Investigation of optical emission spectroscopy in diamond chemical vapor deposition by Monte Carlo simulation

Zhijun Wang (王志军), Lifang Dong (董丽芳), Panlai Li (李盼来), Yong Shang (尚 勇), and Shoujie He (何寿杰)

College of Physics Science and Technology, Hebei University, Baoding 071002

Received August 14, 2007

The optical emission spectra (atomic hydrogen (H_α, H_β, H_γ), atomic carbon C ($2p3s \rightarrow 2p^2$: $\lambda = 165.7$ nm) and radical CH ($A^2\Delta \rightarrow X^2\Pi$: $\lambda = 420 - 440$ nm)) in the gas phase process of the diamond film growth from a gas mixture of CH_4 and H_2 by the technology of electron-assisted chemical vapor deposition (EACVD) have been investigated by using Monte Carlo simulation. The results show that the growth rate may be enhanced by the substrate bias due to the increase of atomic hydrogen concentration and the mean temperature of electrons. And a method of determining the mean temperature of electrons in the plasma *in-situ* is given. The strong dependence on substrate temperature of the quality of diamond film mainly attributes to the change of gas phase process near the substrate surface.

OCIS codes: 300.2140, 310.1860, 160.4670.

Due to the outstanding properties, diamond film is expected to become a very advanced and promising material for many applications, such as integrated circuit (IC) heat sinking and packaging materials, semiconductor devices, infrared windows. The technology of electron-assisted chemical vapor deposition (EACVD) has been developed substantially in recent years for the fabrication of diamond films, such as polycrystalline diamond films, textured diamond films, oriented diamond and nanocrystallite diamond films[1−3]. Though the fundamental understanding about EACVD of diamond growth has been advanced with the development of gas phase analysis techniques, the exact mechanism in the gas phase environment is not yet clear.

In order to obtain accurate information about the nature and mole fractions of all the present species, various *in-situ* diagnostic techniques have been developed, such as optical emission spectroscopy (OES), along with laser techniques such as cavity ring down spectroscopy, two-photon laser-induced fluorescence[4] and resonance-enhanced multiphoton ionization. However, the results obtained from experiments are not adequate. For example, in the experiments using OES, the measured intensity ratio of atomic hydrogen emission line (H_β/H_α) is usually used to represent the mean temperature of electrons in the plasma on the assumption that the gas phase process of EACVD is of thermodynamic equilibrium[5]. In fact, it is a nonequilibrium system. Consequently the mean electron temperature of electrons obtained in those conventional experiments is not accurate enough. Therefore, theoretical simulation for nonequilibrium gas phase process of EACVD is desirable.

Previously we have investigated the electron behavior and dissociation and excitation process in EACVD by using Monte Carlo simulation, and it is believed that atomic hydrogen H and radical CH_3 play important roles in diamond film deposition[6,7]. In this work, the optical emission processes of atomic H, atomic C and radical CH in EACVD are simulated, and the effects of the experimental parameters on emission spectra and synthesis of diamond films are discussed.

The model has been described detailed in our previous work[6,7], and so here we just present it in brief. The filling gas is a mixture of H_2 and CH_4. The distance between filament and substrate is 10 mm. The filament temperature is 2273 K and the gas temperature decreases rapidly with the distance from the filament. The variance of gas temperature is cited from the measurements of Yarbrough[8]. A positive bias voltage is applied to the substrate with respect to the filament. A simplified three-dimensional (3D) model is used. Two directions parallel to the substrate are defined as the x and y axes, the z axis is the direction perpendicular to the substrate surface.

There are many types of reactions such as electron+molecule, molecule+molecule, molecule+radical and H+CH_x ($x = 1, 2, 3$) in gas phase during EACVD process. And in these types, electron-molecule collision is the most important. So only the electron-molecule collision is considered in the initial simulation.

According to the statistical physics, the electron may collide with a molecule while it flies through the mean free path λ_e which is defined as

$$\lambda_e = \frac{1}{S_T(\varepsilon) \cdot N}, \tag{1}$$

where $S_T(\varepsilon) = (1 - c) \cdot \sigma_{H_2} + c\sigma_{CH_4}$ is the total cross section for electron with energy ε, σ_{H_2} and σ_{CH_4} are total cross sections of e-H_2 and e-CH_4 for electron with energy ε respectively, c is CH_4 concentration in the filling gas, $N = P/kT$ (P is gas pressure in reaction chamber, k is Boltzmann's constant and T is gas temperature) is gas number density.

Elastic collision, vibrational excitation, dissociation, electronic excitation, dissociative excitation[9] (H_α, H_β, H_γ included) and ionization are considered in e-H_2 collision. The scattering is anisotropic for e-H_2 elastic collision[10], and isotropic for e-H_2 inelastic collisions. Among the collisions between electron and methane molecule, elastic momentum transfer, vibrational ex-

1671-7694/2008/030218-04

citation, neutral dissociation, dissociative excitation[11] (H_α, H_β, H_γ, C ($2p3s \rightarrow 2p^2$: $\lambda = 165.7$ nm) and CH ($A^2\Delta \rightarrow X^2\Pi$: $\lambda = 420 - 440$ nm) included), ionization and dissociation ionization are considered. In the case of all e-CH_4 collisions, the scattering is considered isotropic for simplification.

It is generally believed that the emission intensity ratio of the species is helpful for determining the relationship between plasma-generated species and diamond film growth[12]. And the emission intensity of the species does not represent its absolute concentration. For the same species, the emission intensity ratio of two lines, for example, H_β/H_α or H_γ/H_β is proportional to the rate constant of excitation of the species, which reflects an electron mean energy in the plasma, i.e., the electron temperature. For different species, 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 we will mainly discuss the relative intensities below.

Figure 1 shows the variation of the intensity ratios of CH/H_γ and H_γ/H_β as functions of methane concentration. It can be seen that increasing the methane concentration promotes the intensity ratio of CH to H_γ, which implies that higher methane concentration leads to relatively low level of atomic H. McMaster *et al.*[13] measured reaction radicals near the substrate by mass spectrum method and found atomic H concentration decreases with the increase of methane concentration. At the same time, it is well known that atomic H is particularly important as it plays several roles, such as selective etching of graphic deposits and stabilization of the sp^3 bonds necessary for the formation of diamond. Therefore, the methane concentration is generally controlled in the range of $0.5\% - 2.0\%$ when a diamond film begins to grow on a substrate. Otherwise, the surface morphology of diamond films would change from well-defined facets to cauliflower structures with the increase of methane concentration and influence the quality of the diamond film.

From Fig. 1 we can also see that the intensity ratio of H_γ/H_β slightly drops with the increase of methane concentration, i.e. an increase in methane concentration reduces the mean temperature of electrons, which may be by the reason that the ionization collisions of CH_4 are dominant at lower gas pressure. Thus an increase in methane concentration promotes the probability of ionization, consequently the loss of the threshold energy of electrons rises, and the mean temperature of electrons decreases. Figure 2 shows the relevant experiment result[14], and it can be obviously seen that our calculation results are in a good agreement with the experiment.

In summary, the increase of methane concentration changes the chemical properties of the gas phase near the substrate, and further influences the deposition of diamond films.

Figure 3 shows the intensity ratio of H_β/H_α as a function of substrate bias voltage. We can see that H_β/H_α increases with bias voltage, which indicates that the higher bias voltage can present an increase of mean temperature of electrons. We calculated the mean temperature of electrons under different bias voltages, as shown in Fig. 4. It is apparent that the mean temperature of electrons increases with the bias voltage. This result may be because the mean free path of electron is proportional to $1/N$ as shown in Eq. (1), and the energy gain after an electron flying through the mean free path increases with the rise of bias voltage. Consequently, the kinetic energy of electron is approximately proportional to E/N (E is electric field). Therefore, when N is settled, the mean temperature of electrons increases with increasing E, namely bias voltage.

In addition, the relationship between the mean temperature of electrons and H_β/H_α can be obtained by combining Fig. 3 with Fig. 4, as shown in Fig. 5. It can be seen that the mean temperature of electrons increases with increasing H_β/H_α, thus the mean temperature of electrons can be represented indirectly by intensity ratio of H_β/H_α.

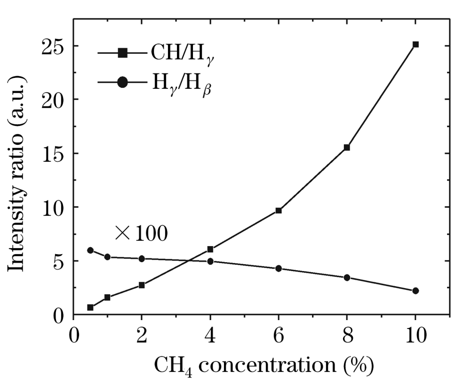

Fig. 1. Intensity ratios of H_γ to H_β and CH to H_γ as functions of CH_4 concentration.

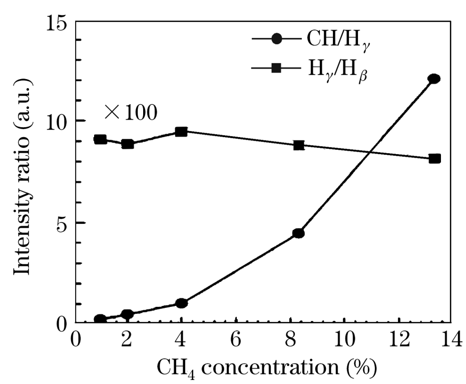

Fig. 2. Intensity ratios of H_γ to H_β and CH to H_γ as functions of the CH_4 concentration in Ref. [14].

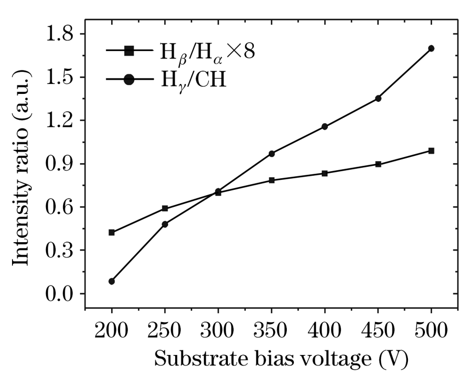

Fig. 3. Intensity ratios of H_β to H_α and H_γ to CH as functions of bias voltage under the condition $P = 1.0$ kPa.

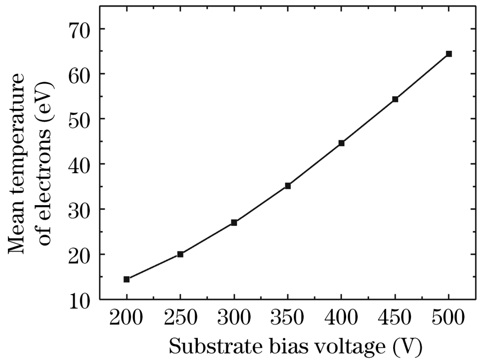

Fig. 4. Mean electron temperature as a function of bias voltage under the condition $P = 1.0$ kPa.

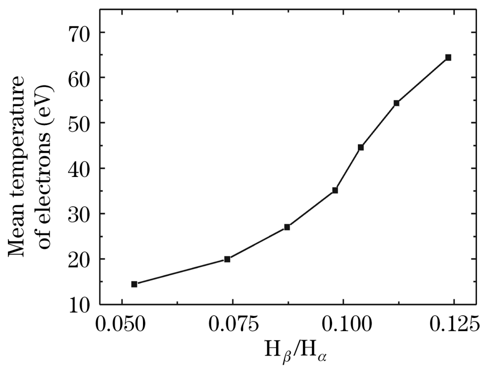

Fig. 5. Relationship between the mean electron temperature and the ratio of atomic hydrogen emission intensity.

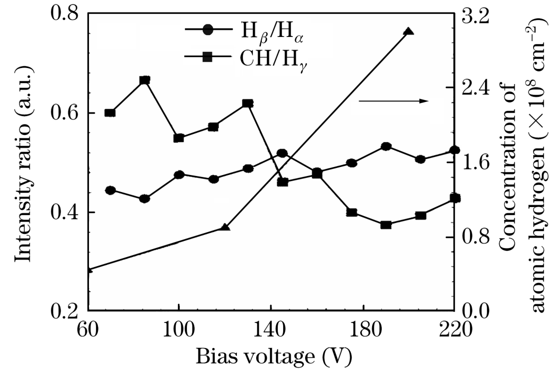

Fig. 6. Intensity ratios of H_β to H_α and CH to H_γ as functions of bias voltage under the condition in Ref. [14].

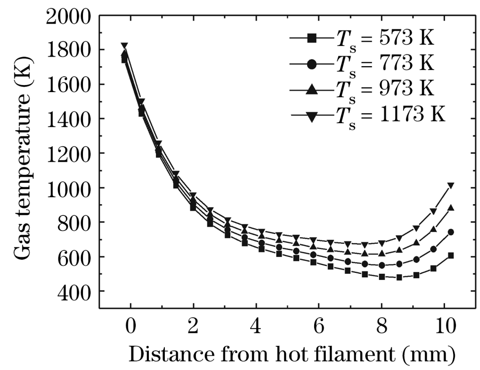

Fig. 7. Gas temperature as a function of the distance from hot filament under different substrate temperatures.

For example, when H_β/H_α is 0.1, the corresponding mean temperature of electrons is 44.6 eV. And it is worth pointing out that EACVD is considered thermodynamic nonequilibrium when the above relationship is obtained. Therefore, the result will be more accurate than that from conventional experiments. Thus a method of determining the mean temperature of electrons in the plasma of EACVD *in-situ* is proposed.

From Fig. 3 we can also see that the intensity ratio of H_γ/CH increases with the increase of bias voltage, which suggests that the higher bias voltage will be beneficial to increase the relative concentration of atomic hydrogen near the substrate, which agrees well with the experiment[14] (Fig. 6 shows the relevant experiment result). That can be explained as follows. In conventional hot filament chemical vapor deposition (CVD) system, most of the H_2 dissociation occurs on the filament surface. The atomic hydrogen concentration decreases rapidly to 25% near the substrate. Therefore, sufficient amount of hydrogen atoms cannot be provided on the substrate under some conditions. By applying bias voltage, additional hydrogen atoms are generated by the dissociation of H_2 resulting from electron impact in the gas phase, thus the higher bias will be more helpful to increase the relative concentration of atomic hydrogen near the substrate. Because the atomic hydrogen is an important species promoting diamond growth while suppressing nondiamond carbon deposition, the deposition rate of diamond film is effectively enhanced. Moreover, the rise of the mean temperature of electrons will result in more probability of the collisions between electron and other radicals as well as substrate surface, which may lead to the more product of atomic hydrogen. In conclusion, the growth rate of diamond film may be enhanced by the substrate bias due to the increase of atomic hydrogen concentration and the mean temperature of electrons.

We also investigated the influence of the substrate temperature on the optical emission spectra. The variance of gas temperature is cited from the measurements of Yarbrough[8], and the spatial variation of gas temperature under different substrate temperatures is obtained, as plotted in Fig. 7. It can be seen that the gas temperature at the surface of hot filament is the highest, then drops rapidly with the distance from the hot filament, and at last rises near the substrate. In the mass, the gas temperature in the reactor increases with increasing substrate temperature, and the substrate temperature has much more effect on the gas temperature near the substrate surface than that far from the substrate.

Figure 8 shows the spatial distribution of intensity ratio of H_β/H_α under different substrate temperatures. We can notice that the higher substrate temperature produces higher H_β/H_α, i.e. higher mean temperature of electrons, which can be interpreted as follows. The kinetic energy of electrons is approximately proportional to E/N (the ratio of electric field to gas molecule density, $N = P/kT$), thus the electron energy is proportional to gas temperature T, and since the gas temperature in the reactor is influenced by the substrate temperature, as shown in Fig. 5, the increase of the mean temperature of electrons is the result of raising substrate temperature.

In addition, from Fig. 8, we can also see that the change extent of H_β/H_α near the substrate surface is relatively greater than that far from the substrate, which indicates

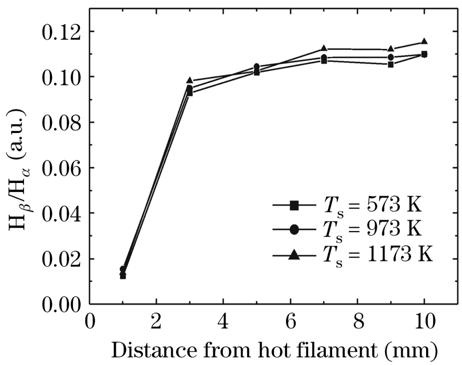

Fig. 8. Intensity ratio of H_β to H_α as a function of the distance from hot filament under different substrate temperatures.

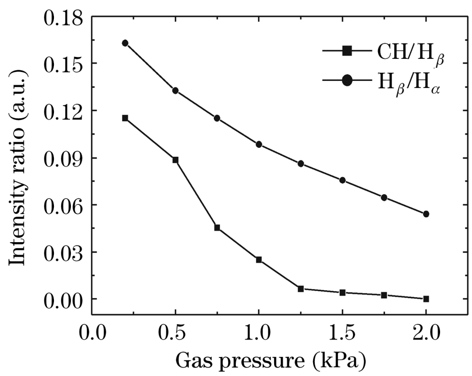

Fig. 9. Intensity ratios of H_β to H_α and CH to H_β as functions of gas pressure.

that the substrate temperature has more effect on the mean temperature of electrons near the substrate surface compared with that far from the substrate. It implies that the substrate temperature affects the gas phase reaction process near the substrate surface more greatly because the gas phase process is determined by the electron kinetic energy. So, we can conclude that the strong dependence on substrate temperature of the quality of diamond film is mainly attributed to the change of gas phase process near the substrate surface[14].

Figure 9 shows the intensity ratios of H_β/H_γ and CH/H_β as functions of gas pressure. It can be seen that H_β/H_α decreases with increasing gas pressure, i.e. the increase of gas pressure depresses the mean temperature of electrons. It may be because the higher gas pressure decreases the mean free path of electrons in the plasma, thus the more probability of collisions between electrons and other radicals occurs, as well as the increase of the loss of electron energy and the decrease of the mean energy of electrons.

From Fig. 9, we can also find that the intensity ratio CH/H_β decreases with increasing gas pressure, which indicates that the addition of gas pressure enhances the relative concentration of atomic H to CH.

In conclusion, the optical emission spectra of atomic hydrogen, atomic carbon and radical CH in EACVD have been investigated by using Monte Carlo simulation from CH_4/H_2 gas mixture. Effects of the experimental parameters on emission spectra and synthesis of diamond films are discussed. The growth rate may be enhanced by the substrate bias due to the increase of atomic hydrogen concentration and the mean temperature of electrons. The strong dependence on substrate temperature of the quality of diamond film is mainly attributed to the change of gas phase process near the substrate surface. And a method of determining the mean temperature of electrons *in-situ* in the plasma of EACVD is obtained. These results will be helpful to the understanding of the plasma process in EACVD and the model of plasma CVD.

This work was supported by the National Natural Science Foundation of China (No. 10647123) and the Youth Natural Science Foundation of Hebei University (No. 2005Q31). Z. Wang's e-mail address is wangzhijunmail@yahoo.com.cn.

References

1. R. Kuschnereit, P. Hess, D. Albert, and W. Kulisch, Thin Solid Films **312,** 66 (1998).
2. G. Fu, X. Wang, W. Yu, L. Han, L. Dong, and X. Li, Appl. Phys. Lett. **70,** 1965 (1997).
3. Y.-K. Kim, Y.-S. Han, and J.-Y. Lee, Diam. Relat. Mater. **7,** 96 (1998).
4. L. Schäfer, C.-P. Klages, U. Meier, and K. Kohse-Höinghaus, Appl. Phys. Lett. **58,** 571 (1991).
5. Y. Shigesato, R. E. Boekenhauer, and B. W. Sheldon, Appl. Phys. Lett. **63,** 314 (1993).
6. L. Dong, B. Ma, Y. Shang, and Z. Wang, Plasma Sci. Technol. **3,** 2845 (2005).
7. L. Dong, B. Ma, and Z. Wang, Chin. Phys. **13,** 1597 (2004).
8. W. A. Yarbrough, K. Tankala, M. Mecray, and T. Debroy, Appl. Phys. Lett. **60,** 2068 (1992).
9. H. Tawara, Y. Ltikawa, H. Nishimura, and M. Yoshino, Phys. Ref. Data **19,** 617 (1990).
10. G. M. Webb, Phys. Rev. **47,** 384 (1935).
11. K. Motohashi, H. Soshi, M. Ukai, and S. Tsurubuchi, Chem. Phys. **213,** 369 (1996).
12. Y. Liao, C. Li, Z. Ye, C. Chang, G. Wang, and R. Fang, Diam. Relat. Mater. **9,** 1716 (2000).
13. M. C. McMaster, W. L. Hsu, M. E. Coltrin, and D. S. Dandy, J. Appl. Phys. **76,** 7567 (1994).
14. J. Cui, Y. Ma, and R. Fang, Science in China (A) (in Chinese) **26,** 1038 (1996).