EFFECT OF H$_2$/CH$_4$ RATIOS ON THE STRUCTURE AND PROPERTIES OF COATINGS FOR HERMETICALLY CARBON-COATED OPTICAL FIBER PREPARED BY PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION METHOD

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Key Words: amorphous carbon, optical fibers, structure, plasma deposition.

ABSTRACT

The amorphous hydrogenated carbon (a-C:H) films for hermetical optical fiber coatings are prepared by plasma enhanced chemical vapor deposition method with different hydrogen/methane (H$_2$/CH$_4$) ratio. The structure and properties of a-C:H films are examined by Fourier transform infrared spectroscopy, Raman scattering spectroscopy, UV/V is spectrophotometer, nanoindentation, atomic force microscopy and field emission scanning electron microscopy. It is found that the sp$^3$-C-C bonds are changed to the sp$^3$-CH$_x$ bonds as the H$_2$/CH$_4$ ratio increases. The optical band gap of a-C:H films increases with increasing the H$_2$/CH$_4$ ratio, while the hardness, Young's modulus, and roughness of a-C:H films decrease. As a result, the a-C:H film is shifted toward the polymer-like films with increasing the H$_2$/CH$_4$ ratio, and the color of a-C:H films is changed from dark brown to light yellow. The outer surface of a-C:H films includes many nano-crystalline grains. The nano-crystalline grain size decreases with increasing the H$_2$/CH$_4$ ratio. There exists an optimum H$_2$/CH$_4$ ratio to obtain a-C:H films with high mechanical strength.
1. INTRODUCTION

Recently, various properties of diamond-like carbon (DLC) films have been found, such as wide band gap, high hardness, inert chemical attack, infrared transparency and high water resistance [1,2]. Many researches successfully applied DLC films to the commercial applications such as hard disk, frictional resistance films, protective optical materials, biomedical products and so on. Meanwhile, the excellent properties of DLC films have been also applied to become hermetical coatings of optical fibers and the carbon-coated optical fiber is expected to be a key technology for optical transmission lines [3-10].

Preparation of DLC films can be carried out at a low substrate temperature and high deposition rate using various methods, such as radio-frequency plasma enhanced chemical vapor deposition (rf-PECVD) [7,10-13], plasma enhanced chemical vapor deposition with electron cyclotron wave resonance source [14], microwave plasma chemical vapor deposition [15], sputtering deposition [16], filtered cathodic vacuum arc deposition [17] and ion beam deposition [18]. The carbon film prepared by rf-PECVD using methane (CH₄) and hydrogen (H₂) as the precursor gases contains a more percentage of hydrogen, so it is usually classified as the amorphous hydrogenated carbon (a-C:H) film in the literature [2]. Recently, a-C:H films for hermetical optical fiber coatings prepared by rf-PECVD method were studied [7,10]. However, the structure and properties of a-C:H films were not clearly addressed. In
this article, the structure and properties of a-C:H films for hermetical optical fiber coatings deposited using rf-PECVD method with different H<sub>2</sub>/CH<sub>4</sub> ratio are investigated. The structure of the a-C:H film is evaluated by the Fourier transform infrared (FTIR) spectroscopy and Raman scattering spectroscopy (RSS). The optical band gap and mechanical property of a-C:H films are measured by the U/VUV is spectrophotometer and nanoindentation (NI), respectively. Meanwhile, the surface roughness and morphology of carbon-coated optical fibers are checked by the atomic force microscope (AFM) and field emission scanning electron microscope (FESEM), respectively. Finally, the effect of H<sub>2</sub>/CH<sub>4</sub> ratios on the structure and properties of a-C:H films is discussed.

2. EXPERIMENTAL DETAILS

The experimental details proceeded as follows. First, silica glass fibers and silica glass plates were cleaned in ultrasonic bath of ethanol, acetone, and de-ionized water in sequence. These pre-treatments were typically applied to improve the adhesion of a-C:H films onto these substrates. Second, the a-C:H films were simultaneously deposited on silica glass fibers and silica glass plates using a 13.56 MHz capacitively coupled rf-PECVD system in which a cylindrical stainless steel reaction chamber with two parallel planar electrodes was employed. The distance between two parallel planar electrodes was 3 cm. The a-C:H films were deposited with working pressure of 120 mTorr (about 16 Pa) and induced negative self-bias which is related to the ion energy corresponding to a RF power of 250 W. Nine kinds of a-C:H films were prepared with the H<sub>2</sub>/CH<sub>4</sub> ratio being 0, 0.67, 1.33, 2, 2.67, 3.33, 4, 4.67 and 5.33, respectively, where the flow rate of CH<sub>4</sub> gas was fixed at 9 sccm. The deposition time was kept at 30 min, and the substrate temperature was set at 523 K (250 °C). Third, the thicknesses of a-C:H films were obtained by measuring the cross section of the carbon-coated optical fiber using the FESEM. An example of the cross section of the carbon-coated optical fiber is illustrated in Fig. 1, where the H<sub>2</sub>/CH<sub>4</sub> ratio is 2. After the thickness of the a-C:H film is obtained, the deposition rate is calculated from the film thickness and deposition time. The deposition rate is 13, 12.8, 12.5, 12.3, 11.7, 11.5, 10.9, 9.8 and 6.8 mm/min for the H<sub>2</sub>/CH<sub>4</sub> ratio being 0, 0.67, 1.33, 2, 2.67, 3.33, 4, 4.67 and 5.33, respectively, where the flow rate of CH<sub>4</sub> gas was fixed at 9 sccm. The deposition time was kept at 30 min, and the substrate temperature was set at 523 K (250 °C). Third, the thicknesses of a-C:H films were obtained by measuring the cross section of carbon-coated optical fibers using the FESEM (JEOL JSM - 6700 F). Each thickness was estimated from the average value of ten data with the same deposition condition. Fourth, the structure of a-C:H films were examined by the FTIR (Thermo - Nicolet NEXUS 470) and RSS (Renishaw system 2000). The FTIR can identify the nature of bonding (C-H vibration modes) by absorbance spectrum at 298 K. All spectra were detected in the range of 2700 - 3200 cm<sup>-1</sup> with 128 scans at resolution of 1 cm<sup>-1</sup>. The RSS was measured in the back-scattering geometry with the 532 nm line of an Nd:YAG laser at room temperature in the spectral range from 800 to 2000 cm<sup>-1</sup>. The laser power was 25 mW and irradiation time of the laser on the films was 20 sec / point. Fifth, the optical property was measured with UV/V is spectrophotometer (HITACHI U - 3010) for wavelength ranging from 200 to 1100 nm with a bare silica glass plate at the reference beam to eliminate the substrate contribution. Sixth, the mechanical property of a-C:H films was measured by the NI (UMIS Nanoindenter, Based Model, CRISO, Australia). In each of indentation experiment, the indenter was loaded and unloaded three times at the maximum penetration depth ~10 % of the film thickness. Seventh, the roughness of a-C:H films was examined by the AFM (Digital Instrument NS4 / D3100CL / MultiMode). The value of surface roughness, Ra, was estimated by tapping mode method and was evaluated in the area of 1×1 μm. Each datum was obtained from the average value of three different positions on the same specimen surface. Finally, the outer surfaces of a-C:H films for the hermetical optical fiber coatings were observed by the FESEM. Notably, the thickness and the outer surface of a-C:H films were measured using the samples with silica glass fiber substrates. Nevertheless, the other properties of a-C:H films were measured using the samples with silica glass plate substrates.

3. EXPERIMENTAL RESULTS

3.1 Deposition Rate

The thickness of the a-C:H film is obtained by measuring the cross section of the carbon-coated optical fiber using the FESEM. An example of the cross section of the carbon-coated optical fiber is illustrated in Fig. 1, where the H<sub>2</sub>/CH<sub>4</sub> ratio is 2. After the thickness of the a-C:H film is obtained, the deposition rate is calculated from the film thickness and deposition time. The deposition rate is 13, 12.8, 12.5, 12.3, 11.7, 11.5, 10.9, 9.8 and 6.8 mm / min for the H<sub>2</sub>/CH<sub>4</sub> ratio being 0, 0.67, 1.33, 2, 2.67, 3.33, 4, 4.67 and 5.33, respectively. It is shown that the deposition rate of a-C:H films decreases with increasing the H<sub>2</sub>/CH<sub>4</sub> ratio. During the deposition process, the most abundant
reactive species delivered by methane plasmas are hydrocarbon radicals (mainly CH3), atomic hydrogen as neutrals, and CH3+ and CH4+ as ions [19]. The sticking coefficient of CH3 during deposition can be enhanced through the creation of dangling bonds (DBs) [20]. While a large amount of hydrogen gas adds to the methane atmosphere, the continuous reaction near the film surface should be retarded. In other words, the DBs near the film surface decrease and the most hydrocarbon radicals can not stack on the film surface as the H2/CH4 ratio increases. Hence, the deposition rate of a-C:H films decreases with increasing the H2/CH4 ratio.

3.2 FTIR AND RSS Measurements

The FTIR spectra of a-C:H films prepared by various H2/CH4 ratios are shown in Fig. 2. Fig. 2 depicts that the prominent absorption band occurs at 2875 cm⁻¹ and 2920 cm⁻¹ which are corresponding to the sp³-CH₃ symmetric and sp³-CH₂ asymmetric C-H stretching mode, respectively. It is also observed that the sp³-CH₂ symmetric C-H stretching mode at 2850 cm⁻¹ and the sp³-CH₃ asymmetric C-H stretching mode at 2959 cm⁻¹ are considerably strengthened for the a-C:H film deposited at a higher H2/CH4 ratio. In FTIR spectra, sp²-CHₓ modes appear in the wavenumber ranging from 2800 to 2970 cm⁻¹, but sp²-CHₓ modes are existed in the wavenumber range of 2970 - 3100 cm⁻¹ [21].

![Carbon coating](image1.png)

Fig. 1 Scanning electron microscope picture to demonstrate the cross section of the carbon-coated optical fiber, where the H2/CH4 ratio is 2.

![FTIR spectra](image2.png)

Fig. 2 FTIR spectra of a-C:H films with different H2/CH4 ratio.

![IR spectra](image3.png)

Fig. 3 Typical IR spectra obtained in C-H stretching band region for (a) H2/CH4 = 0 and (b) H2/CH4 = 5.33.
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Table I. The characterization of a-C:H films for various H₂/CH₄ ratios.

<table>
<thead>
<tr>
<th>H₂/CH₄ ratio</th>
<th>0</th>
<th>0.67</th>
<th>1.33</th>
<th>2</th>
<th>2.67</th>
<th>3.33</th>
<th>4</th>
<th>4.67</th>
<th>5.33</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp³/sp² CHₓ</td>
<td>1.77</td>
<td>1.91</td>
<td>1.97</td>
<td>2.05</td>
<td>2.19</td>
<td>2.27</td>
<td>2.50</td>
<td>2.65</td>
<td>2.70</td>
</tr>
<tr>
<td>ω₀ (cm⁻¹)</td>
<td>1350</td>
<td>1355</td>
<td>1365</td>
<td>1367</td>
<td>1372</td>
<td>1376</td>
<td>1382</td>
<td>1384</td>
<td>1390</td>
</tr>
<tr>
<td>ω₉ (cm⁻¹)</td>
<td>1540</td>
<td>1541</td>
<td>1543</td>
<td>1544</td>
<td>1546</td>
<td>1547</td>
<td>1551</td>
<td>1552</td>
<td>1555</td>
</tr>
<tr>
<td>A_D/A_G</td>
<td>0.41</td>
<td>0.43</td>
<td>0.47</td>
<td>0.49</td>
<td>0.53</td>
<td>0.53</td>
<td>0.56</td>
<td>0.63</td>
<td>0.65</td>
</tr>
<tr>
<td>I_D/I_G</td>
<td>0.69</td>
<td>0.76</td>
<td>0.88</td>
<td>0.94</td>
<td>1.06</td>
<td>1.06</td>
<td>1.18</td>
<td>1.41</td>
<td>1.48</td>
</tr>
<tr>
<td>FWHM_D (cm⁻¹)</td>
<td>304</td>
<td>309</td>
<td>316</td>
<td>318</td>
<td>328</td>
<td>324</td>
<td>334</td>
<td>341</td>
<td>342</td>
</tr>
<tr>
<td>FWHM_G (cm⁻¹)</td>
<td>180</td>
<td>175</td>
<td>167</td>
<td>166</td>
<td>163</td>
<td>161</td>
<td>157</td>
<td>151</td>
<td>147</td>
</tr>
</tbody>
</table>

Fig. 4  Raman scattering spectra of a-C:H films with different H₂/CH₄ ratio.

In order to view the detail of FTIR spectra, the FTIR spectra are decomposed into the sp³-C₁ₓ and sp²-C₁ₓ modes. Two examples of the FTIR fitting results are shown in Fig. 3(a) and 3(b) for H₂/CH₄ = 0 and 5.33, respectively. Fig. 3(a) and 3(b) reveal that the absorption bands of sp³-C₁ₓ modes increase as the H₂/CH₄ ratio increases, while the absorption bands of sp²-C₁ₓ modes decrease. The ratios of sp³-C₁ₓ modes to sp²-C₁ₓ modes (that is, sp³/sp²CHₓ) for various H₂/CH₄ ratios are listed in Table I. Table I depicts that the sp³/sp² CHₓ ratio increases with increasing the H₂/CH₄ ratio.

The RSS of a-C:H films prepared by various H₂/CH₄ ratios is shown in Fig. 4. Fig. 4 indicates that the RSS of a-C:H films consists of two peaks, in which one peak named D band approximately 1350 - 1390 cm⁻¹ is attributed to the breathing mode of the sp³ sites only in aromatic rings and makes Raman active by disorder effect, and the other peak named G band approximately 1540 - 1555 cm⁻¹ is resulting from stretching vibrations at all sp² sites [22-24].

The RSS with different deposition condition is decomposed into two Gaussian distributions (D band and G band) and a linear background. Table 1 reveals the fitting results of RSS for various H₂/CH₄ ratios. Here symbols ω₀, A, I, and FWHM represent the peak position, peak intensity, integrated intensity and full width half maximum, respectively, and subscripts D and G indicate the D band and G band, respectively. Table 1 shows that if the H₂/CH₄ ratio increases, the peak positions (roD and roG), peak intensity ratio of D band and G band (AD/I_G), integrated intensity ratio of D band and G band (I_D/I_G) and the full width half maximum of D band (FWHM_D) increase. Nevertheless, the full width half maximum of G band (FWHM_G) decreases as the H₂/CH₄ ratio increases.

3.3 Optical and Mechanical Properties

The optical band gap (Eₜ) is a very useful parameter to rapidly identify the fundamental characterization of amorphous semiconductor film, such as a-C:H films. It can be extracted from the so-called Tauc formula, which is most common throughout the literature [25]. Based on the Tauc formula, the
determination of optical band gap is given by
\[ \alpha E = B (E - E_g)^n \]  
(1)

where \( \alpha \) is absorption coefficient; \( E \) is photon energy; \( B \) is disorder parameter, and \( n \) is an index which is characterized by the optical absorption process. For a-C:H films, the optical absorption process belongs to the indirect allowed transition process and \( n \) is equal to 2. Fig. 5 reveals that the \( E_g \) depends on the H\(_2\)/CH\(_4\) ratio. It is shown that the \( E_g \) increases from 1.17 to 1.40 eV as the H\(_2\)/CH\(_4\) ratio increases from 0 to 5.33.

The hardness and Young’s modulus of a-C:H films as a function of the H\(_2\)/CH\(_4\) ratio are shown in Fig. 6. Fig. 6 reveals that the hardness and Young’s modulus of a-C:H films decrease with increasing the H\(_2\)/CH\(_4\) ratio. It means that the a-C:H films become softer at a higher H\(_2\)/CH\(_4\) ratio. Usually, the measured Young’s modulus \( E \), is not the exact Young’s modulus \( E \); can be expressed as

\[ \frac{1}{E} = \left[ \frac{(1-\nu_i^2)}{E_i} \right] + \left[ \frac{(1-\nu_j^2)}{E_j} \right] \]  
(2)

where \( E_i \) is Young’s modulus of the indenter, and \( \nu_i \) and \( \nu_j \) are Possion’s ratios of the sample and indenter, respectively. Because \( E_i \) is much larger than \( E \), so the last term \( (1-\nu_i^2) / E \), on the right-hand side of Eq. 2 can be omitted. On the other hand, \( \nu \) is commonly smaller than 0.3 for most of the coating materials [34]. Therefore, the measured Young’s modulus is close to Young’s modulus of the sample.

### 3.4 Surface Characterization

AFM measurement depicts that the average surface roughnesses, \( R_a \), of these nine samples are 1.21, 1.04, 0.81, 0.63, 0.54, 0.42, 0.37, 0.36 and 0.35 nm, respectively as shown in Fig. 7. Fig. 7 reveals that the roughnesses of these carbon coatings decrease with increasing the H\(_2\)/CH\(_4\) ratio. During the deposition, the etching effect of hydrogen atom plays a significant role. Atomic hydrogen sputters the surface of carbon coatings, and thus the coating roughness decreases with increasing the H\(_2\)/CH\(_4\) ratio [26].
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Fig. 8  Morphology of outer surfaces of the carbon coating examined by FESEM. The H<sub>2</sub>/CH<sub>4</sub> ratios are (a) 0, (b) 0.67, (c) 1.33, (d) 2, (e) 2.67, (f) 3.33, (g) 4, (h) 4.67, and (i) 5.33, respectively.
After the examination of FESEM, Fig. 8(a) - 8(i) indicate the morphologies of carbon-coated optical fibers with H$_2$/CH$_4$ ratios being 0, 0.67, 1.33, 2. 2.67, 3.33, 4, 4.67 and 5.33, respectively. Fig. 8 reveals that the outer surface of a-C:H films exhibits a lot of nano - crystalline grains. The nano - crystalline grain size decreases with increasing the H$_2$/CH$_4$ ratio. Notably, the color of a - C:H films is changed from dark brown to light yellow. As stated above, the deposition rate decreases with increasing the H$_2$/CH$_4$ ratio. Consequently, the grain size of a-C:H films decreases with increasing the H$_2$/CH$_4$ ratio. Notably, the nano - crystalline grain size is inversely proportional to the integrated intensity ratio, $I_D/I_G$, and this is in good agreement with that proposed in the previous literature [27,28].

4. DISCUSSION

In order to clearly identify the structure of a-C:H films, FTIR, RSS, $E_g$ and hardness should be measured simultaneously. The FTIR measurement results show that the sp$^3$/sp$^2$ CH$_4$ ratio increases as the H$_2$/CH$_4$ ratio increases. Meanwhile, the RSS measurement results reveal that the integrated intensity ratio, $I_D/I_G$, increases with increasing the H$_2$/CH$_4$ ratio. It was suggested that if the integrated intensity ratio, $I_D/I_G$, increases, the sp$^3$/sp$^2$ C-C ratio should be decreased [2,18]. Hence, it is regarded that the sp$^3$/sp$^2$ C-C ratio would be decreased with increasing the H$_2$/CH$_4$ ratio. Based on the above FTIR and RSS measurement results, two possible situations about the change of film structure would be suggested. First, the sp$^3$ C-C bonded content decreases as the H$_2$/CH$_4$ ratio increases, while the sp$^3$ CH$_4$ bonded content increases. In this case, the sp$^3$ C-C bonds are changed to the sp$^3$ CH$_4$ bonds, so the a-C:H films would be shifted toward the polymer-like films. Second, the sp$^3$ C-C bonded content increases as the H$_2$/CH$_4$ ratio increases, while the sp$^3$ CH$_4$ bonded content decreases. In this case, the sp$^2$ C - H bonds are changed to the sp$^2$ C - C bonds, and thus the a-C:H films would be shifted to the graphite - like films. Whenever the a-C:H film becomes the polymer - like film, the $E_g$ would increase while the hardness would decrease [22,29]. On the other hand, if the a-C:H films shift to the graphite - like films, the $E_g$ would trend to zero value [30]. Additionally, Ferrari and Robertson [22] proposed the relationships between visible Raman spectra (514 nm) and the sp$^3$ C-C fraction in a-C:H films, it stated that the sp$^3$ C-C content decreased with the simultaneous increase of $\omega_G$ and $I_D/I_G$ ratio. Tamor and Vassell [31] proposed that the hardness was a function of the G band width for a - C:H films. When the G band width decreased, the hardness would decrease simultaneously. Consequently, viewing the FTIR, RSS, $E_g$, and hardness measurement results, it is confirmed that the a-C:H film is changed to the polymer-like film as the H$_2$/CH$_4$ ratio increases. When the a-C:H film is changed to the polymer - like film, $E_g$ increases, while Hardness and Young’s modulus decrease. Additionally, the color of the a-C:H film is changed from dark brown to light yellow. Notably, it is difficult to measure the FTIR, RSS, $E_g$, Nl, and Ra of a-C:H films using the samples with silica glass fiber substrates, so these properties of a-C:H films are measured using the samples with silica glass plate substrates. The difference of the measured results between these two kinds of substrates is not clear. However, it is believed that the qualitative variation of these properties with the H$_2$/CH$_4$ ratio for these two kinds of substrates would be the same.

In the real application, the carbon - coated optical fibers must sustain the mechanical and thermal stresses. Once the mechanical fracture or thermally induced stress voids occur on the carbon coating, the hermetically carbon - coated optical fiber will lose their prevention of mechanical fatigue [6,7,10]. The mechanical strength of the a-C:H film is strongly dependent on its Young’s modulus and surface roughness. The a-C:H film with high Young’s modulus and low surface roughness would possess high mechanical strength [4,10]. It can be seen in Fig. 6 and 7 that Young’s modulus and the surface roughness of a-C:H films decrease with increasing the H$_2$/CH$_4$ ratio. Hence, there exists an optimum H$_2$/CH$_4$ ratio to obtain a-C:H films with high mechanical strength. It was suggested that $I_D/I_G$ and the surface roughness should not exceed 1.233 and 0.783 nm,
respectively, to acquire a-C:H films for the optical fiber coatings with high mechanical strength [10]. As a result, the optimal H₂/CH₄ ratio of this work should be selected between 2 and 4. In the PECVD process, many factors affect the structure and properties of a-C:H films, such as fluctuation in the vapor arrival flux, surface diffusion, self-shadowing, as well as the working pressure, substrate temperature, bias voltage and so on [32, 33]. Hence, the optimum H₂/CH₄ ratio to obtain a-C:H films with high mechanical strength is strongly dependent on the PECVD processing condition.

5. CONCLUSIONS

The structure and properties of a-C:H films for hermetical optical fiber coatings prepared by rf-PECVD method with different H₂/CH₄ ratio are investigated. It is found that the sp³ C-C bonds are changed to the sp³ CHₓ bonds as the H₂/CH₄ ratio increases. The a-C:H films would be shifted toward the polymer-like films at a high H₂/CH₄ ratio. The E_g of a-C:H films increases with increasing the H₂/CH₄ ratio, while the hardness, Young's modulus, and roughness of a-C:H films decrease. The outer surface of a-C:H films includes a lot of nano-crystalline grains. The nano-crystalline grain size decreases with increasing the H₂/CH₄ ratio. Additionally, the color of a-C:H films is changed from dark brown to light yellow. There exists an optimum H₂/CH₄ ratio to obtain a-C:H films with high mechanical strength, and the optimum H₂/CH₄ ratio is strongly dependent on the PECVD processing condition.

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