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# Monte Carlo simulation of the behaviour of electrons during electron-assisted chemical vapour deposition of diamond*

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The behaviour of electrons during electron-assisted chemical vapour deposition of diamond is investigated using Monte Carlo simulation. The electron energy distribution and velocity distribution are obtained over a wide range of reduced field $E/N$ (the ratio of the electric field to gas molecule density) from 100 to 2000 in units of $1Td{=}10^{-17}\mathrm{Vcm}^2$. Their effects on the diamond growth are also discussed. The main results obtained are as follows. (1) The velocity profile is asymmetric for the component parallel to the field. The velocity distribution has a peak shift in the field direction. Most electrons possess non-zero velocity parallel to the substrate. (2) The number of atomic H is a function of $E/N$. (3) High-quality diamond can be obtained under the condition of $E/N$ from 50 to $800Td$ due to sufficient atomic H and electron bombardment.

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

## 1. Introduction

The technology of electron-assisted chemical vapour 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.[1−4] It is well known that electron-assisted technology can increase the nucleation density and growth rate, make the charged radicals aligned in a certain direction, and thus promote the oriented growth.[2]

Although the detailed growth mechanism is still not clear, the key role that electrons accelerated by the dc electric field play in EACVD has long been recognized. In the gas phase, the dissociation of $H_2$ and hydrocarbons was enhanced due to the impact with energetic electrons, thus the deposition rate of the diamond film was effectively enhanced.[5] The electrons emitted from hot filament and accelerated by the biased field bombard the substrate surface. This can strongly affect the oriented growth of diamond particles. The electron bombardment can also provide kinetic energy to the atomic species residing on the substrate surface and enhance their surface mobility, which may result in an improvement in the growth of facets of diamond crystallites.[6] It is worth emphasizing that the processes mentioned above are directly related to electron behaviour for the following reasons. The atomic H near the substrate, which plays an important role during the CVD process, is generated mainly by dissociation of $H_2$ resulting from electron impact. The dissociative collisions are directly related to electron energy. On the substrate surface, a series of effects of electron bombardment, such as improving nucleation density and initializing oriented growth, are dependent upon the electron incident angle as well as their energy. Thus, it is very important to clarify the behaviour of the electrons accelerated by the dc electric field in the gas phase during EACVD for a better understanding of the diamond reaction process.

Saitoh *et al.*[7] have described a semi-quantitative electron energy distribution in the diamond deposition process using the results of Monte Carlo computer simulation. However, quantitative calculation of electron behaviour, especially its variation with the applied electric field, gas pressure and gas temperature, is still lagging.

In this paper, we investigate the behaviour of electrons during EACVD of diamond using Monte Carlo simulation. The electron velocity distribution and energy distribution changing with the reduced field $E/N$

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(the ratio of the electric field to gas molecule density in units of $1Td{=}10^{-17}\mathrm{Vcm}^2$) are obtained, and their effects on the diamond growth are discussed.

## 2. Model

The EACVD process is studied using a straightforward Monte Carlo method. The feed gas is a mixture of $H_2$ and $CH_4$. The total gas pressure is varied between 0.1 and 10kPa. A positive voltage is applied to the substrate with respect to the filament. The applied voltage is varied from 0 to 300V. The distance from the filament to the substrate is 1cm. The thermal source is assumed to consist of several strands of uncoiled filaments at least 5cm in length to approximate the idealized infinitely large planar hot-filament geometry.[8] The filament temperature is 2273K. The potential between the filament and the substrate is thus roughly a linear function of the distance from the hot filament. The collisions between electrons and hydrocarbons can be neglected due to the much smaller volume fractions for the hydrocarbons compared with that of $H_2$ (about 1:99) in the filling gas. Thus only e–$H_2$ collision processes are considered for studying the behaviour of electrons.

Because of the deficiency in memory and calculation speed of the personal computer we used, $10^5$ electrons are provided for the computer simulation. The electrons are emitted from the hot filament and accelerated towards the biased substrate. The initial velocity distribution of electrons follows a Maxwell–Boltzmann energy distribution function. A simplified three-dimensional model is selected for calculating the kinetic energy and velocity of electrons. 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. Three components of the electron velocity $v_x$, $v_y$ and $v_z$ were computed. Very few electrons can get rid of the electric field because the displacement along $z$ ($\mathrm{d}z$) is larger than that along $r$ ($\mathrm{d}r$) within a mean free path since the electric field drives the electrons along the direction of $-z$ and the possibility of sustained increase in $\mathrm{d}r$ after several collisions is very small. Thus, the $x$ and $y$ boundaries can be assumed to be infinite. So the electron position was computed only in the direction of $z$.

According to statistical physics, the electron may collide with a hydrogen molecule while it flies through the mean free path $\lambda_\mathrm{e}$. The mean free path of electron $\lambda_\mathrm{e}$ is defined as

$$\lambda_\mathrm{e} = \frac{1}{S_\mathrm{T}(\varepsilon)\cdot N}, \qquad (1)$$

where $S_\mathrm{T}(\varepsilon)$ is the total cross section for electrons with energy $\varepsilon$, and $N$ is the gas molecule density.

There are two basic types of collision between electrons and hydrogen molecules: elastic collision and inelastic collision. Considering the large mass difference between the electron and hydrogen molecule, no energy transfer occurs in an elastic collision, implying no energy loss of the electron. In the case of inelastic collision, further consideration should be given. On the basis of a general survey of the cross sections of the electron and hydrogen molecule, four types of inelastic process have been considered, namely the vibrational excitation, dissociation, electron excitation and ionization. Inelastic collisions involve energy transfer from the electron. In the case of vibrational excitation, 20% energy loss from the electron is supposed.[9] Other processes require transfer of the threshold energy for each process. The threshold energy is 8.8eV for dissociation reaction and 15.4eV for ionization and electron excitation. All the cross sections of e–$H_2$ are taken from Saelee.[9]

The scattering angle $\theta$ of the electron after an elastic collision is given by

$$\frac{\int_0^\theta \sigma(\theta,\varepsilon)\sin\theta\mathrm{d}\theta}{\int_0^\pi \sigma(\theta,\varepsilon)\sin\theta\mathrm{d}\theta} = \xi \qquad (0<\xi\le 1), \qquad (2)$$

where $\xi$ is a random number, and $\sigma(\theta,\varepsilon)$ is the elastic differential scattering cross section for electrons with energy $\varepsilon$.[10,11]

For inelastic scattering, the differential cross-section data are incomplete. However, the limited results of Opal *et al.*[12] have shown that the scattering is not so pronounced in the forward direction as in the scattering due to elastic collisions. We thus assume that the scattering by inelastic collision is isotropic for all electron energies. So, after an inelastic collision, the scattering angle $\theta$ is given by

$$\cos\theta = 1-2\xi \quad (0<\xi\le 1). \qquad (3)$$

The angle $\alpha_m$ of the electron velocity with respect to the $z$-axis after the $m$th collision is given by

$$\cos\alpha_m = \cos\alpha_{m-1}\cos\theta + \sin\alpha_{m-1}\sin\theta\cos\chi, \quad (4)$$

where $\chi$ is the azimuth, and $\alpha_{m-1}$ is the angle between the electron velocity and the $z$-axis after the $(m-1)$th collision. The electron flies to the next $\lambda_\mathrm{e}$ with the angle $\alpha_m$ and velocity determined by the type of collision.

## 3. Results and discussion

Figure 1(a) shows the electron velocity distribution $\rho(v_z, v_\parallel)$ (contour diagram) at the substrate surface for $E/N$=236.7$Td$. (The bias voltage is 200V, the gas pressure is 1.6kPa and the gas temperature is 1373K. The gas temperature decreases with the distance from the filament. In order to simplify the calculation, we chose 1373K as an average temperature in the gas phase.[13]) $\rho(v_z, v_\parallel)$ is the electron number normalized by the maximum value. It is drawn as functions of $v_z$ and $v_\parallel = \sqrt{v_x^2 + v_y^2}$ in units of $\sqrt{\text{eV}}$. It is clear that the velocity profile is asymmetric. The effect of the field on the velocity distribution is noticeable between the component in accelerated electrons ($\alpha \leq \pi/2$) and that in decelerated electrons ($\alpha > \pi/2$). The electron velocity distribution has a peak shift in the field direction at $\alpha \sim 5\pi/12$. As a result, most electrons possess non-zero velocity parallel to the substrate. 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 result in an improvement in the growth of facets of diamond crystallites. Moreover, the kinetic energy of particles on the substrate surface is raised and these particles become a nucleation centre, therefore the nucleation density is improved.

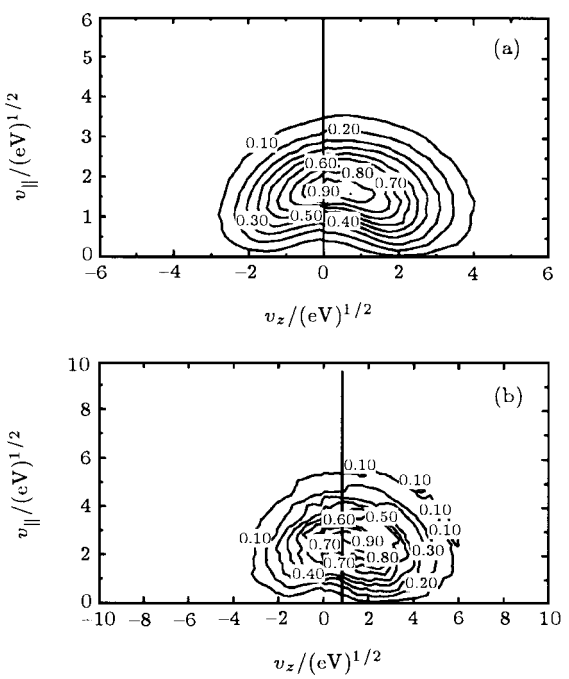



**Fig.1.** Electron velocity distribution (contour diagram) at the substrate surface for (a) $E/N$=236.7$Td$ and (b) $E/N$=602.3$Td$.

The velocity distribution is more asymmetric and the peak also shifts to a smaller angle with increasing $E/N$ (as shown in Fig.1(b)). The deflection of the peak velocity from the field direction is due to the fact that electrons moving along the $-E$ direction gain higher energy and have a higher collision rate per unit time than the electrons released perpendicular to the field.

In order to test the reliability of the model, we calculate the electron drift velocity using the velocity distribution as a function of $E/N$ with the following equation:

$$v_\text{d} = \frac{\int v_z f(v)\text{d}v}{\int f(v)\text{d}v}. \tag{5}$$

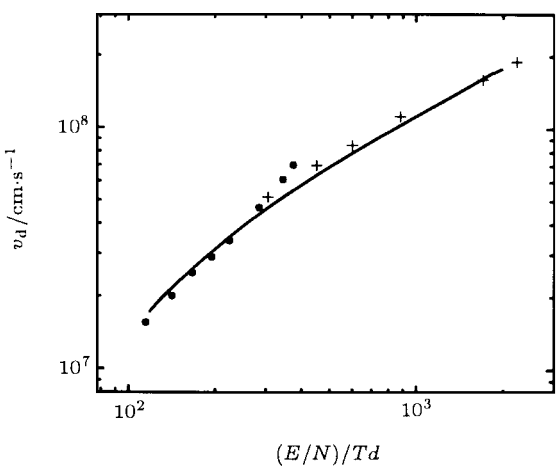



**Fig.2.** Electron drift velocity as a function of $E/N$ in hydrogen: •, Saelee[14]; +, Schlumbohm[15].

As shown in Fig.2, the calculation results are in good agreement with the experimental data reported previously,[14,15] suggesting that our model is feasible and can be used to evaluate electron behaviour and its effects on diamond growth.

Figure 3 shows the mean energy of electrons as a function of $E/N$ at the substrate surface. Curve $a$ represents the mean electron energy, and curve $b$ represents $(1/2)mv_\parallel^2$, where $v_\parallel$ is the velocity in a direction parallel to the substrate surface. The mean energy of electrons increases from 5eV to about 20eV with increasing $E/N$ from 100 to 500$Td$. Furthermore, the mean energy of electrons increases rapidly under the condition of high $E/N$. The $(1/2)mv_\parallel^2$ changes more slowly than the mean energy and reaches about 10eV at 800$Td$.

A common feature of most diamond deposition techniques is the abundance of molecular hydrogen in the gas phase. Atomic H is particularly important as it plays several roles including: (1) selective etching of graphic deposits[16] and stabilization of the $sp^3$ bonds necessary for the formation of diamond;[17] (2) reacting with hydrocarbons to form species such as $CH_3$ and $C_2H_2$ that are considered important for diamond depositions;[18,19] and (3) stabilizing the diamond surface during growth.[20] So first we consider the dissociation collision process.

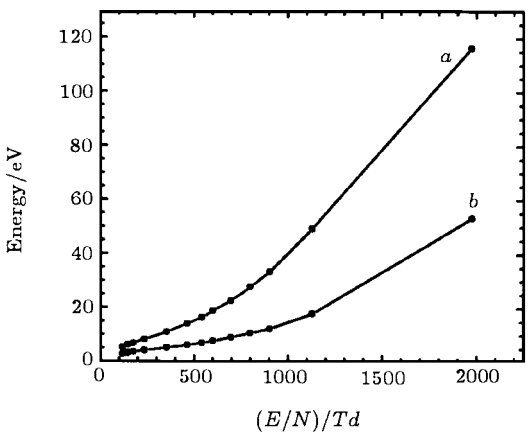



**Fig.3.** Electron energy as a function of $E/N$ at the substrate surface. Curve $a$ represents the mean energy, and curve $b$ represents the $\frac{1}{2}mv_{\parallel}^2$, where $v_{\parallel}$ is the velocity parallel to the substrate.

In conventional hot filament systems, most of the $H_2$ dissociation is catalytic, that is, occurring on the filament surface. But atomic H concentration is decreased rapidly and down to 25% near the substrate.[21] Therefore, a sufficient amount of atomic H cannot be provided on the substrate under some conditions. By applying bias voltage, additional H atoms are generated by dissociation of $H_2$ resulting from electron impact in the gas phase, thus the deposition rate of the diamond film is effectively enhanced. So dissociation of $H_2$ resulting from electron impact during EACVD is the main process for atom H generation, especially near the substrate surface.

Figure 4 shows the energy distribution of electrons as a function of $E/N$ at the substrate surface. The solid curves represent the energy distribution of total electrons. The grey diagrams represent the energy distribution of electrons experiencing dissociative collisions. It can be seen that the maximum electric energy increases with increasing $E/N$. Electrons with energy less than 100eV can be obtained with $E/N$ up to $464.5Td$ (Fig.4 $a$–$e$). A further increase of $E/N$ leads to electrons with energy over 100eV (Fig.4 $f$–$l$).

From Fig.4, one can also notice that the number of dissociations changes with $E/N$. This can be explained as follows. The mean free path of electrons is proportional to $1/N$, and the energy gain after an electron flying through the mean free path increases with the rise of applied biased voltage. Consequently, the kinetic energy of electrons is approximately proportional to $E/N$. The cross section for dissociation collision is a function of electron energy. The number of dissociations thus changes with $E/N$.

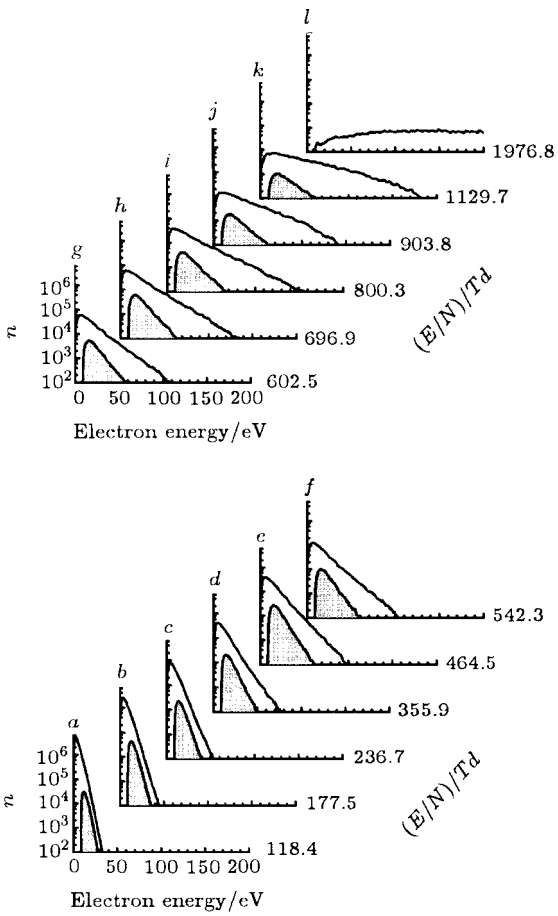



**Fig.4.** Energy distribution of electrons as a function of $E/N$ at the substrate surface. Solid curves represent the energy distribution of total electrons, and grey diagrams represent the energy distribution of electrons which have undergone dissociative collisions.

The $E/N$ dependence of the number of dissociative collisions $N_d$ is depicted in Fig.5. The peak is at $E/N$=$150Td$. This can be explained using the relationship between the cross section of e–$H_2$ and electron energy for inelastic collisions. The mean electron energy is increased with increasing $E/N$. More and more electrons possess energy over 8.8eV (the threshold energy of dissociative collision), so the num-

ber of dissociative collisions are increased. When the electron energy reaches 17eV, the dissociation cross section reaches a maximum. Moreover, the scope of electron energy contributing to the dissociation is widened. Thus the dissociative collisions reach a maximum. Once most electrons possess energies of more than 20eV, ionization collisions become dominant instead of dissociation collisions. Therefore $N_{\rm d}$ decreases.

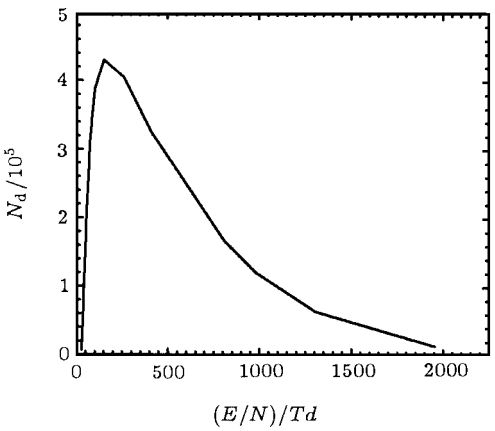



**Fig.5.** The number of dissociative collisions as a function of $E/N$ at the substrate surface.

During the EACVD process, the electrons bombarding the substrate with energies of several tens of eV produce vacancies on the substrate surface. Plenty of carbonaceous species arriving at the surface move and add to the oriented or misoriented $sp^3$ and $sp^2$ bond carbon clusters. Consequently, they are grown to stable nuclei due to adding the carbonaceous species. At the same time, the carbon clusters are intensively etched away by abundant atomic H prepared by electron impact. The non-diamond carbon components are especially preferentially etched away because the etching rate is 50 times higher than that of diamond.[22,23] So plenty of atomic H are required during the process. On the other hand, the value of $(1/2)mv_{\parallel}^2$ is also important because electrons with parallel velocity can push carbonaceous species to move, thus enhancing the growth of oriented diamond. So high-quality diamond film with a high growth rate can be deposited by choosing an appropriate $E/N$ value, for which not only sufficient atomic H but also a larger value of $(1/2)mv_{\parallel}^2$ can be reached. From the experimental reports,[2,3] highly oriented diamond has been deposited at $E/N$ ranging from 50 to $200Td$ under the substrate temperature of 1000K. One can see in Fig.5 that high-quality diamond film can be deposited at $E/N$=$50Td$ with $N_{\rm d}$=$1.5\times10^5$. Moreover, the number of dissociation collisions over $1.5\times10^5$ can be obtained with $E/N$ ranging from 50 to $800Td$, implying that highly oriented diamond can be obtained in this range.

## 4. Conclusion

In summary, we have investigated the behaviour of electrons during EACVD of diamond using Monte Carlo simulation. The electron energy distribution and velocity distribution were obtained over a wide range of $E/N$. Their effects on the diamond growth were also discussed. The main results obtained are as follows. (1) The velocity profile is asymmetric for the component parallel to the field. The velocity distribution has a peak shifted in the field direction. Most electrons possess non-zero velocity parallel to the substrate. (2) The number of atomic H is a function of $E/N$. (3) High-quality diamond can be obtained under the condition of $E/N$ from 50 to $800Td$ due to sufficient atomic H and electron bombardment. We believe that these results will be helpful to understanding the growth mechanism in EACVD and plasma CVD processes. It is also important for the research on electron swarm motion in a dc electric field.

In future work, we will consider the shape of the electric field and the temperature gradient to improve the accuracy of the simulation.

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