Deposition of Diamond-Like Carbon on Inner Surface by Hollow Cathode Discharge*

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Abstract A cylindrical hollow cathode discharge (HCD) in CH$_4$/Ar gas mixture at pressure of 20-30 Pa was used to deposit diamond-like carbon (DLC) films on the inner surface of a stainless steel tube. The characteristics of the HCD including the voltage-current curves, the plasma images and the optical emission spectrum (OES) were measured in Ar and CH$_4$/Ar mixtures. The properties of DLC films prepared under different conditions were analyzed by means of Raman spectroscopy and scanning electron microscopy (SEM). The results show that the electron excitation temperature of HCD plasma is about 2400 K. DLC films can be deposited on the inner surface of tubes. The ratio of $sp^3$/sp$^2$ bonds decreases with the applied voltage and the deposition time. The optimizing CH$_4$ content was found to be around CH$_4$/Ar = 1/5 for good quality of DLC films in the present system.

Keywords: diamond-like carbon, hollow cathode discharge, film deposition, inner surface

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

1 Introduction

Since the introduction by Aisenberg and Chabot [1], diamond-like carbon (DLC) has drawn a great deal of attention as a promising material owing to its unique characteristics, such as high hardness, low friction coefficient, chemical inertert, gas barrier property and biocompatibility, etc. DLC is an amorphous carbon with mixture of $sp^3$ and $sp^2$ bonds synthesized by various techniques, such as radio frequency plasma enhanced chemical vapor deposition (RF-PECVD), plasma immersion ion implantation and deposition (PIII-D) and filtered cathodic vacuum arc (FCVA) [2–4], and the properties of DLC are affected by the deposition techniques and the synthesis conditions employed. The deposition of DLC films on the inner surface of tubes, however, is usually difficult. One of the alternative ways is to employ hollow cathode discharge (HCD) which is a type of gas discharge between hollow-structured cathodes and an arbitrarily shaped anode [5]. Hollow cathode effect (HCE), a unique characteristics of HCD, can be achieved when the negative glow regions from two opposite cathode surfaces overlapped. In this regime, high energy electrons can oscillate between the negative glows and the excitation/ionization will be greatly enhanced, and thus high density plasma and active species can be generated inside the hollow cathode. Extensive investigations and wide applications of HCD have been achieved in the past decades [6–10]. With high density plasma inside the cathode cavity, HCD becomes a feasible approach to deposit DLC films on the inner surface of tubes [11,12].

In this work, we developed a localized cylindrical HCD technique to deposit DLC film on the inner surface of metal tube. This type of DLC-deposition device is simple to operate and easy to control. The discharge characteristics of the HCD and the properties of the DLC films have been investigated experimentally.

2 Experimental details

The experimental apparatus is shown in Fig. 1. It is composed of a vacuum system and a discharge system. A cylindrical metal tube (stainless steel, type of 316L) acts as the hollow cathode. The inner diameter of the tube is 12 mm and the length is 20 mm. A pair of anodes is 10 cm away from the cathode. The HCD plasma is excited by a negative DC power source (WWL-LDG 2000V/1A). A ballast resistor $R = 100 \text{k}\Omega$ is connected in series with the cathode. The applied voltage is recorded by a digital oscilloscope (Tektronik TDS3054B) and the averaged current is measured by an Ampere-meter connected in series with the anode. There is a glass window on the vacuum chamber so that the optical characteristics of the discharge plasma can be acquired. A digital CCD camera (Canon A950) is used to record the plasma images from the end-on of the tube. The spectrum lines of the active groups were captured by optical emission spectroscopy (OES,
Omni-λ500). The deposition was performed in CH$_4$/Ar mixtures. The range of the total pressure $p$ is 10 Pa to 100 Pa and the ratio of CH$_4$/Ar ranges from 10% to 50% during the deposition.

Before deposition experiment, the substrates were polished and cleaned ultrasonically in acetone, ethanol and deionized water in sequence to remove the impurities on substrates. To prepare the DLC’s samples, stainless chips made of the same material of the tube with dimensions of 20 mm $\times$ 5 mm $\times$ 0.4 mm were fixed inside of the steel tube along the axis. The chip and the inner surface of metal tube were cleaned by Ar glow plasma at pressure of 20-30 Pa for 10 min. Thereafter DLC films were deposited in CH$_4$/Ar plasma at different deposition time, applied voltages and CH$_4$/Ar ratios.

The morphology of DLC films was analyzed by scanning electron microscopy (SEM, Hitachi JSM-5600). The bonding state was analyzed by Raman spectroscopy (PI SpectraPro 2500i). The structure of deposited DLC film is evaluated by the ratio of integrated spectrum intensity of D-peak and G-peak (or the ratio of $sp^3/\text{sp}^2$) from Raman spectrum which is one of the popular methods to evaluate the DLC feature [13]. The thickness of DLC films is determined by surface profiler (Veeco Dektak 150).

![Fig.1 Schematic of the experimental apparatus](image)

### 3 Results and discussion

#### 3.1 Plasma diagnostics

Firstly we investigated the characteristics of the HCD. Voltage-current ($V$-$I$) curves were measured under different discharge conditions and the emission of the plasma was recorded. In the OES method an Omni-λ spectrograph was used for the wavelength ranging from 300 nm to 600 nm.

A typical $V$-$I$ curve of the HCD in pure argon is shown in Fig. 2. The images from end-on are also shown with increasing currents. The argon pressure is 20 Pa.

It is seen that the HCD starts from diffuse glow of small current, with two separated spots located at each end of the cavity (see Fig. 2(a) at 0.2 mA). This is the first stage of pre-discharge mode. When the current increases above 1.0 mA, the voltage decreases suddenly from 396 V to 336 V. Meanwhile the discharge image changes distinctly accordingly. A weak, solid column forms along the axis of the cavity to connect the two separated spots (see Fig. 2(b)), demonstrating that the discharge goes into the second stage. There are two modes exist in this stage. In the first one (see Fig. 2(b)-(d)) the voltage increases with the current, but the brightness of the plasma column is still weak. The differential resistivity at this stage is smaller than that in pre-discharge mode and decreases slightly as the current rises, indicating that the discharge is in abnormal glow discharge (AGD) mode. In this mode the reduced current density ($J/\rho^2$) ranges from 9.4 mA·Torr$^{-2}$·cm$^{-2}$ to 31.3 mA·Torr$^{-2}$·cm$^{-2}$ which is much larger than that of a normal glow (of the order of 0.2 mA·Torr$^{-2}$·cm$^{-2}$) [8]. The positive differential resistivity on the $V$-$I$ curve together with the high current density also strongly refers to the signature of AGD. When the current rises up to a critical value of 4.5 mA, the slope of the $V$-$I$ curve becomes a constant. The luminance suddenly becomes much intense and a bright line appears in the center of the plasma column (see Fig. 2(d) at 5 mA), indicating a change in the discharge mode. The luminous solid column associated with the overlapping of the negative glows (NGs) is the typical feature of HCE. No significant normal glow discharge was found under the present condition. The above results indicate that the onset of HCE is achieved by transition from AGD. It was also noticed that the transition from pre-discharge to AGD is not stable and there is a drop in the applied voltage (see the $V$-$I$ curve around point (b) in Fig. 2). From (d) to (e) the discharge operates in the HCE mode. The voltage is proportional to the current with a differential resistance of $R_p = 10.6$ kΩ. The radius of the bright plasma column increases (i.e. the thickness of cathode fall deceases) with increasing current. As the current increases further a new mechanism will appear and the discharge is suggested to be a hybrid mode in combination of AGD and HCE modes. The transition of discharge mode into this localized HCD was well described in Ref. [14].

![Fig.2 The discharge images with different currents and the $V$-$I$ curve of HCD in pure Ar at 20 Pa](image)
The characteristic of HCD in CH4/Ar mixture is similar to that in pure Ar at the initial phase. But as the time goes by, in CH4/Ar discharge the current will deceases while the voltage increases. This should be caused by the deposition of DLC films on the inner surface of the cathode. The OES of the CH4/Ar discharge is different from that in pure Ar, as shown in Fig. 3.

It is seen that the Ar(4p5-1s5) line at 355.5 nm appears in both Ar and CH4/Ar discharges. But in CH4/Ar plasma, the spectra of CH (A2∆-X2II) group at 431.4 nm and CH (A2∆-X2II) at 462.9 nm can be observed. These carbon groups have also been found in the gas phase of all DLC deposition [16], indicating that the precursors to deposit DLC are produced in the CH4/Ar plasma in the present configuration.

From the result of OES, the radical number density of CH(X2II) NCH might also be determined from the density of the excited Ar (1s5) NAr by the actinometry method. In this method, both species (e.g. Ar and CH in our experiment) should be excited by direct electron impact from their lower energy state to irradiative excited states, respectively, and the energy of the two irradiative excited states should be almost the same [16]. The excitation energy of CH(A2∆) radical from the ground level of CH(X2II) radical is ~3 eV, and Ar(4p5) excited atoms is also situated at ~3 eV from Ar(1s5) metastable atoms. By comparing the spectra intensity of CH(A2∆-X2II) at 431.4 nm and Ar (4p5-1s5) at 355.5 nm, NCH can be calculated as follow [16]:

\[ N_{CH} = \left( \frac{A_{ji}^{Ar} I_{OES}^{CH}}{A_{ji}^{CH} I_{OES}^{Ar}} \right) N_{Ar}, \]

where NAr is the density of Ar (1s5), AjiAr is the Einstein coefficient of Ar transition from 4p5 to 1s5, AjiCH is the Einstein coefficient of CH transition from A2∆ to X2II (=1.8x10^8 s⁻¹) [17]. Under the present conditions, NCH = (0 – 3.3) x 10⁻⁴ NAr according to the CH4 ratio, indicating that the content of CH4 influences the OES intensity of the CH(A2∆-X2II) line at 431.4 nm (I_{OES}^{Ar}) and hence the CH(X2II) radical number density (NCH).

The electron excitation temperature can be calculated from Boltzmann plot [18]. For this, the plasma is assumed to be in local thermal equilibrium. The electron excitation temperature is about 2400 K under the above conditions when the Ar spectrum lines 763.51 nm (with intensity of 463) and 772.42 nm (with intensity of 273) were used.

### 3.2 DLC film deposition

With HCD, a film was deposited on the inner surface of metal tube. We firstly confirmed the existence of DLC, and then investigated the effects of the deposition time, the applied voltage and the ratio of CH4/Ar on the properties of DLC films.

Fig. 4 shows the Raman spectrum of a DLC film sample. It was deposited for 10 min in HCD plasma of CH4/Ar mixture (ratio of 1:5) at 26 Pa under applied voltage of 300 V. The result is a typical spectrum of DLC films, i.e., a pair of asymmetric peaks of D-peak (disorder) around 1370 cm⁻¹ and G-peak (graphite) around 1570 cm⁻¹. It means that the films contain both sp³-bond and sp²-bond. The proportion of sp³-bond is estimated by the value of ID/IG. The higher the content of sp³-bond, the better the quality of DLC films. By Gaussian fitting, one can obtain the ratio ID/IG = 0.4, which is a typical value for DLC film. Generally the ratio ID/IG of DLC film is 0.2-3.5 [19,20].
The surface morphology of this DLC film characterized by SEM is shown in Fig. 5. One can see that the film is uniform and has a high density. But there are some cracks on the surface. This may be due to the poor quality of the substrate surface. From the surface profiler, the thickness of the above DLC film (i.e. deposited for 10 min in CH$_4$/Ar mixture with ratio of 1:5 under voltage of 300 V) is about 290 nm. The thickness depends on the deposition time as well as other conditions.

![SEM image of the DLC film](image)

At given applied voltage, pressure and CH$_4$/Ar content, the ratio of $I_D/I_G$ increases with the deposition time, as shown in Table 1. According to the theory that the relative intensity of D-peak against G-peak ($I_D/I_G$) by Gaussian fitting decreases with the $sp^3$ content [21], the content of $sp^3$-bond in the present conditions will decrease with the deposition time. The possible reason is that as the time goes by, the HCD becomes weaker inside the tube due to the deposited DLC films on the surface, which will reduce the conductivity of the metal surface. In this experiment, the maximum current appears at 9 minutes or so. Thereafter the discharge current deceases significantly and so do the active species. The plasma condition becomes worse for the DLC deposition. Therefore, the deposition time should not be too long.

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>D-peak position (cm$^{-1}$)</th>
<th>G-peak position (cm$^{-1}$)</th>
<th>$I_D/I_G$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1376</td>
<td>1566</td>
<td>0.306</td>
</tr>
<tr>
<td>20</td>
<td>1381</td>
<td>1568</td>
<td>0.390</td>
</tr>
<tr>
<td>30</td>
<td>1388</td>
<td>1573</td>
<td>0.475</td>
</tr>
</tbody>
</table>

At a constant deposition time, the ratio of $I_D/I_G$ increases with the applied voltage, as shown in Table 2. This should be explained that at higher voltage the electrons will be more energetic to dissociate the methane molecule into smaller molecules or ions including C and C$^+$, which will reduce the number of the precursors (CH/CH$^+$) of DLC films. This suggests that a high voltage is not optimal for DLC deposition in this HCD system. The applied voltage should be as low as possible.

<table>
<thead>
<tr>
<th>Discharge voltage (V)</th>
<th>D-peak position (cm$^{-1}$)</th>
<th>G-peak position (cm$^{-1}$)</th>
<th>$I_D/I_G$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1362</td>
<td>1568</td>
<td>0.355</td>
</tr>
<tr>
<td>350</td>
<td>1390</td>
<td>1569</td>
<td>0.450</td>
</tr>
<tr>
<td>400</td>
<td>1381</td>
<td>1580</td>
<td>0.878</td>
</tr>
</tbody>
</table>

The property of DLC films is also influenced by the gas ratio of CH$_4$/Ar. Generally, increasing the content of CH$_4$ results in an increase of the ratio $I_D/I_G$, as shown in Table 3. Also the large content of CH$_4$ influences the stability of HCD. Therefore, the CH$_4$ concentration should be suitable for the DLC deposition. The optimal ratio is CH$_4$/Ar $\sim$ 1/5 in the present system.

<table>
<thead>
<tr>
<th>Gas ratio CH$_4$/Ar position</th>
<th>D-peak position (cm$^{-1}$)</th>
<th>G-peak position (cm$^{-1}$)</th>
<th>$I_D/I_G$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:5</td>
<td>1382</td>
<td>1565</td>
<td>0.405</td>
</tr>
<tr>
<td>1:4</td>
<td>1367</td>
<td>1570</td>
<td>0.548</td>
</tr>
<tr>
<td>1:3</td>
<td>1387</td>
<td>1572</td>
<td>0.678</td>
</tr>
</tbody>
</table>

4 Conclusion

In this work we demonstrated that DLC films could be deposited on the inner surface of steel tube by DC HCD. The HCD is typically localized inside the cathode cavity. The OES shows that the precursors (i.e., CH and CH$^+$ groups) are produced in HCD in CH$_4$/Ar mixtures. The Raman spectrum and SEM were used to analyze the DLC properties. The results show that the DLC film was indeed deposited on the inner surface and the content of $sp^3$-bond decreases with the deposition time and the applied voltage. An appropriate CH$_4$ concentration could result in a higher content of $sp^3$-bond. This technology may find applications in depositing DLC films on the inner surface of long metal tubes.

References

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