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Gas phase study and oriented self-standing diamond film fabrication in high power DC arc plasma jet CVD

G.C. Chen [a,*], B. Li [b], H. Lan [a], F.W. Dai [a], Z.Y. Zhou [a], J. Askari [a], J.H. Song [a], L.F. Hei [a], C.M. Li [a], W.Z. Tang [a], F.X. Lu [a]

[a] *Sch. Metal. Ecolo., Uni. Sci Technol. Beijing, Beijing, 10083, P. R. China*
[b] *Sch. Mater. Sci. Eng., Uni. Sci Technol. Beijing, Beijing, 10083, P. R. China*

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Abstract

Gas phase species were diagnosed by *in situ* spatially resolved OES in high power DC arc plasma jet CVD system. CH, C_2, H were found as main species in this deposition plasma environment. Concentration of species was studied with the variation of deposition parameters such as methane concentration, substrate temperature and gas flow rate. C_2 was found to be the most sensitive species to deposition parameters. The electron mean temperature was deduced from H_γ/H_β, and changed little no matter how the deposition parameters varied. Self-standing diamond films with (111) orientation were grown within the modified species atmosphere where the intensity ratio of CH/C_2 was higher than 0.41.

Keywords: Diamond film; OES; Orientation; DC arc jet

1. Introduction

With the increase in the requirement of high properties of device in MEMS, SAW and sensors, highly oriented CVD diamond films become more and more attractive [1–3]. So far, a number of different chemical vapor deposition (CVD) techniques for producing oriented film have been developed, including hot filament CVD [4], microwave CVD [5], and combustion flame CVD [6]. As growth rate is concerned, significant high rate occurs in DC arc plasma jet CVD. Over 1 mm/h has been reported [7]. However, few results about oriented film by this high rate technique are reported. Orientation is strongly dependent on gas species. For example, Harris [8], ??Goodwin [9] and Conltrin [10] regarded that CH_3 dominated the formation of (100) orientation, though CH and C_2H_2 were the key species regarded by Frenklach [11], Battaile [12] and Okkerse [13]. To detect gas species, various *in situ* detection methods have been used that include mass spectrometry [14], resonance-enhanced multiphoton ionization [15], laser induced fluorescence [16], and infrared absorption spectroscopy [17]. Optical emission spectroscopy (OES) has been used in microwave plasma CVD [18], hot filament CVD [19], and low power DC jet [20,21]. There have been fewer diagnostic reports on diamond deposition by high power DC arc plasma jet CVD than any of the other CVD techniques mentioned above. Therefore, the gas phase chemistry of this technique is very blurry. In this paper, we provide plasma diagnostic data with the help of OES *in situ* detection, and reported the stable growth of self-standing diamond film with (111) orientation in C_2 dominant plasma environment by high power DC arc plasma jet CVD.

2. Experiment

Diamond film deposition apparatus was a high power (30 kW) DC Arc Plasma Jet CVD reactor with a methane/hydrogen/argon source gas mixture. The flow rate of each gas is 1–8 slm for Ar, 1–8 slm for H_2, and 10–50 sccm for CH_4. The system with a magnetically controlled plasma torch was similar to that reported from our previous publications [22]. The

* Corresponding author.
E-mail address: gcchen_ustb@163.com (G.C. Chen).

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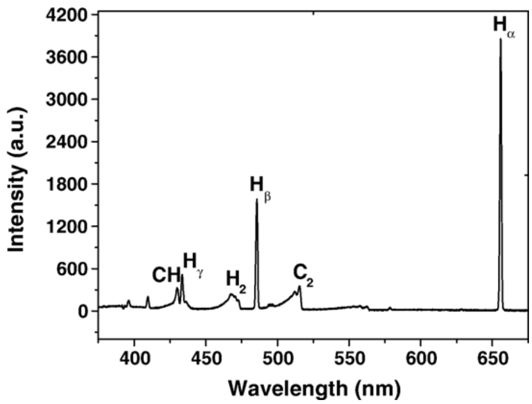

Fig. 1. Typical optical emission spectrum from the CH_4–H_2–Ar mixture in the high power DC arc plasma jet CVD system.

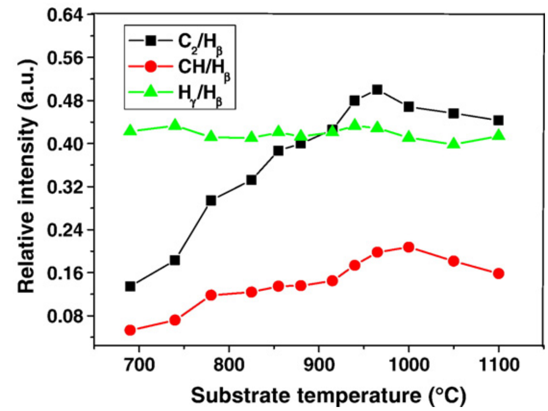

Fig. 3. Optical emission intensity ratios of C_2, CH and H_γ to H_β *v.s.* the substrate temperature (C_m = 1.8%, F_g = 16 slm).

chamber pressure was 4–8 kPa during deposition. Diamond films were deposited on molybdenum substrates and obtained under different deposition parameters (methane concentration, substrate temperature, ratio of Ar/H_2, etc.). In order to enhance the nucleation density, the molybdenum substrates were cleaned in an ultrasonic bath with acetone and then rubbed with 20, 10, 5 and 0.5 μm diamond powder in turn, at last drying after an ethanol rinse. The power was maintained at 15 kW.

The gas phase species in the reaction region were examined by OES during diamond films growth. The emission light from the reaction region was transferred to the entrance slit of a monochrometer (WDP500-2A) through the quartz window and a lens system with an optical fiber. Scan rate was 200 nm/min, and collection time was 1 s/step controlled by a computer. The detection position was focused 0.8 mm above the substrate.

3. Results and discussion

Fig. 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 300 and 700 nm). We studied the relationship between the emission intensities of CH, C_2 and H_γ with the deposition parameters. 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 concentration. The intensity ratio of I_{H_β}/I_{H_α} or I_{H_γ}/I_{H_β} is proportional to the rate constant of excitation of H, which reflects an electron mean energy in the plasma, i.e. the electron temperature [23].

Variation of the intensity ratios of H_γ, C_2 and CH to H_β, as a function of methane concentration (C_m) under 945 °C substrate temperature (T_{sub}) and 16 slm gas flow rate (F_g), 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 higher methane concentration leads to relatively high levels of C_2 and CH. Harris and Weiner measured the atomic H concentration near the substrate surface. They found that the atomic H concentration was higher at low methane concentrations than that at high methane concentrations [24]. Therefore, increase of non-diamond phase would occur at high methane concentration due to less H etching. Slight increase in the intensity ratio of H_γ/H_β indicates that electron mean temperature is enhanced with the increase of methane concentration.

Fig. 3 shows the intensity ratios of C_2, CH and H_γ to H_β as a function of the substrate temperature under C_m = 1.8% and F_g = 16 slm. The intensity ratios of C_2 to H_β and CH to H_β increase

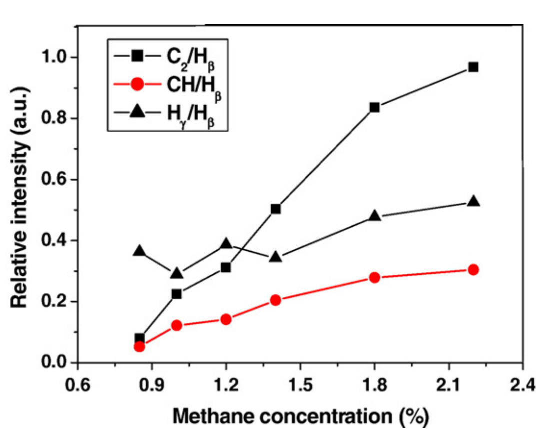

Fig. 2. Optical emission intensity ratios of C_2, CH and H_γ to H_β *v.s.* the methane concentration (T_{sub} = 945 °C; F_g = 16 slm).

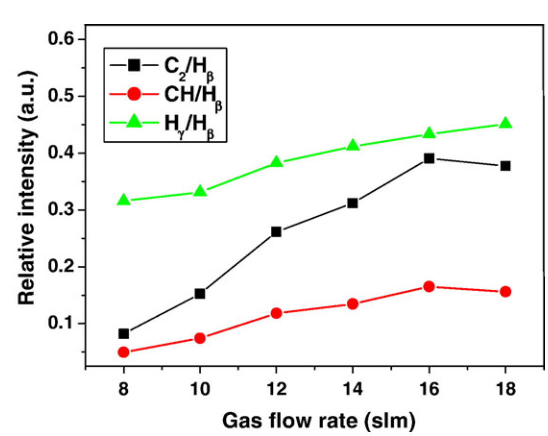

Fig. 4. Optical emission intensity ratios of C_2, CH and H_γ to H_β *v.s.* gas flow rate (T_{sub} = 945 °C and C_m = 1.8%).