Mechanism of high growth rate for diamond-like carbon films synthesized by helicon wave plasma chemical vapor deposition

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Abstract
A high growth rate fabrication of diamond-like carbon (DLC) films at room temperature was achieved by helicon wave plasma chemical vapor deposition (HWP-CVD) using Ar/CH4 gas mixtures. The microstructure and morphology of the films were characterized by Raman spectroscopy and scanning electron microscopy. The diagnosis of plasma excited by a helicon wave was measured by optical emission spectroscopy and a Langmuir probe. The mechanism of high growth rate fabrication for DLC films by HWP-CVD has been discussed. The growth rate of the DLC films reaches a maximum value of 54 μm h⁻¹ at the CH4 flow rate of 85 sccm, which is attributed to the higher plasma density during the helicon wave plasma discharge. The CH and Hα radicals play an important role in the growth of DLC films. The results show that the Hα radicals are beneficial to the formation and stabilization of C=C bond from sp² to sp³.

Keywords: helicon wave plasma, diamond-like carbon film, sp³ content, Raman spectra

(Some figures may appear in colour only in the online journal)

1. Introduction
Diamond-like carbon (DLC) is a metastable form of amorphous carbon containing a significant fraction of sp² bonds [1]. It has attracted much attention due to its outstanding performance in physical-chemical characteristics such as high optical transparency in the wavelength ranging from the ultraviolet to infrared region, high hardness, self-lubrication, excellent wear resistance, atomic smoothness and good adhesion [2–4]. Many practical products such as heart valves, cardiovascular stents, orthopedic devices, magnetic data storage disks and field emission displays have been applied in commercial fields [5–8]. In general, there are many methods for the synthesis of DLC films, including microwave plasma [9], vacuum arc discharge [10], pulsed-DC hollow cathode discharge [11], magnetron sputtering [12] and so on. Various approaches have been tried to improve the quality and growth rate for DLC films. For example, the DLC films deposited by low-pressure inductively coupled plasmas can achieve a growth rate of 75.1 nm min⁻¹ (i.e. 4.5 μm h⁻¹) [13], and meshed plasma immersion ion deposition can attain a high deposition rate of 6.5 μm h⁻¹ [14].

The helicon wave plasma (HWP) source has many advantages compared with conventional plasma sources, such as higher plasma density and lower ion energy, which can result in a greater efficiency in the breaking of C–H and Si–H
bonds within the feedstocks [15]. Furthermore, the achieved plasma density $n$ is almost an order of magnitude higher than that in other discharges at comparable pressures and input powers [16, 17]. Therefore, HWP is attracting considerable attention as a new plasma source due to these features. In this paper, we report the synthesis of DLC films by helicon wave plasma chemical vapor deposition (HWP-CVD) using Ar/CH$_4$ gas mixtures at room temperature. The mechanism of high growth rate fabrication for DLC films by HWP-CVD has been investigated by optical emission spectroscopy (OES), Langmuir probe, scanning electron microscopy (SEM) and Raman spectroscopy.

2. Experimental details

A schematic diagram of the self-designed HWP-CVD apparatus is shown in figure 1. The apparatus consists of many parts, mainly including the vacuum discharge chamber with a diameter of 228 mm and a length of 800 mm, the vacuum deposition chamber with a diameter of 400 mm and a length of 400 mm, magnetic coil, water-cooled Nagoya III-type internal helicon antenna with a diameter of 50 mm and a length of 180 mm, substrate holder, turbo pump, and so on. This apparatus can excite the plasma wave to a helicon mode and generate high-ionized plasma in the source chamber, and then diffuse into the reaction chamber. It is worth noting that our helicon antenna is located inside the source chamber, while most helicon antennas for other apparatuses are placed around the source chamber [18, 19]. The main characteristic of this internal helicon antenna is that we can change the jet direction of the generated high-density plasma by varying the axial direction of the internal helicon antenna. Using this characteristic, the apparatus with the internal helicon antenna can also be used in the research of plasma-wall interaction [17].

P-type Si (100) wafers with the dimension of $40 \times 40 \times 0.5$ mm were cleaned by the conventional RCA method, and finally placed on the substrate holder in the reaction chamber. The Ar/CH$_4$ gas mixtures were introduced into the source chamber to generate high-density plasma. The CH$_4$ flow rate was varied from 45–145 sccm, while the Ar flow rate was maintained at 50 sccm. Table 1 shows the deposition parameters for the DLC films.

The diagnosis of plasma excited by helicon wave was measured by OES (MS 5204i) and Langmuir probe (Hiden ESPION). The morphology of the DLC films was characterized using SEM (SU8010). Visible and UV Raman spectra for the deposited DLC films were measured using an excitation light with a wavelength of 514 and 325 nm from a tunable Ar ion laser (HR800), respectively.

3. Results and discussion

The cross-section SEM images of the DLC films at different CH$_4$ flow rates are presented in figures 2(a)–(f) in order to investigate the variation in growth rate for DLC films. Based on the cross-section SEM images for the DLC films, the growth rates of the DLC films at different CH$_4$ flow rates are shown in figure 3. When the CH$_4$ flow rate increases, the growth rate of the DLC film increases at first and reaches a maximum value of 54 $\mu$m h$^{-1}$ at the CH$_4$ flow rate of 85 sccm, and then decreases with the further increase of the CH$_4$ flow rate. The growth rate of 54 $\mu$m h$^{-1}$ achieved in our experiment is much higher than that by other preparation methods that have been mentioned above [13, 14].
In order to calculate the plasma density at different CH$_4$ flow rates, the current–voltage ($I$–$V$) curves are measured by Langmuir probe. Then, the electron energy probability function $f(\varepsilon)$ and plasma density $N_i$ can be calculated from the Druyvesteyn formula [20].

$$f(\varepsilon) = \frac{2e\lambda_0}{\varepsilon A} \frac{dI}{dV}$$

$$N_i = \int_0^\infty \varepsilon^{1/2} f(\varepsilon) d\varepsilon$$

where $m_e$ and $e$ are the electron mass charge, $I$ and $V$ are the probe current and voltage, respectively, $A$ is the probe surface area, and $\varepsilon$ is measured in units of electron volt. The calculated plasma density $N_i$ at different CH$_4$ flow rate is also plotted in figure 3. When the CH$_4$ flow rate increases, the plasma density first increases up to a maximum value of about $3.8 \times 10^{-19}$ m$^{-3}$ at the CH$_4$ flow rate of 85 sccm, and then decreases with the further increasing CH$_4$ flow rate. Therefore, there is an optimum CH$_4$ flow rate that maximizes plasma density for the given discharge parameters. As can be seen in other helicon experiments, there is a threshold discharge pressure for sustaining the high-density helicon mode. Above the threshold, the change in the plasma density with increasing discharge pressure is insignificant or shows a downtrend [21]. The higher CH$_4$ flow rate (i.e. the higher discharge pressure) increases the energy cost of electron-ion production, and leads to a decrease of the plasma density [18].

The achieved maximum value of plasma density $n$ is almost an order of magnitude higher than that in other discharges at comparable pressures and input powers [22, 23].

![Figure 2](image-url)
Moreover, as can be seen from figure 3, the variation trend of plasma density is similar to that of the growth rate of DLC films with the increase of CH4 flow rate. The phenomenon seems to illustrate that the variation of the growth rate of DLC films is closely related to that of the plasma density during the discharge process. The high growth rate of DLC films can be ascribed to the high plasma density during the HWP discharge.

OES can be used to explore the relationship between the formation of DLC films and the different active species. The spectra for the HWP at different CH4 flow rates are presented in figure 4(a). The strong emissions including CH (431.5 nm), C2 Swan bands (516.5 nm), Ar (750.3 nm), Balmer atomic hydrogen Hα (486.1 nm) and Hβ (656.3 nm) are observed. The CH, Hα and Hβ are ascribed to the breakdown of CH4, and the production of CH from CH4 by electron impact dissociation expressed via \( \text{CH}_4 + e^- \rightarrow \text{CH}_3, \text{CH}_2, \text{CH}, \text{C} \) [24]. Here, CH4 and CH2 radical lines have not been detected in the optical emission spectrum. As is well known, the disappearance of the CH3 radical line is because it does not emit light in the spectrograph range [25]. In addition, the absence of the CH2 radical line can be expressed via \( \text{CH}_2 \rightarrow \text{CH} + \text{H} \) [26]. The C2 species are formed from the recombination reaction of CH4 and other carbon-containing radicals (CHx species) spread all over the chamber [27]. In a hydrogen-poor environment, the main reaction of the C2 radical production might be \( \text{C}_2\text{H}_2 + \text{Ar} \rightarrow \text{C}_2 + \text{H}_2 + \text{Ar} \) [28].

The optical emission intensities of the C2, CH, Hα, and Ar radicals at different CH4 flow rates are displayed in figure 4(b). It is observed that Hα and CH emission intensities increase with the increasing CH4 flow rate and reach a maximum value at a CH4 flow rate of 65 and 85 sccm, respectively, then decrease with the further increase of CH4 flow rate. The variation of CH emission intensity is similar to that of the growth rate of DLC films along with increasing CH4 flow rate. The phenomenon seems to illustrate that the CH radicals are related to the growth of DLC films. In view of the general belief, the CH radical should be considered as a precursor species in the diamond-like film growth reaction, and an increase in CH radical enhanced DLC film growth [29, 30]. Atomic hydrogen plays a role in enhancing chemical etching with respect to growth [31], and is beneficial to the formation and stabilization of C=C bond from sp2 to sp3 [32]. Hence, the presence of CH and Hα radicals plays an important role in the growth of DLC films. Meanwhile, the emission intensity of the C2 dimer monotonously increases, while the emission intensity of Ar decreases with increasing the CH4 flow rate. The increase in C2 is related to the enhanced nondiamond growth, and promotes the formation of more sp2 hybridized carbon domain and graphitic-like bonds in the DLC matrix [24, 33]. Argon is believed to play a role in the methane ionization and dissociation.

The Raman spectrum is a conventional technique for the confirmation of diamond phase, and is widely applied to characterize sp3 and sp2 phases in DLC films. As shown in figures 5(a) and (b), the visible (514 nm) and UV (325 nm) Raman spectra of the deposited DLC films exhibit two distinct peaks, namely, the G peak and D peak at different CH4 flow rates. According to [1], the G peak is due to the bond stretching of all pairs of sp2 atoms in both rings and chains, and the D peak is attributed to the breathing mode of sp3 sites only in six-fold rings, respectively. The relative content of sp3 ((sp3/(sp3 + sp2))) is one of the most important parameters that relate to the properties and structures of DLC films. Usually, the intensity ratio of the D peak and G peak, \( I(D)/I(G) \), has been widely applied to estimate the sp3 content in DLC [34, 35]. However, \( I(D)/I(G) \) can only give accurate measurements of sp3 content less than 20% for H-free DLC or

![Figure 3. Growth rate of the DLC films and the plasma density during the discharge process at different CH4 flow rates.](image)

![Figure 4. (a) OES spectra for the HWP at different CH4 flow rates. (b) Absolute emission intensities of C2, CH, Hα, and Ar bands as a function of CH4 flow rates.](image)
40% for hydrogenated DLC [35, 36]. Therefore, the dispersion rate of the G peak, Disp(G) was also used for confirming the sp³ content. We can calculate Disp(G) using the following formula [37]:

\[
Disp(G) = \frac{\text{Pos}(G)@\lambda_2 - \text{Pos}(G)@\lambda_1}{\lambda_2 - \lambda_1} \quad \text{[cm}^{-1}/\text{nm}] \tag{3}
\]

where \(\lambda_1\) and \(\lambda_2\) take values of 325 and 514 nm, respectively. Pos(G)@\(\lambda_1\) and Pos(G)@\(\lambda_2\) are the position values of the G peaks measured by 325 and 514 nm Raman, respectively. Based on the values of Pos(G)@\(\lambda_1\) and Pos(G)@\(\lambda_2\), the Disp (G) is calculated using formula (1) and is plotted in figure 6.

The sp³ content can be calculated from Disp(G) using the following formula [37]:

\[
\text{sp³ content} = -0.07 + 2.50 \times \text{Disp(G)}[\text{cm}^{-1}/\text{nm}] \\
\pm 0.06. \tag{4}
\]

Table 2. sp³ content is calculated from the formula (4).

<table>
<thead>
<tr>
<th>CH4 (sccm)</th>
<th>45</th>
<th>65</th>
<th>85</th>
<th>105</th>
<th>125</th>
<th>145</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp³ content (± 0.06)</td>
<td>0.21</td>
<td>0.33</td>
<td>0.25</td>
<td>0.20</td>
<td>0.12</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The results are listed in table 2 and also plotted in figure 6. The achieved maximum value of sp³ content at CH4 flow rate of 65 sccm is about 0.33. The sp³ content circuitously decreases, while the CH4 flow rate increases from 65 to 145 sccm, which can be ascribed to the increase of C2 radical in the plasma leading to the formation of more sp² hybridized carbon domain [7]. Ferrari proposed a three-stage model to interpret the Raman spectra of disordered and amorphous carbon [35]. This model considers an amorphisation trajectory, consisting of three stages from graphite to ta-C (or diamond):

1. graphite → nanocrystalline graphite (nc-G)
2. nanocrystalline graphite → sp² a-C
3. a-C → ta-C (→ 100 sp³ ta-C, defected diamond).

In passing from a-C to ta-C, the sp³ content rises from ~10%–20% to ~85% [36]. Because the achieved sp³ content varies from 33%–12% with different CH4 flow rates in our experiments, the deposited DLC films seem closer to amorphous carbon (a-C) containing a significant fraction of sp³ bonds.

The variation trend for sp³ content with increasing CH4 flow rate is similar to that for the Hα optical emission intensity observed in figure 4. This illustrates that the Hα radical is beneficial to the formation and stabilization of C=C bond from sp² to sp³. Therefore, in order to increase the sp³ content in the deposited DLC film, using CH4/H2/Ar gas mixtures in the fabrication of DLC film is a good idea in the next stage of research.

4. Conclusions

A high growth rate fabrication of the DLC film at room temperature was achieved by HWP-CVD using Ar/CH4 gas
mixtures. The growth rate of the DLC films reaches a maximum value of 54 μm h⁻¹ at the CH₄ flow rate of 85 sccm. The growth rate achieved in our experiment is much higher than that by other preparation methods. The reason for the high growth rate can be ascribed to the high plasma density during the HWP discharge. The presence of CH radical plays an important role in the growth of DLC films. The sp³ content in the DLC film is calculated from the dispersion rate of the G peak, and it reaches a maximum of 0.33 at the CH₄ flow rate of 65 sccm. The variation trend for sp³ content with the increase of CH₄ flow rate is similar to that for Hₖ optical emission intensity. The results show that the Hₖ radical is beneficial to the formation and stabilization of C=C bond from sp² to sp³. Meanwhile, the C₂ must be associated with the formation of more sp² hybridized carbon domain and graphitic-like bonds in the DLC matrix.

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