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Intertwisted fibrillar diamond-like carbon films prepared by electron cyclotron resonance microwave plasma enhanced chemical vapour deposition*

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In this paper, the structures, optical and mechanical properties of diamond-like carbon films are studied, which are prepared by a self-fabricated electron cyclotron resonance microwave plasma chemical vapour deposition method at room temperature in the ambient gases of mixed acetylene and nitrogen. The morphology and microstructure of the processed film are characterized by the atomic force microscope image, Raman spectra and middle Fourier transform infrared transmittance spectra, which reveal that there is an intertwisted fibrillar diamond-like structure in the film and the film is mainly composed of sp^3 CH, sp^3 C—C, sp^2 C═C, C═N and C_{60}. The film micro-hardness and bulk modulus are measured by a nano-indenter and the refractive constant and deposition rate are also calculated.

Keywords: ECR microwave plasma, diamond-like carbon films, AFM, FTIR
PACC: 5250D, 8115H, 6800

1. Introduction

Compared with chemical vapour deposition (CVD) diamond, diamond-like carbon films (DLCs) have many excellent properties such as low friction, high transmission, and they can be deposited under gentler conditions and are easier to dope with plenty of elements.[1−8] Since DLCs are carbon-based materials with structure, composition and properties that are variable over a wide range, they have been widely used as protective coatings in several areas such as optical windows, magnetic storage discs, car parts, biomedical coatings and micro electromechanical devices.

Several methods have been developed to deposit DLCs on various substrates, which can be categorized as the physical vapour deposition (PVD) and CVD methods. For example, the PVD methods include those using ion beam, ion sputtering, magnetic-controlled glow discharge, cathode arc, pulsed laser deposition and pulsed-high-energy-density plasma gun; and the CVD methods include those using microwave plasma, RF plasma, hot filament and so on.[9−13] Compared with the above methods, electron cyclotron resonance (ECR) microwave plasma has the advantages of higher ionization ratio, larger deposition area, better deposition uniformity and easier doping with other elements. In this paper, DLCs are deposited in the ambient gases of acetylene and nitrogen using ECR microwave plasma enhanced CVD method. Raman spectra, atomic field microscope, nano-indenter, middle and near-infrared transmittance spectra are used to characterize the structures, morphologies, and properties of DLCs.

2. Experiment

Figure 1 is a schematic diagram of the self-fabricated ECR equipment. Acetylene and nitrogen are inputted separately from different gas input hollows in the ratio of N_2/C_2H_2=0.01. The microwave power is controllable up to 1.5kW and is 400W in this experiment. The magnetic field is about 0.0875T in the centre of discharge area, which matches to the calculated magnetron intensity. No additional electric field is applied in the experiment. Other parameters in the experiment include: the total working gas pressure is about 5Pa and the deposition time is about 2.5h. A Quartz substrate with a diameter of 2cm and thick-

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ness of 0.15cm is kept at room temperature, which is cleaned by ultrasonic in alcohol for 15min, and then rinsed by using de-ionized water before deposition.

The surface morphology of the deposited film is measured by atomic force microscope (AFM, Digital Instruments, Nano-scope IIIA) operated in a contact mode. The film structure is measured by Raman spectra at 1cm^{-1} / step using the Ar 488nm line (Stex-1403). Transmission spectra are recorded in a range of 400–4000cm^{-1} at 2cm^{-1} /step on a Fourier transform spectrometer (FTS-60V) to clearly distinguish the chemical configuration. The film optical property is characterized by the transmission spectra ranging between 4000 and 15000cm^{-1} (FTIR, FTS-6000, 2cm^{-1} /step). Vicker's hardness of the deposited film is obtained by nano-indentation measurement (Nano-indenter^{TM} III, MTS).

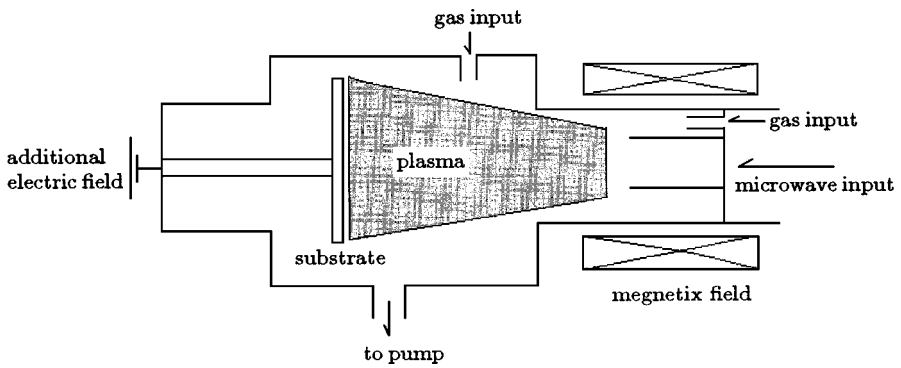


Fig.1. Schematic diagram of the self-fabricated ECR-MPECVD equipment.

3. Results and discussion

3.1. Surface morphology

Figure 2 is the AFM surface morphology of the processed film in an area of 1μm× 1μm. The surface roughness is 0.127nm evaluated over an area of 10μm× 10μm. The surface morphology shows an intertwisted fibrillar structure, with its fibrillar diameter about 40nm and a length larger than 300nm, indicating that the film may be composed mainly of hydrogenated carbon nanotubes (CNTs). Such surmise is supported in two aspects: first, CNTs can be prepared by a similar process but it needs a higher substrate temperature and different substrate pretreatment.[14–17] Secondly, when the film is artificially peeled from the substrate, most crushed pieces look like strips with a width less than 1mm and a length larger than 20mm. This can verify that the film has a high anisotropic structure similar to CNTs.

3.2. Structure analysis

It is well known that the Raman spectra of carbon are very sensitive to its structures. Usually, the broadened D peak (1358cm^{-1}) and G peak (1580cm^{-1}) can indicate that the sample consists of DLCs.[18,19] Fig. 3 illustrates the Raman spectra of the deposited films. The broadened D peak and G peak can evidently prove the existence of DLCs. The central D and G peaks appearing at 1348 and 1607cm^{-1} are displaced from the standard peak positions, which can be

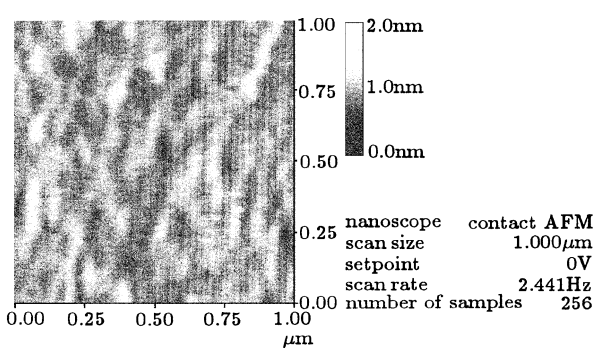


Fig.2. AFM image of the intertwisted fibrillar DLCs.

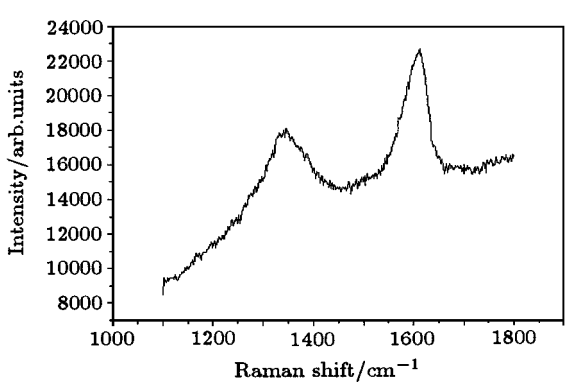


Fig.3. Raman spectra of the intertwisted fibrillar DLCs.

attributed to the effects of nitrogen mingling and film stress. The background Raman intensity is very high, which means that the film has a high-fluorescence ability.

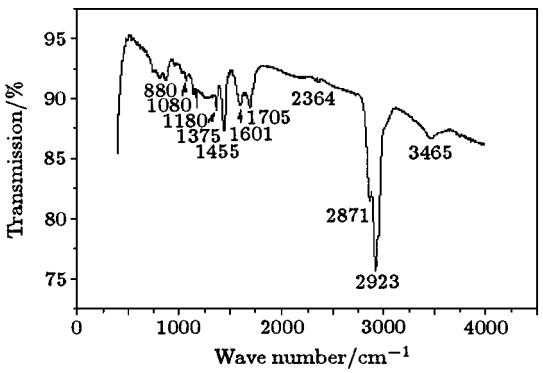


Fig.4. Middle-infrared FTIR transmittance spectra of the intertwisted fibrillar DLCs.

The middle-infrared spectrum is a sensitive method to characterize the bonding in DLC films.[20–23] To identify the DLC structure clearer, the film is deposited on a KBr substrate, and the middle FTIR is shown in Fig.4, with the absorption peaks labelled, the most conspicuous absorption peaks of 2871 and 2923cm^{-1} can be attributed to the sp^3 CH band. The 880 and 2364cm^{-1} absorption peaks correspond to the sp^3 C—C band. The 1080cm^{-1} peak may be induced by the impurities of N and the 1705cm^{-1} peak may be caused by the C=N band vibrating absorption. The peaks of 1375, 1455, 1601 and 3465cm^{-1} correspond to the sp^3 CH band, the CH_2 band, the C=C band and the NH band, respectively. The 1180cm^{-1} peak corresponds to the fullerenes of C_{60}. From the above analysis we can conclude that the films are composed mainly of sp^3 CH, sp^3 C—C, sp^2 C=C, C=N and C_{60}. The absorption peaks and the corresponding configurations are summarized in Table 1.

Table 1. Absorption peaks and the corresponding configurations of DLCs.

Wavenumber/cm^{-1}	Configuration	
880	sp^3	C—C
1080	impurity	N
1180	sp^{2+s} $(0 < s < 1)$	C_{60}
1375	sp^3	CH
1455	sp^3	CH_2
1601	sp^2	C=C
1705	sp^2	C=N
2364	sp^3	C—C
2871	sp^3	CH_2, CH_3
2923	sp^3	CH, CH_2
3465		NH

3.3. Optical and mechanical properties

Figure 5 is the transmission spectra of the film ranging between 4000 and 15000cm^{-1}, obtained by taking the substrate as the background. Evidently, there are little absorptions when the wavenumber is larger than 9000cm^{-1}. The wavenumber can characterize the interference of the film (see Table 2). The wave crests are induced by interference enhancement, where no rays are reflected, and the wave valleys are induced by interference weakening, where the absorptions can be neglected. Under such a circumstance, the reflectivity R in valleys can be calculated by

$$R = 1 - T,$$

where T is the transmission of the film.

In the range of 4000–9000cm^{-1}, the absorption of the film can be neglected. Using the reflectivity of 94.5%, the refractive index n is calculated to be 1.6. The film thickness d can be calculated from the adjacent wave crests,[24]

$$d = 1/[2n(k_2 - l_1)],$$

where k_2 and k_1 are the wavenumbers of adjacent crests (or valleys). The film thickness d is 1.42μm calculated from the FTIR data (see Table 2). Dividing d by the deposition time of 2.5h, we can obtain the deposition rate of about 0.57μm/h.

In addition, the microhardness and bulk elasticity modulus of the film are measured by a nano-indenter. The average micro-hardness is about 4GPa and the bulk modulus about 11GPa.

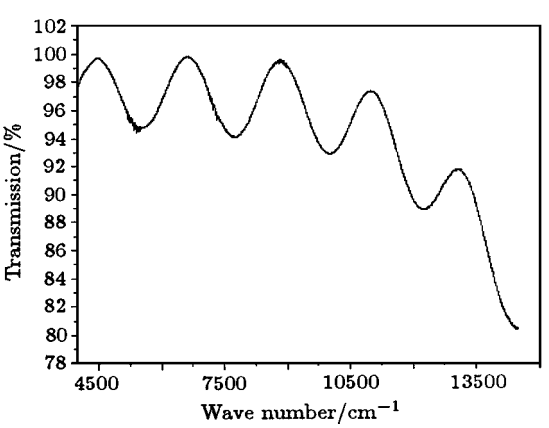


Fig.5. Near-infrared FTIR spectra of the intertwisted fibrillar DLCs.

Table 2. Extrema of the wavenumbers and the corresponding transmissions induced by film interference.

Wave crest		Wave valley	
Wavenumber/cm^{-1}	Transmission/%	Wavenumber/cm^{-1}	Transmission/%
4486.4	99.6	5514.5	94.7
6621.6	99.7	7738.4	94.0
8830.1	99.4	10039.5	92.8
11013.5	97.2	12259.5	88.7

4. Conclusion

Intertwisted fibrillar DLCs are obtained using ECR microwave plasma enhanced CVD method. AFM image of the DLC shows that its fibrillar diameter is about 40nm and its length is larger than 300nm. Middle infrared FTIR transmission spectra reveal that the film is composed mainly of sp^3 CH, sp^3 C—C, sp^2 C═C, C═N and C_{60}. The micro-hardness and bulk modulus of the film measured by a nano-indenter are about 4GPa and 11GPa, respectively. Calculated by using Fourier transform infrared transmittance spectra in the near-infrared area, the refractive constant is about 1.6 and the deposition rate is about 0.57μm/h.

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