Vol 15 No 5, May 2006
1009-1963/2006/15(05)/0980-05

Chinese Physics

© 2006 Chin. Phys. Soc.
and IOP Publishing Ltd

OES study of the gas phase during diamond films deposition in high power DC arc plasma jet CVD system*

Zhou Zu-Yuan(周祖源)†, Chen Guang-Chao(陈广超),
Tang Wei-Zhong(唐伟忠), and Lü Fan-Xiu(吕反修)

School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, *China*

(Received 21 July 2005; revised manuscript received 27 December 2005)

This paper used optical emission spectroscopy (OES) to study the gas phase in high power DC arc plasma jet chemical vapour deposition (CVD) during diamond films growth processes. The results show that all the deposition parameters (methane concentration, substrate temperature, gas flow rate and ratio of H_2/Ar) could strongly influence the gas phase. C_2 is found to be the most sensitive radical to deposition parameters among the radicals in gas phase. Spatially resolved OES implies that a relative high concentration of atomic H exists near the substrate surface, which is beneficial for diamond film growth. The relatively high concentrations of C_2 and CH are correlated with high deposition rate of diamond. In our high deposition rate system, C_2 is presumed to be the main growth radical, and CH is also believed to contribute the diamond deposition.

Keywords: gas phase, OES, diamond film, high power DC arc plasma jet CVD
PACC: 0765, 5270K

1. Introduction

A number of different chemical vapour deposition (CVD) techniques for producing diamond films have been developed in recent years, including hot filament CVD, microwave CVD, and DC plasma jet CVD. Although these techniques could produce nearly identical polycrystalline diamond films, great differences have been observed in the linear diamond growth rate.[1−4] And many proposed applications for diamond require the overcoming of several remaining problems. One barrier for overcoming these problems is that the fundamental mechanisms of diamond growth and the gas phase under CVD conditions are not well understood. Although many researchers have studied the growth process of CVD diamond films, the role of reactive radicals has not been completely clarified. Various *in situ* detection methods have been used, including mass spectrometry,[5] resonance-enhanced multiphoton ionization,[6] laser induced fluorescence,[7] and infrared absorption spectroscopy.[8] Optical emission spectroscopy (OES) has been used in microwave plasma CVD,[9] hot filament CVD,[10] and low power (below 3 kW) DC jet.[11,12] However, there have been fewer diagnostic reports on the gas phase of diamond films deposition by high power (up to 100 kW) DC arc plasma jet CVD. Therefore, the gas phase chemistry of this technique is not clear yet. In this paper, we provide OES diagnostic data for this technique so that the useful information can be applied to modelling the diamond growth process.

2. Experimental details

The diamond film deposition apparatus is a high power DC arc plasma jet CVD reactor with a methane/hydrogen/argon source gas mixture. The total pressure in the chamber was 4–8kPa. Diamond films were deposited on molybdenum substrates and obtained under different deposition parameters (methane concentration, substrate temperature, etc.) This high power DC arc plasma CVD system with a

*Project supported by the Key Research Project of Chinese Hi-Tech (Grant No 2002AA305508); the National Natural Science Foundation of China (Grant No 50472095); SRF for ROCS, SEM (Grant No 2003-14) and Beijing Novel Project (Grant No 2003A13).

†Corresponding author. E-mail: zuyuanzhou@163.com

magnetically controlled plasma torch is similar to that reported from our previous publications.[13]

The gas phase radicals in the reaction region were examined by OES during the diamond films growth. The emission light from the reaction region was transferred to the entrance slit of a monochrometer (WDP 500-2A) through the quartz window and a lens system with an optical fibre. The OES system was controlled by a computer.

3. Results and discussion

Figure 1 shows the typical optical emission spectrum from the CH_4–H_2–Ar mixture in the high power DC arc plasma jet CVD system. The major optical emission lines from atomic H, CH and C_2 were observed. No Ar related emission lines, like 714 nm, 750 nm, 763 nm, were found due to the limit of narrow scanning band of the monochrometer (between 400 and 700 nm). We studied the relationship between the emission intensities of CH, C_2 and $H_\gamma$with the deposition parameters. For the same radicals, the intensity ratio of two lines, e.g. I_{H_β}/I_{H_α} or I_{H_γ}/I_{H_β} is proportional to the rate constant of excitation of the radicals, which reflects an electron mean energy in the plasma, i.e. the electron temperature.[14] For different radicals, the intensity ratio is correlated with their rate constants of excitation and their concentrations. When they exist in an excited environment and have two emission lines of close energy, the intensity ratio reflects their relative concentrations. So the intensity ratio of H_γ (434.1 nm) to H_β (486.1 nm) was used as a measure of electron temperature in the gas phase. And the intensity ratios of CH (431.4 nm) and C_2 (516.5 nm) to H_β (486.1 nm) were used as a measure of CH and C_2 concentrations.

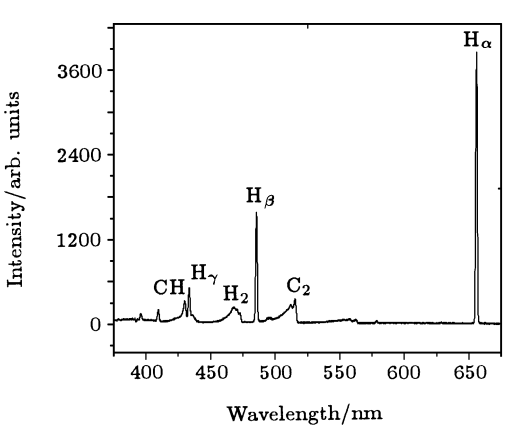


Fig.1. Typical optical emission spectrum from the CH_4–H_2–Ar mixture in the high power DC arc plasma jet CVD system.

Methane concentration is a key parameter in diamond film depositions where methane and hydrogen are used as feed gases. And high methane concentration would increase the diamond film growth rate. The variation of the intensity ratios of H_γ, C_2 and CH to H_β, as a function of methane concentration is plotted in Fig.2. It can be seen that increasing the methane concentration promotes the intensity ratio of C_2 and CH to H_β, which implies that the higher methane concentration led to relatively high levels of C_2 and CH. And this may be correlated with diamond growth rate, i.e. C_2 and CH radicals could be correlated with high deposition rate of diamond.

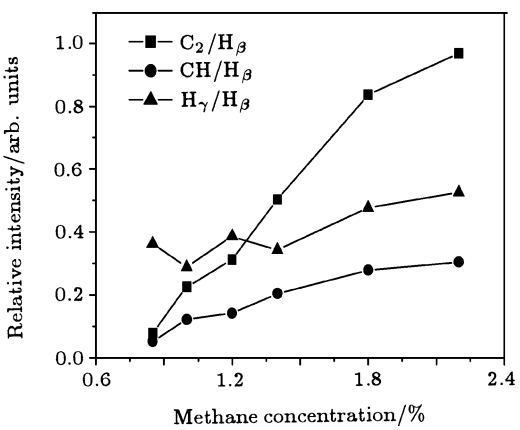


Fig.2. Optical emission intensity ratios of C_2, CH and H_γ to H_β vs the methane concentration.

From Fig.2, one can see the slight increase in the intensity ratio of H_γ/H_β with increasing methane concentration, i.e. the increase of methane concentration enhanced the electron mean temperature. Hence, the increase of methane concentration changed the chemical property of the gas phase near the substrate surface, and further influenced the deposition of the diamond films.

Figure 3 shows the intensity ratios of C_2, CH and H_γ to H_β near the substrate surface as a function of the substrate temperature. The intensity ratios of C_2 to H_β and CH to H_β increase as the substrate temperature is improved. However, the intensity ratio of H_γ to H_β shows little change with the substrate temperature. It is well known that the deposition of high quality diamond film needs reasonably high substrate temperature. This temperature corresponds to higher intensity ratios of C_2 and CH to H_β. The low substrate temperature results in the non-diamond phase deposition and the low growth rate. The intensity ratios of C_2, CH and H_γ to H_β measured 5 mm above the substrate surface do not change with the increase of

substrate temperature. It indicates that the gas composition far away from the substrate is independent of the substrate temperature.

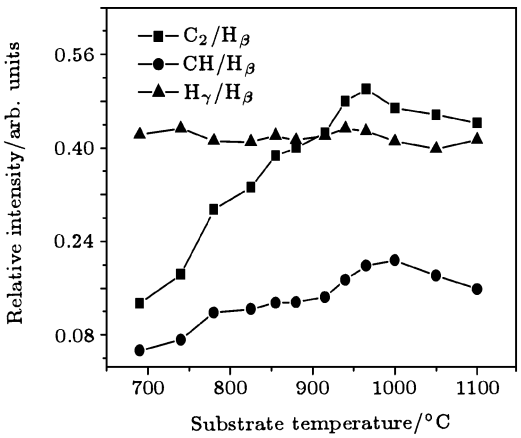


Fig.3. Optical emission intensity ratios of C_2, CH and H_γ to H_β vs the substrate temperature.

McMaster *et al* reported that the hydrogen atom mole fraction near the substrate is independent of the substrate temperature as studied by molecular beam mass spectroscopy.[15] However, Corat and Goodwin found that the signal of CH_3 radicals 4 mm above the substrate is independent of the substrate temperature but near the substrate it is dependent on the substrate temperature,[16] which is consistent with our observation. These results suggest that the dependence of diamond film growth on the substrate temperature results not only from the change of the chemical reaction kinetics at different temperatures, but also from the change of gaseous environment near the substrate.

Figure 4 shows the relationship between optical emission intensity ratios of C_2, CH, H_γ to H_β and gas flow rate. It is found that the influence of the gas flow rate on the intensity ratios of CH and H_γ to H_β is slightly more than that of C_2, the intensity ratio of C_2/H_β increased strongly with the improvement of the gas flow rate. Although the addition of gas flow rate has little influence on the electron mean temperature and the relative concentration of CH to H_β, it added the probability of a collision among the radicals in the gas phase.

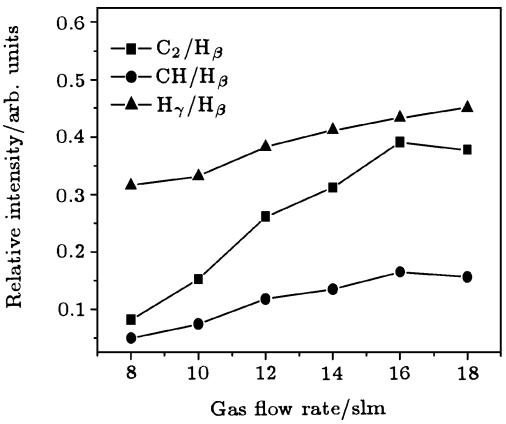


Fig.4. Optical emission intensity ratios of C_2, CH and H_γ to H_β vs gas flow rate.

Figure 5 shows the relationship between the emission intensity ratios of C_2, CH, H_γ to H_β and the ratio of H_2/Ar. It is found that the emission intensity ratios of CH and H_γ to H_β decrease slightly, but that of C_2 decreases strongly. Because change of the ratio of H_2/Ar influences not only on the gas composition, but also on the arc plasma properties.

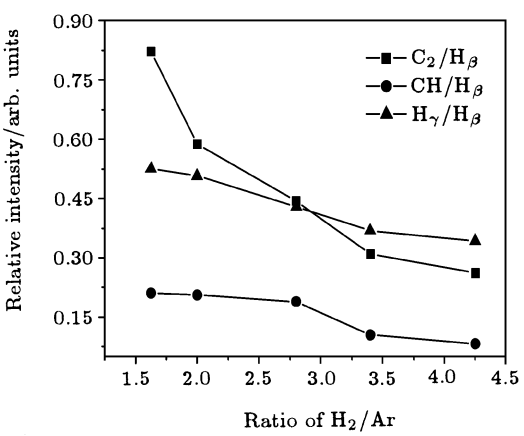


Fig.5. Optical intensity ratios of C_2, CH and H_γ to H_β vs ratio of H_2/Ar.

Figure 6 gives the vertical, spatially resolved OES by changing the detection point between the anode and the substrate. From Fig.6, we can see that the relative concentration of C_2 and CH to atomic H drops when the detection point was close to the substrate surface. It shows that a relative high concentration of atomic H exists, which is beneficial to the high quality of diamond film.

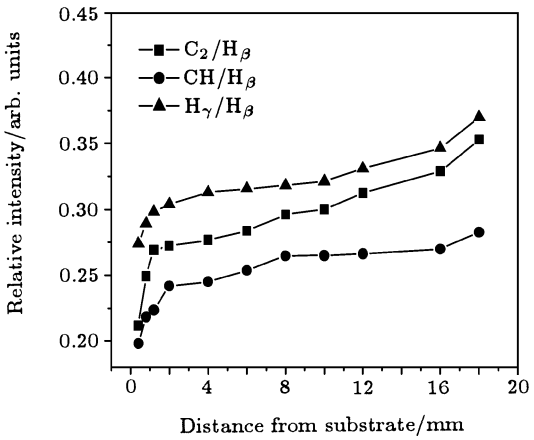


Fig.6. Optical emission intensity ratios of C_2, CH and H_γ to H_β as a function of the distance from substrate surface.

Under the conditions of diamond growth by using either microwave plasma CVD or hot-filament CVD, the temperature of the gas found in the CVD reactor is fairly low. Therefore, it is impossible for C and C_2 radicals to be presented in the reactor at those temperatures.[17] But the DC arc plasma jet CVD process employs relatively higher deposition temperature compared to hot-filament and microwave CVD processes. H, Ar, H_2, C, C_2H_2, CH, C_2H and C_2 are the most abundant radicals, whilst the concentration for CH_4 and CH_3 is negligibly small,[18] and therefore the C, C_2H_2, CH, C_2H and C_2 radicals are discussed as the main carbonaceous radicals in this CVD process. And under the conditions in our DC arc plasma jet CVD system, if the atomic hydrogen supply is rich, C_2 and CH can be found in high concentrations.[18–20] Our observations are consistent with our previous works.[17–20] So it is important to investigate the effect of the C_2 concentration on the growth rate under the condition of high hydrogen concentration.

Figure 7 shows the relation between the growth rate of diamond films and emission intensity ratio of C_2 to H_β from the CH_4–H_2–Ar mixture plasma. In light of Fig.7, it could be found that a lower emission intensity ratio of C_2 to H_β is accompanied by a correspondingly low growth rate about 5μm/h. As the relative intensity of C_2 increases, the growth rate of diamond films is increased significantly. The close relationship between the growth rate and the C_2 concentration shown in Fig.7 suggests that the concentration of C_2 in the CH_4–H_2–Ar plasma is the factor determining the film growth rate under conditions of high H_2 concentration. Our observations demonstrate that C_2 is the main growth radical for diamond in our DC arc plasma jet CVD system, and CH radical could be believed to play certain role in diamond film deposition.

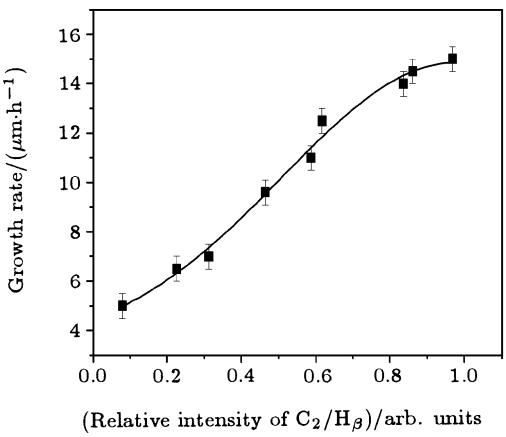


Fig.7. The growth rate of diamond films and emission intensity ratio of C_2 to H_β from the CH_4–H_2–Ar mixture plasma.

4. Conclusions

Characterization of the reaction radicals and electron temperature in DC arc plasma jet CVD system diamond growth process was investigated by *in situ* spatially resolved OES. The results show that all the deposition parameters (methane concentration, substrate temperature, gas flow rate and ratio of H_2/Ar) could strongly influence the gas phase. C_2 is found to be the most sensitive radical to deposition parameters among the radicals in gas phase. Spatially resolved OES implies that a relative high concentration of atomic H exists near the substrate surface, which is beneficial for diamond film growth. Correlation between atomic hydrogen concentration and diamond film quality proves the important role of the hydrogen atom in diamond formation. C_2 in the CH_4–H_2–Ar plasma is the factor determining the film growth rate under conditions of high H_2 concentration. Our observations demonstrate that C_2 is the main growth radical for diamond in our DC arc plasma jet CVD system, and CH radical also plays certain role in the diamond film deposition.

References

[1] Harris S J, Weiner A M and Perry T A 1988 *Appl. Phys. Lett.* **53** 1605

[2] Weiner W A, Cerio F M and Johnson C E 1991 *J. Mater. Res.* **6** 2134

[3] Snail K A and Hanssen L M 1991 *J. Cryst. Growth* **112** 651

[4] Ohtake N and Yoshikawa M 1990 *J. Electrochem. Soc.* **137** 717

[5] Hsu W L 1991 *Appl. Phys. Lett.* **59** 1427

[6] Celii F G and Butler J E 1992 *J. Appl. Phys.* **71** 2877

[7] Meler U, Kohse-Hoinghaus K, Schafer L and Klages C P 1990 *Appl. Opt.* **29** 4993

[8] Celii F G, Pehresson P E, Wang H T and Butler J E 1988 *Appl. Phys. Lett.* **52** 2043

[9] Locher R and Wild C 1994 *Appl. Phys. Lett.* **65** 34

[10] Liao Y, Li C H, Ye Z Y, Chang C, Wang G Z and Fang R C 2000 *Diam. and Relat. Mater.* **9** 1716

[11] Stalder K R and Sharpless R L 1990 *J. Appl. Phys.* **68** 6187

[12] Cubertafon J C, Chenevier M, Campargue A, Priem T and Verven G 1995 *Diam. and Relat. Mater.* **4** 350

[13] Lu F X, Tang W Z, Zhong G F, Huang T B, Liu J M, Li G H, Lo T L, Zhang Y G and Sun Z L 2000 *Diam. and Relat. Mater.* **9** 1655

[14] Kampas F T 1983 *J. Appl. Phys.* **54** 1983

[15] McMaster M C, Hsu W L, Coltrin M E and Dandy D S 1994 *J. Appl. Phys.* **76** 7576

[16] Corat E J and Goodwin D G 1993 *J. Appl. Phys.* **74** 2021

[17] Huang T B, Tang W Z and Lu F X 2005 *Surface & Coatings Technology* **190** 48

[18] Lu F X, Huang T B, Tang W Z and Liu J M 2002 *Inter. J. Mod. Phys.* B **16** 887

[19] Lu F X, Tang W Z, Huang T B, Liu J M, Song J H, Yu W X and Tong Y M 2001 *Diam. Relat. Mater.* **9** 1551

[20] Lu F X, Zhong G F, Sun J G, Fu Y L, Tang W Z, Wang J J, Li G H, Zang J M and Pan C H 1998 *Diam. Relat. Mater.* **7/6** 737