results will contribute to the realization of low-cost and high-speed DLC film deposition technique.

Keywords: Diamon-like carbon, nanosecond pulsed glow discharge

1. Introduction

Diamond-like carbon (DLC) films have attracted broad interest in a wide range of industrial fields because of its excellent material properties such as high mechanical hardness, low coefficient of friction, chemical inertness, and biological compatibility [1]. At present, physical vapor deposition (PVD) with a solid target material [2] and plasma chemical vapor deposition (CVD) with a source gas [3] under low gas pressures, typically below 10 Pa, are widely used for DLC film preparation. One of the research issues of DLC film preparation using conventional plasma CVD processes is the low deposition rate of 0.013 μm/min [3]. Recently, we have demonstrated a high-speed preparation technique for DLC film preparation using a high-repetition nanosecond pulsed glow discharge under sub-atmospheric pressure [4]. It has been shown that the deposition rate was 0.1 μm/min and the film hardness was sufficiently large at 13 GPa. In our previous study, a process gas of methane (CH_4) was diluted by helium (He) in order to obtain a stable glow discharge at sub-atmospheric pressure. However, He is a rare and expensive gas. Thus, it is necessary to find out a low-cost alternative dilution gas for further cost reduction of DLC film preparation. In this presentation, we report the results of DLC deposition using argon (Ar)/CH_4 as the process gas.

2. Experimental setup

Figure 1 shows a schematic view of an experimental device in this study. A discharge source has two parallel plate electrodes made of stainless steel [diameter of upper (bottom) electrode: 50 (70) mm, thickness: 10 (5) mm, and gap length: 30 mm]. The electrodes were installed in a vacuum chamber, and the chamber was evacuated with a dry scroll pump. A prosess gas was CH_4 diluted with Ar or He. The gas flow rates of Ar (He) and CH_4 were 3 and 0.6 L/min, respectively. In this experiment, the gas pressure during the deposition was varied from 0.36 to 1.2 kPa.

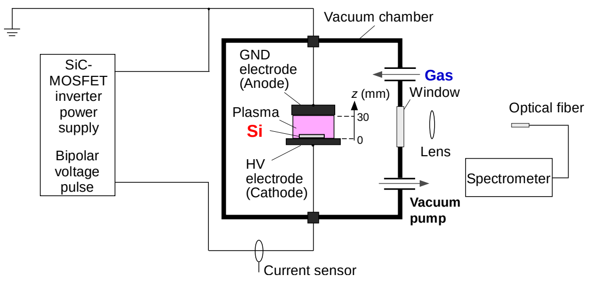

Fig. 1. Experimental setup

The upper electrode was grounded, and the bottom one was powered with a SiC-MOSFET inverter power supply. This power supply can produce high-voltage nanosecond bipolar pulses. The repetition frequency of bipolar voltage pulses was 150 kHz, and the duration of the pulsed voltage defined by the full width at half maximum (FWHM) was 250 ns in this study. The peak values of the voltage and current between the electrodes at gas pressures of 0.36 kPa and 1.2 kPa were 0.68 kV, 3.8 A, 0.76 kV, and 3.4 A, respectively. Time-integrated optical emission spectroscopy (OES) measurements were carried out in order to discuss effects of the gas pressures on the plasma parameters. For DLC film deposition experiments, silicon wafers (25×25×0.6 mm^3) were used as substrates. The substrates were pretreated in acetone shampoo with an ultrasonic vibrator, and then installed on the water-cooled high voltage electrode. After Ar/H_2 plasma irradiation at a gas pressure of 100 Pa for 20 min, the substrate was exposed to a repetitive nanosecond pulsed glow Ar (He)/CH_4 discharge plasma for 5 min.

The thickness, film structure and hardness of the DLC films were evaluated by FE-SEM, Raman spectroscopy and nanoindenter.

3. Experimental results

Figure 2 shows the deposition rate of DLC films deposited by the Ar/CH_4 and He/CH_4 plasma irradiation. It can be seen that the deposition rate decreases as the gas pressure is decreased. This is attributed to the decrease in plasma density. Furthermore, the deposition rate of the Ar/CH_4 plasma is higher than that of the He/CH_4 plasma at the same gas pressure, which is thought to be due to the higher plasma density in the Ar/CH_4 plasma. To obtain a deposition rate of approximately 0.1 μm/min, which is the deposition rate in our previously reported He/CH_4 plasma irradiation experiment, we investigated the gas pressure at which a hard DLC film can be obtained by the Ar/CH_4 plasma irradiation.

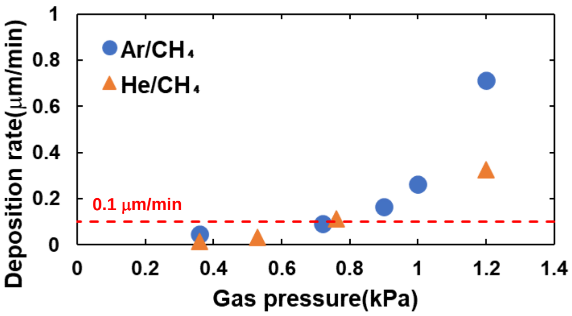

Fig. 2. Deposition rate of the DLC films deposied by the Ar/CH_4 and He/CH_4 plasma irradiation as a function of Ar gas pressure.

Figure 3 shows the obtained Raman spectra of the DLC films. The Raman spectra can be deconvoluted into two Gaussian components centered at the D band (1350 cm^{-1}) and the G band (1550 cm^{-1}). The hydrogen content in the DLC film was determined using the relationship between the slope of the Raman spectra at 1050 cm^{-1} to 1800 cm^{-1} and the intensity of the G peak [5]. Figure 4 shows the relationship between gas pressure and hydrogen content in the DLC film. In the case of the Ar/CH_4 plasma at a gas pressure of 1.2 kPa, the hydrogen content is very high at 57%. The deposition rate is very high at 0.83 μm/min compared to 0.1 μm/min in the case of the He/CH_4 plasma irradiation, but the DLC film is considered to have low hardness due to the high hydrogen content in the film. As

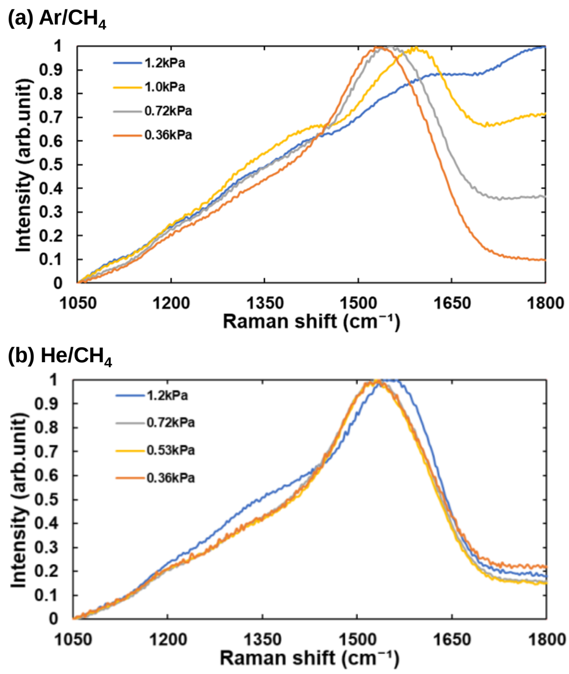

Fig. 3. Raman spectra of the DLC films deposited by (a) Ar/CH_4, and (b) He/CH_4 plasma irradiation.

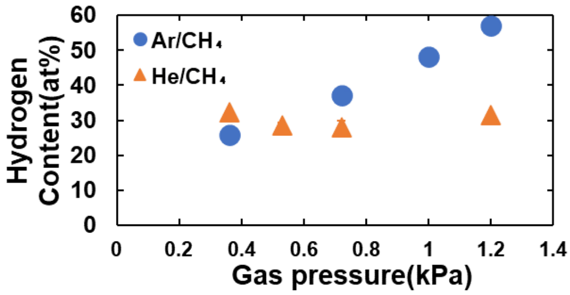

Fig. 4. Hydrogen content in the DLC films deposited with Ar/CH4 and He/CH4 plasmas as a function of gas pressure.

the gas pressure was decreased, the hydrogen content decreased to 26% at 0.36 kPa. The deposition rate of 0.045 μm/min was obtained, respectively. On the other hand, in the case of the He/CH_4 plasma, the hydrogen content in the DLC film is almost constant at about 30% in this gas pressure range. By adjusting the gas pressure, it is thought that a DLC film with Raman spectra similar to those deposited by the He/CH_4 plasma irradiation can be achieved in the Ar/CH_4 plasma irradiation.

Figure 5 shows the gas pressure dependence of film hardness and hydrogen content in the DLC films deposited by the Ar/CH_4 plasma irradiation. Here, the film thickness at each gas pressure is 1 ± 0.2 μm, and the indentation depth of the nanoindenter measurment is about 1/10 of the film thickness, so that the effect of the Si substrate does not appear in the film hardness. It can be seen that as the gas pressure is decreased, the hydrogen content decreases and the film hardness increases. At a gas pressure of 0.36 kPa, the film hardness is about 12 GPa. As the hydrogen content in the DLC film decreases, the film density increases [6], which in turn causes an increase in film hardness [7]. On the other hand, substrate temperature is also known to affect the hydrogen content in the DLC film [8]. The substrate temperatures of 118, 141, 182, and 187°C were obtained at gas pressures of 0.36, 0.72, 1.0, and 1.2 kPa

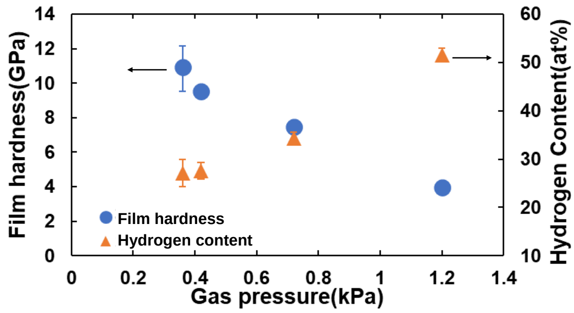

Fig. 5. Film hardness and hydrogen content in the DLC films deposited by the He/CH4 plasma irradiation Raman spectra of the DLC films as a function of gas pressure.

during the deposition. It is known that hydrogen abstraction in the DLC film is caused by hydrogen radical irradiation, which is accelerated as subtrate temperature increases [8]. Therefore, the main mechanism of the decrease in the hydrogen content in the DLC films in this experiment is considered to be the change in plasma parameters due to the decrease in gas pressure.

To investigate changes in plasma parameters as the gas pressure was varied, OES measurements were conducted. Figure 6 shows the gas pressure dependences of Ar ion (Ar II, 465.8 nm) and carbon ion (C II, 426.7 nm) emission intensities normalized by Ar neutral emission intensity (Ar I, 750.8 nm). As shown in Fig. 6(a), the Ar II/Ar I intensity ratio increases with decreasing gas pressure, suggesting an increase in electron temperature. Furthermore, the increase in the intensity ratio C II/Ar I shown in Fig. 6(b) suggests that the decrease in gas pressure promotes the dissociation and ionization of CH_4. It is also known that ion irradiation conditions such as ion bombardment energy and ion flux are important to obtain DLC films with high hardness [?, ?]. The lower gas pressure is expected to reduce the collision frequency between ions and neutral particles in the sheath region near the substrate, resulting in higher incident ion energy to the substrate. Therefore, the main mechanism for the decrease in hydrogen content and increase in film hardness due to the decrease in the gas pressure is thought to be the increase in incident ion energy and ion flux to the substrate.

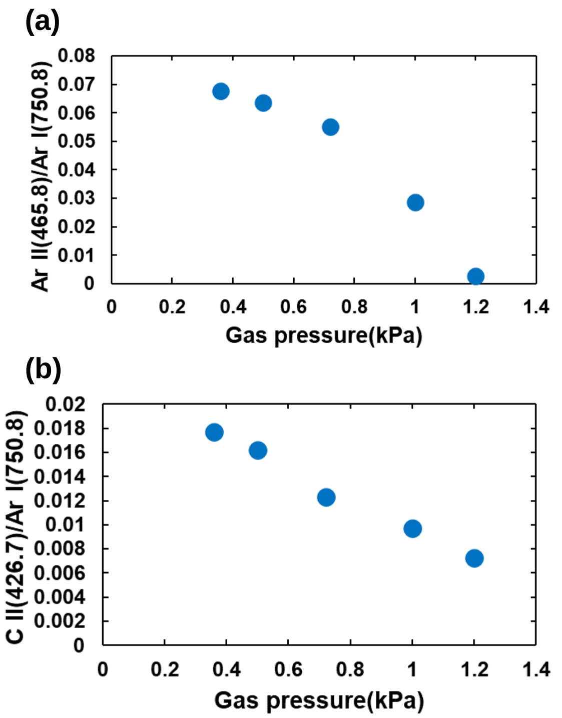

Fig. 2. Intensity ratio of (a) Ar II/ Ar I and (b) C II/ Ar I as a function of gas pressure.

4. Summary

In this study, DLC deposition experiments were conducted using nanosecond pulsed Ar/CH_4 glow discharge plasmas with the repetition frequency of 150 kHz. The film hardness of about 12 GPa, the hydrogen content of about 26%, and the deposition rate of 0.045 μm/min were obtained by adjusting the gas pressure. In the future, by increasing the power supply frequency and optimizing the gas flow rate and pressure, it is expected that a deposition rate comparable to that of the He/CH_4 plasma irradiation can be achieved.

5. References

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