[Article ID] 1003 - 6326(2000)04 - 0502 - 03

Emission spectra of microwave plasma and MPCVD transparent diamond film①

ZHOU Jian(周 健)[1], HE Wei(何 伟)[2], YUAN Run-zhang(袁润章)[1], JIANG De-sheng(姜德生)[2], WANG Jian-hua(汪建华)[1]

(1. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P.R.China;

2. Fiber Optic Sensing Technology Research Center, Wuhan University of Technology, Wuhan 430070, P.R.China)

[Abstract] The emission spectra of microwave plasma was in-line measured in visible light wave-band using a self-made optical fiber spectrometer, the change rule of the atomic hydrogen (H) and double-carbon radical(C_2) was given under different CH_4/H_2 ratios of volume flow. The effect of atomic hydrogen (H) on CVD diamond, deposited high quality and transparent diamond film by microwave plasma CVD (MPCVD) was analyzed according to the measured results by scanning electron microscopy(SEM), laser Raman spectrometry(Raman), and Fourier transform infrared spectrometry (FTIR). The results showed that the diamond film consisted of (220) orientation and it was homogeneous, compact, low-defective, high-quality film, its infrared transmissibility was about 70%, approached theoretical transmissibility of diamond. It was key conditions that a large number of atomic hydrogen (H_γ) and double-carbon radical(C_2) exist in the course of high quality diamond film growth. The research provided a rapid method for technology exploration of microwawe plasma CVD, and a reliable basis for research on growth mechanism of diamond film.

[Key words] emission spectra; H_γ; C_2; MPCVD; tansparent diamond film

[CLC number] TN304.05; TN304.1; O657.31 **[Document code]** A

1 INTRODUCTION

Microwave plasma is formed by excited deposition gas in the action of microwave energy. Electrons violently vibrate under the action of a high frequency electromagnetic field which greatly promotes the collision among atoms, radicals and molecules[1], thus the ionization degree of gas increases and plasma with high density is produced. Due to the characteristics with no inner electrodes, no eletrode discharging pollution, high energy transformation, easily controlling of plasma parameters and causing a large quantity of uniform plasma, it is one of predominate methods of preparing high quality diamond film with large area.

Atom luminescence is an important kind of atom appearance, which reflects the change in atom internal structure and energy eigen-state. Optical fiber spectometer is a kind of spectral analysis instrument by optical fiber channelling optical signal. It has some characteristics such as reducing intereference and loss, improve the quality of spectrum, so it can be used as precise measurement of atomic luminescence. Optical fiber spectrometer becomes commercial instrument only in oversea developed countries such as America, Germany and Japan, domestic optical fiber spectrometer was gap in China. In order to measure spectra of plasma and furnish spectrum data for the mechanism and technology of microwave plasma chemical vapor deposition (MPCVD), a self-made optical fiber spectrometer[2] was used to in-line measure the emission spectrum and analyze the results in this paper. It is very significant to further revealing the mechanism of microwave plasma chemical vapor deposition and to shortening time of technology research, and to monitoring the deposition course.

2 EXPERIMENTAL AND ANALYSES

2.1 Measurement of emmission spectra

The optical fiber probe of the domestic optical fiber spectrometer is put in the front of observation window of the microwave plasma equipment and aligned to plasma zone, then the optic signal emitting from microwave plasma enters the optic and measuring system, thus the spectra testing of microwave plasma can be performed. The wavelength of the spectrum line is calculated by computer processing according to the site of the spectrum line obtained by measurement, and the amplitude of the spectrum line is obtained according to measuring the voltage of optic signal. The relative strength is based on the maximum amplitude as constant 100.

The spectra curves of plasma under various $V(CH_4)$: $V(H_2)$ when the amount of H_2 being a cer-

① **[Foundation item]** Project (99J070) supported by the Natural Science Foundation of Hubei Province

[Received date] 2000 - 04 - 10; **[Accepted date]** 2000 - 06 - 06

tain value and deposition pressure being 6.0 kPa.

2.2 Results and analyses

The visible spectrum lines series in the spectra of hydrogen atom are called Balmer series, the wavelength of the spectrum line is calculated by its following empirical formula:

$$\lambda = B\frac{n^2}{n^2 - 4}$$

where B is 3645.7 Å, n is quantum number which is a positive integer. When $n = 3$, 4 or 5, the wavelengths of H_α, H_β and H_γ spectra are calculated to be 6562.26 Å, 4860.93 Å and 4340.12 Å, respectively.

It is shown from Fig.1 that a large number of H_γ spectra are contained in the microwave plasma, this is different from hot-filament plasma in which a large number of H_α spectra are contained[3,4]. H_γ spectrum is in blue region conforming to the blue plasma ball. H_α is in red region and is going to form red plasma ball. Based on the quantum energy formula $E = hv$, where h is Planck constant and equals to 6.63×10^{-34} J·s, v is frequency. Base on the above formula, the energy of atom hydrogen is $E_{H_\alpha} = 1.89$ eV, $E_{H_\beta} = 2.56$ eV, $E_{H_\gamma} = 2.86$ eV, respectively. It is shown that the energy of H_γ is higher than that of H_α due to the shorter wavelength of H_γ. The above data illustrate that the activity of hydrogen atom increases by the action of microwave electromagnetic field, and the results further prove that the activity of microwave plasma is increased and the ionization degree of gas rises.

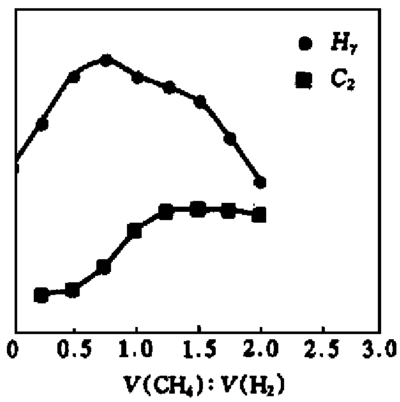

Fig.1 Relations of $V(CH_4)$: $V(H_2)$ with relative strength

The predominate roles which atom H plays in realizing the metastable growth of low pressure CVD diamond are as following:

1) Stabilizing the sp^3 hybridized orbital of growing surfacial carbon of diamond. The carbon atom in the metastable zone of diamond maintains its sp^3 hybridized state, in the meantime, the sp^2 bond is etched, therefore, the nucleation and growth of non-diamond phases such as graphite and non-crystalline carbon phases are restained selectively[5,6].

2) Forming an adsorptive layer on the surface of solid substrate, lowering the interfacial energy between gaseous carbon source and solid substrate, and activating the growth surface through compounding the hydrogen on the growth surface[7~9].

3) Participating in the chemical reaction between gas phases and the growth surface[10].

The increase of energy of atom hydrogen will strengthen the above roles and improve the quality of CVD diamond film.

The tested results show that an emission peak of double-carbon atomic radical C_2 is found at 516.5 nm. The results also reveal that the relative strength of H_γ of atom hydrogen rapidly increases with the increase of $V(CH_4)$: $V(H_2)$, however, it reaches maximum when the ratio is equal to 0.75% and then decreases sharply with the increase of $V(CH_4)$: $V(H_2)$. This is due to the fact that the increase of $V(CH_4)$: $V(H_2)$ leads to the hydrogen atoms ionized from CH_4 increasing the concentration of atomic hydrogen, meanwhile leads to a rise in strength of C_2 atomic radical, thus more hydrogen atoms are required to be depleted to etch graphite carbon, which lowers the concentration of atom hydrogen. Consequently, it is proposed that the optimum deposition parameter is that $V(CH_4)$: $V(H_2)$ is 0.75%. The further study of CVD diamond film is performed on a laboratory-prepared microwave plasma equipment of stainless resonant cavity type in the condition above mentioned.

3 MPCVD DIAMOND FILMS

In order to judge the results right or not, MPCVD experiments have finished. The SEM micrograph of diamond film which deposited on a single-crystal silicon (100) substrate (d76.2 mm) is showed in Fig.2 when $V(CH_4)$: $V(H_2)$ is 0.75% and the deposition pressure is 6.0 kPa and the deposi-

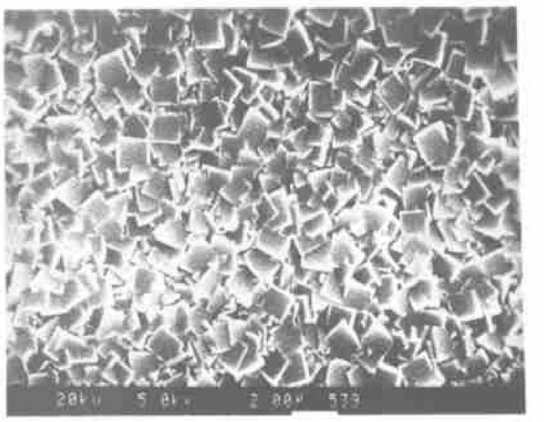

Fig.2 SEM micrograph of diamond film

tion time is 55 h. The Raman spectra of the diamond film is shown in Fig.3. It is shown from the figures that a characteristic peak at 1 332 cm^{-1} sharply appears but the characteristic peak of graphite does not appear obviously and diamond film is high quality.

The silicon substrate was removed by an acid leaching method ($V(HF)$: $V(HNO_3)$ = 1:3) from the central part of the diamond film above, a perfect transparent diamond film with d50 mm was produced after corrosion while the edge was protected by paraffin wax. The FTIR transmission spectra of the transparent diamond film is shown in Fig.4, the transmissivity is close to its theoretical one.

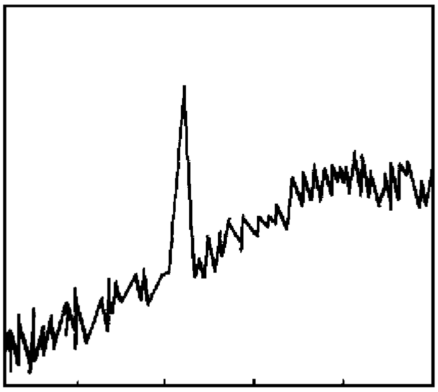

Fig.3 Raman spectrum of diamond film

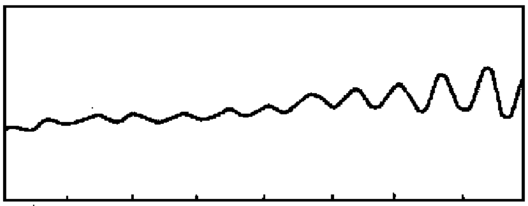

Fig.4 FTIR transmission spectrum of diamond film

4 CONCLUSIONS

1) The results of optical fiber spectrum determination of microwave plasma reveal that there exist H_γ and C_2 in the plasma, and the concentration of atomic hydrogen reaches its maximum when $V(CH_4)$: $V(H_2)$ is 0.75%.

2) Microwave plasma improves the activity and energy of atomic hydrogen.

3) The diamond film obtained is homogeneous and compact. Its quality is high and its defect is low when $V(CH_4)$: $V(H_2)$ is 0.75%, deposition pressure is 6.0 kPa and deposition time is 55 h and its grains are mainly composed of (220) orientation.

[REFERENCE]

[1] ZHOU Jian, CHENG Ji-ping, MEI Bingchu, et al. Research on microwave sinterng alumina ceramics [J]. J Wuhan University of Technology (Mater Sci ed), 1998, 13(3): 34 - 38.

[2] ZHU Wei-jia. The Methods of In-Line Measurement Spectral Analysis in Industry [D], (in Chinese). Wuhan: Wuhan University of Technology, 1999.59.

[3] Muranaka Y, Yamashita H, Sato K, et al. The role of hydrogen in diamond synthesis using a microwave plasma in CO/ H_2 system [J]. J Appl Phy, 1990, 67(10): 6247 - 6254.

[4] Misuda Y, Kojima Y, Yoshida T, et al. The growth of diamond in microwave plasma under low pressure [J]. J Mater Sci, 1987, 22: 1557 - 1562.

[5] Frenlach M. The role of hydrogen in vapor deposition of diamond [J]. J Appl Phys, 1989, 65: 5142 - 5149.

[6] WU Ching-Hsong, Tamor M A, Potter T J, et al. A study of gas chemistry during hot-filament vapor deposition of diamond films using methane/ hydrogen and acetylene/ hydrogen gas mixture [J]. J Appl Phys, 1990, 68: 4825 - 4829.

[7] Spear K. Diamond-ceramic coating of the future [J]. J Am Ceram Soc, 1989, 72: 171 - 192.

[8] Harris S, Martin L R. Methyl versus acetylene as diamond growth species [J]. J Mater Res, 1990, 5: 2313 - 2319.

[9] Chauha S P, Angus J C and Gardner N C. Kinetics of carbon deposition on diamond power [J]. J Appl Phy, 1976, 47: 4746 - 4753.

[10] Joeris P, Benndorf C and Kroger R. Investigations concerning the role of hydrogen in the deposition of diamond films [J]. Surface and Coating Tech, 1993, 59: 310 - 315.

(Edited by HUANG Jin-song)