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Electron behaviour in CH_4/H_2 gas mixture in electron-assisted chemical vapour deposition*

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The behaviour of electrons in CH_4/H_2 gas mixture in electron-assisted chemical vapour deposition of diamond is investigated using Monte Carlo simulation. The electron drift velocity in gas mixture is obtained over a wide range of E/P (the ratio of the electric field to gas pressure) from 1500 to 300000 (V/m kPa^{-1}). The electron energy distribution and average energy under different gas pressure (0.1–20kPa) and CH_4 concentration (0.5%–10.0%) are calculated. Their effects on the diamond growth are also discussed. It is believed that these results will be helpful to the selection of optimum experimental conditions for high quality diamond film deposition.

Keywords: Monte Carlo simulation, chemical vapour deposition, electron swarm, drift velocity
PACC: 0250, 8115H

1. Introduction

Chemical vapour deposition (CVD) diamond films have been paid much attention due to their unique physical and chemical properties in the last decades.[1,2] Electron-assisted chemical vapour deposition (EACVD), which uses a bias between the substrate and the hot filament in HFCVD, has been developed substantially and extensively adopted to deposit the diamond film in recent years.[3–6] It is well known that electron-assisted technique can increase the nucleation density, enhance the diamond growth rate and improve the diamond film quality.

Although the mechanisms of diamond growth are far from being thoroughly understood, the key role that energetic electrons play in EACVD has long been recognized. It is well known that the reactions involving energetic electrons are helpful to the diamond deposition at a high growth rate in the EACVD process, they contribute to the production of particles (methyl CH_3 and atom hydrogen H) essential for diamond deposition, and energetic carbonaceous species which are beneficial to the deposition of smooth diamond film. Thus, the investigation of the behaviour of the electrons in the gas phase in EACVD is very important.

The behaviour of electrons in hydrogen has been investigated by using Monte Carlo simulation.[7,8] However, the research on the behaviour of electron in CH_4/H_2 gas mixture, especially its variation with the CH_4 concentration in the filling gas, and the gas pressure and temperature, is still lagging. In addition, the study on electron swarm in mixture gas is also rare.

In this paper, the behaviour of electrons in CH_4/H_2 gas mixture during EACVD of diamond is investigated using Monte Carlo simulation. The electron drift velocity under different CH_4 concentration over a wide range of E/P are obtained. The electron energy distribution and average energy under different gas pressure (0.1–20kPa) and CH_4 concentration (0.5%–10.0%) are calculated, and their effects on the diamond growth are discussed.

2. Model

The EACVD process is studied using the Monte Carlo simulation. The filling gas is a mixture of $H_2$and CH_4. The distance between filament and substrate is 10mm. The filament temperature is 2273K and the gas temperature decreased rapidly with the distance from the filament. The variation of gas temperature is cited from the measurements of Yarbrough.[9] The total gas pressure is varied between 0.1 and 20kPa. A positive bias voltage (U=300V) is applied to the substrate with respect to the filament. 10^5 electrons are provided for the calculation of their trajectory and kinetic energy. Electrons are emitted from hot filament and accelerated towards the biased substrate. A

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simplified three-dimensional 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 e+molecule, molecule+molecule, molecule+radical and H+CH_x (x=1, 2, 3) radical in gas phase during the EACVD process. Among these types, e+molecule collision is the most important because, (1) experiments to date have shown that the deposition rate can be greatly enhanced in EACVD, it shows that reactions involving energetic electrons are the main processes in EACVD; (2) it is the primary reaction; (3) electrons can obtain sufficient energy from electric field to provide the activation energy for reaction but other particles (such as the molecule, H atom or CH_x radical) cannot. So only the e+molecule collisions are considered in the initial simulation.

According to statistical physics, an electron may collide with a molecule when it flies through the mean free path λ_e. The mean free path of electron λ_e is defined as

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

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 the reaction chamber, k is the Boltzmann constant and T is the gas temperature) is the gas number density.

Elastic collision, vibrational excitation, dissociation, electron excitation and ionization are considered in e–H_2 collision. The cross sections of e–$H_2$are taken from Saelee.[10] The scattering is anisotropic for e–H_2 elastic collision,[11,12] and isotropic for e–H_2 inelastic collisions.

In the collisions between electron and methane molecule, elastic momentum transfer,[10] vibrational excitation,[10] neutral dissociation,[13] ionization and dissociation ionization[14] are considered. In the case of e–CH_4 collisions, the scattering is taken as isotropic for simplicity.

3. Results and discussion

In order to test the reliability of the model, the drift velocity of electrons in CH_4 gas is calculated over a wide range of reduced field E/N (10Td$\leq$ E/N $\leq$2000Td, E/N being the ratio of electric field intensity to gas number density). As shown in Fig.1, the computed values are in good agreement with the experimental data reported previously,[15–17] especially over the E/N range 20$\leq$ E/N $\leq$300Td, suggesting that our model is feasible and can be used to evaluate electron behaviour and its effect on diamond growth.

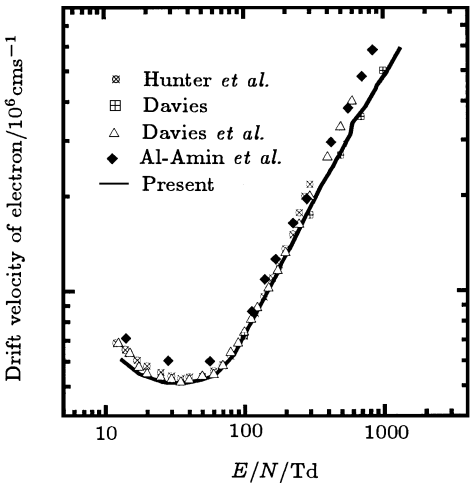


Fig.1. Electron drift velocity as a function of E/N in CH_4.

The drift velocity of electron swarm in CH_4/H_2 gas mixture is calculated first. Figure 2 gives some typical results. The results show that the drift velocity is a function of E/P and gas composition. It increases with increasing E/P for any concentration in gas mixture. It decreases with increasing CH_4 concentration when E/P is in the range of 2000–3.0$\times10^5$V/m kPa^{-1}, while it increases with CH_4 concentration when E/P is in the range of 1500–2000V/m kPa^{-1}.

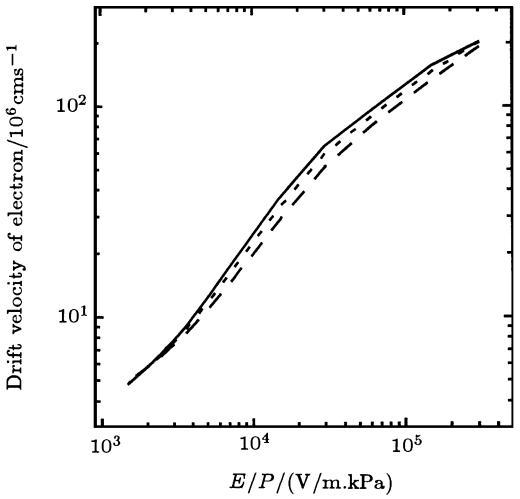


Fig.2. Electron drift velocity as a function of E/P under different CH_4 concentration in CH_4/H_2 gas mixture during EACVD process: — c=0.5%; - - - c=4%; – – – c=10%.

In EACVD, the diamond growth rate depends strongly on the dissociation process of the CH_4 and H_2, which is directly related to electron energy. Thus

the electron energy distribution under different gas pressures and different CH_4 concentrations is computed. Figure 3 gives a typical variation of energy distribution with gas pressure at CH_4 concentration of 0.7%. It is clearly seen that the most probable energy decreases with increasing gas pressure. There are more electrons possessing energy of 8–10eV when gas pressure is in the range of 1.0–8.3kPa, which is beneficial for dissociation of CH_4 and H_2 as the threshold energy of dissociation of CH_4 and H_2 is 9.3eV and 8.8eV, respectively. For clarity, Fig.4 gives the average energy of electrons as the function of CH_4 concentration under different gas pressures. The average energy of electrons decreases with increasing gas pressure. It decreases with increasing CH_4 concentration when gas pressure is in the range of 0.1–4kPa, while increases when in the range of 6–20kPa. From the viewpoint of gas dissociation, the diamond can be obtained at higher rate when the gas pressure is in the range of 2–9kPa.

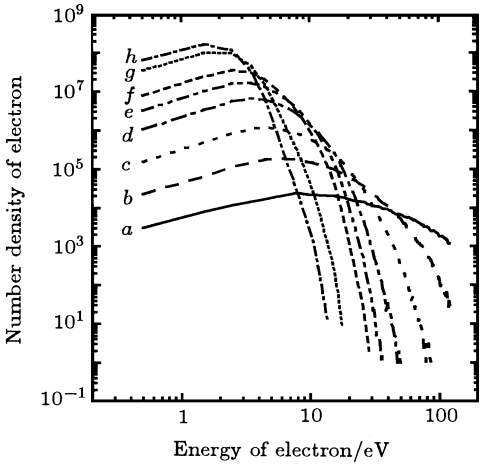


Fig.3. Energy distribution of electron for different gas pressure, under the condition of CH_4 concentration c=0.7% in EACVD process: (a) P=0.5kPa; (b) P=1kPa; (c) P=2kPa; (d) P=4kPa; (e) P=6kPa; (f) P=8.3kPa; (g) P=15kPa; (h) P=20kPa.

It is well known that energetic electrons play an important role in EACVD. In the gas phase, the dissociation of H_2 and hydrocarbons is enhanced due to the impact with energetic electrons, thus the deposition rate is effectively enhanced. When the energetic electrons bombard the substrate surface, they can provide kinetic energy to the atomic species residing on the substrate surface and enhance their surface mobility, which may results in an improvement in the growth of facets of diamond crystallites. Therefore, the value of $\frac{1}{2}mv_{||}^2$ ($v_{||}$ is the velocity parallel to the substrate) is important because electrons with a velocity parallel to the substrate can move the carbonaceous material, thus enhancing the growth of oriented diamond.

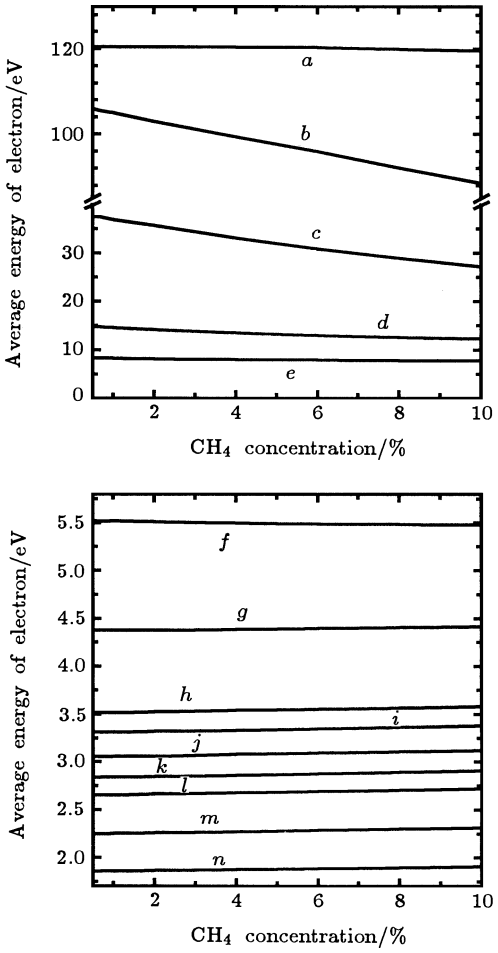


Fig.4. Average energy of electrons as a function of CH_4 concentration in the gas mixture under different gas pressure in EACVD process: (a) P=0.1kPa; (b) P=0.2kPa; (c) P=0.5kPa; (d) P=1kPa; (e) P=2kPa; (f) P=4kPa; (g) P=6kPa; (h) P=8.3kPa; (i) P=9kPa; (j) P=10kPa; (k) P=11kPa; (l) P=12kPa; (m) P=15kPa; (n) P=20kPa.

In order to discuss the influence of gas pressure and gas composition on the diamond growth at the surface, the $\frac{1}{2}mv_{||}^2$ under different gas pressure and CH_4 concentration are calculated. The results show that the $\frac{1}{2}mv_{||}^2$ decreases with the increasing gas pressure under different CH_4 concentration. It decreases with increasing CH_4 concentration when gas pressure is in the range of 0.1–4kPa, while increases when gas pressure is in the range of 6–20kPa. For clarity, only some typical results are shown in Fig.5.

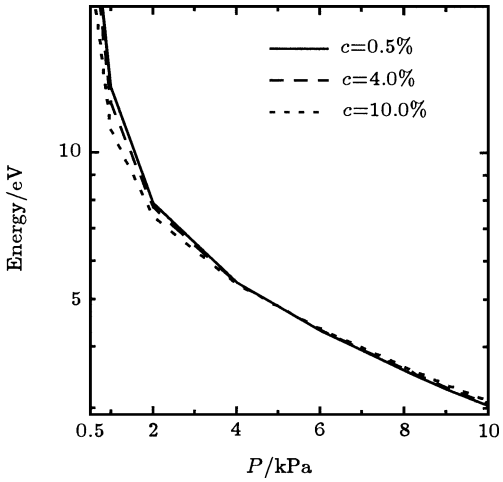


Fig.5. $\frac{1}{2}mv_{||}^2$ (electron energy) as a function of P for different CH_4 concentrations in CH_4/H_2 gas mixture, $v_{||}$ is the velocity parallel to the substrate.

From Figs.4 and 5, we conclude that high-quality diamond with high growth rate can be obtained by choosing appropriate CH_4 concentration and gas pressure, for which not only sufficient atomic H and fragment CH_3 but also large $\frac{1}{2}mv_{||}^2$ can be reached. It is evident that high-quality diamond with high growth rate can be obtained at CH_4 concentration of 0.5% when the gas pressure is in the range of 2–4kPa, and of a little more than 0.5% when gas pressure is in the range of 6–9kPa, which is in good agreement with experiments.

4. Conclusion

The behaviour of electrons in the CH_4/H_2 mixture in EACVD of diamond has been investigated by Monte Carlo simulation. The electron drift velocity under different CH_4 concentration is obtained over a wide range of $1500 < E/P < 300000$ V/m kPa^{-1}. The electron energy distribution and average energy under different gas pressure (0.1–20kPa) and CH_4 concentration (0.5%–10.0%) are calculated. High-quality diamond with high growth rate can be obtained at the condition that CH_4 concentration is 0.5% when gas pressure is in the range of 2–4kPa, and a little more than 0.5% when gas pressure is in the range of 6–9kPa. We believe that these results will be helpful to the selection of optimum experimental conditions for high quality diamond film deposition at a higher rate. It is also important for the research on electron swarm in gas mixture.

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