Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

Monte Carlo Simulation on Generation of Atomic Hydrogen in Diamond Deposition Process

H. Mima[a], H. Saitoh[b], T. Ishiguro[a] and Y. Ichinose[a]

[a] Nagaoka University of Technology,
1603-1 Kamitomioka, Nagaoka, Niigata 940-21, Japan

[b] Department of Materials Science, Faculty of Engineering, Ibaraki University,
4-12-1 Nakanarusawa, Hitachi, Ibaraki 316, Japan

Generation of atomic hydrogen by the electron impact was investigated using a Monte Carlo computer simulation and mass spectroscopy. The simulation result told us that there were optimum conditions for the dissociation of hydrogen by the electron impact when the electric field and the gas pressure were changed. The experimental result using mass spectroscopy suggested that the accelerated electron could dissociate hydrogen under the low pressures required for diamond growth. Electron impact must be an important factor for the formation of diamond even if the reaction system has no plasma state.

1. INTRODUCTION

Research with the diamond films deposited using the chemical vapor deposition (CVD) techniques have been advanced in both scientific and technological interests.[1] Some workers have been recognized that an atomic hydrogen has important roles in the process of CVD-diamond, *i.e.*, (1) to make radicals required to form diamond, (2) to reconstruct surface of the growing diamond to be easy for additional carbon adsorption, and (3) to avoid the nucleation of graphitic material. To generate atomic H from H_2 gas, some low pressure CVD techniques have been developed. The hot filament CVD technique is believed to be one of the powerful methods for the diamond synthesis. In this technique, H atoms are generated by the result of H_2 dissociation on the surface of the hot filament.[2] With applying dc bias voltage on the substrate, the deposition rate of diamond was enhanced effectively.[3] This can be explained as the result of enhancement of the reaction with electron impact to H_2 and hydrocarbons. It is supported by the fact that the thermo-electrons emitted from the hot filament may be accelerated toward the substrate. In addition, the Penn State Univ. group has tried to irradiate electron beam to CH_4-H_2 gas mixture in an environmental scanning electron microscope. With very slow rate, growth of submicron diamond particles was observed.[4] This also implies that the electron related reaction can go on toward the diamond formation, even if reaction system has no plasma state.

It is well known that H_2 molecules can be dissociated into atomic H by the electron impact. It is supported by the result of plasma emission spectroscopy that indicated the evidence of atomic H in the rf plasma induced by impacts of electron accelerated by the electric field.[5] In general, the dissociation of H_2 requires the electron kinetic energy of 10 to 30 eV when the electron-molecule collision occurs. The integrated cross-section for dissociation showed the decreasing in the ranges of the kinetic energies of more than 30 eV or less than 10 eV. It can be understand that there is a maximum in efficiency of atomic H generation, possibly of deposition rate of diamond. We believe that to clarify the behavior of accelerated electrons in the gas phase gives great advances in fundamental understanding for diamond reaction process.

A Monte Carlo computer simulation has been studied with many works, in particular, to investigate behavior of the electron swarm in numerous gases. Recently, Kushnar discussed a model for the rf or dc plasma enhanced CVD of the amorphous hydrogenated silicon films.[6] Saitoh *et al.* have tried to understand the role of the surface bombardment by nitrogen ion in an

ion-nitriding process for steels.[7] In our work, the dissociation model for hydrogen was studied with the results from the Monte Carlo computer simulation to understand the role of accelerated electrons. Furthermore, mass spectroscopy was applied for the vapor phase analysis, to detect atomic H.

2. EXPERIMENTAL

2.1. Computer simulation

We selected a model of electron assisted CVD with the hot filament for the computer simulation. In the typical model, 10^5 electrons are provided for the calculation of their trajectory and kinetic energy. The initial velocities with a Maxwell-Boltzmann energy distribution function are given for each electron in a sample group at the surface of the hot filament. All electrons are accelerated toward positive biased substrate. The electric field in the separation between the hot filament and the substrate has a linear function of distance from the hot filament.

The electron trajectories are calculated using the Monte Carlo method. A simplified three-dimensional model is provided here. In actual, the electron may collide with a hydrogen molecule while it flies to the mean free path, λe. In this model, the divided flying distance is defined as

$$\Delta l = \lambda_e / 10. \quad (1)$$

We assumed that the H_2 could be dissociated by the electron impact only. The collision with the molecule is immediately judged using random numbers after the electron reaches Δl. If judgment indicates the result of collision, then collision type, *i.e.*, elastic or inelastic, is decided. This decision is dependent upon the electron kinetic energy, since the cross sections for each collision are variable as a function of energy. When the judgment is made as the elastic collision, no energy transfer occurs. In the case of inelastic collision, further consideration for the detailed types should be given. Cross sections for each collision type of H_2 were taken from Ref. 8.

Inelastic collisions require the energy transfer from electron. In the case of vibrational excitation, energy loss of electron should be dependent upon the excitation level. Using the calculation results by Saelee *et al.*,[8] it is assumed that 20 % of electron energy is lost by the collision. Dissociation reaction requires an energy transfer of 8.8 eV. The electron excitation, ionization and dissociation consume an energy of 15.4 eV. After collision, the scattering angle θ is calculated immediately using the equation,

$$\cos\theta = 1-2\xi \quad (0 \le \xi \le 1), \quad (2)$$

where ξ are random numbers. The electron is scattered to next Δl with the calculated scattering angle as well as the initial velocity decided by the collision type.

2.2. Mass spectrometry

Mass spectroscopy was performed using a quadrupole mass spectrometer (QMS) attached to a hot filament CVD apparatus as shown in Fig. 1. A tungsten wire having a diameter of 0.5 mm was used as the hot filament. Typical experimental conditions were the gas pressures of 10 and 27 Torr, a filament temperature of 1800 °C and a separation between the filament and the substrate of 20 mm. The thermo-electrons were accelerated by a bias voltage of 200 V applied to the substrate holder. The current density was 100 mA/cm^2. During experiment, H_2 gas was introduced into the chamber. This was flowed close to the hot filament toward the anode. During H_2 gas flowing in the separation, hydrogen molecules were thought to be dissociated by the electron

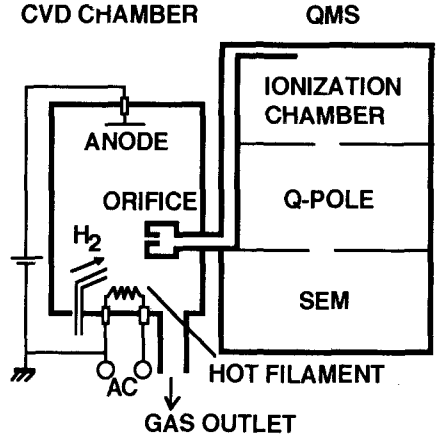

FIG. 1. Schematic diagram of the QMS attached to the CVD chamber.

impact, and possibly by catalytic reaction on the hot filament. Small amount of entire gas flowing toward substrate was sampled into the QMS through an orifice having a diameter of 30 μm. QMS output indicated m/e=1 signal for atomic hydrogen and m/e=2 for H_2.

3. RESULTS AND DISCUSSION

3.1. Simulation

Typical electron energy distributions are shown in Fig. 2. Each distance from the hot filament D represents the position of the spatial zones having 0.4 or 2 mm width. In Fig. 2, 100 V is selected for the bias voltage applied to the substrate. This is corresponding to an electric field of 5 kV/m. The H_2 gas pressure is kept constant at 5 Torr. Therefore, the ratio of the electric field to the gas pressure, E/p, is 1 kV/m·Torr. When the electrons are emitted from the surface of the refractory metal, their initial kinetic energy follows the Maxwell-Boltzmann distribution. At a filament temperature of 1800 °C, however, initial kinetic energy is usually too small to occur the inelastic collision with H_2. Therefore the electrons can increase their kinetic energy by acceleration in the electric field even if the electrons make collision with H_2 several times, as shown in Fig. 2 (a). After the electron possesses sufficient energy to dissociate H_2, number of dissociative collisions is rapidly increased as indicated in Fig. 2 (b).

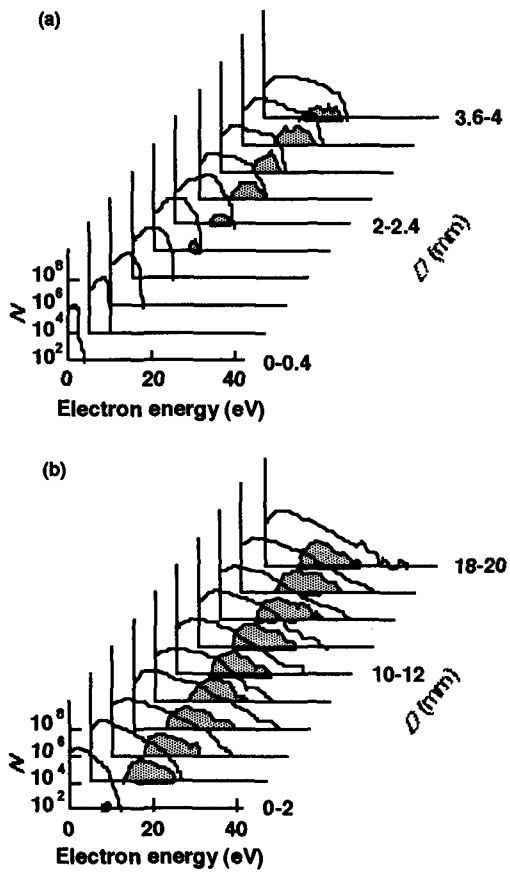

FIG. 2. Energy distribution of accelerated electrons in divided spatial zone. (a) Detail of the spatial zones to the position 2 mm apart from the hot filament. (b) Spatial zones from the hot filament to the substrate. Dark zone represents the number of electrons which contribute to the dissociative collision.

Several simulations were performed to obtain optimum conditions for the atomic H generation. At these calculations, N_d represents the number of dissociative collisions occurred while one electron flied from the hot filament to the anode. To find maximum N_d defined as N_d(max), the gas pressure and the bias voltage were changed at a distance between the hot filament and the anode of 20 mm. In general, mean free path of electron increases with reducing density of gas molecules. This implies that reducing gas pressure develops energy of the accelerated electrons under the condition without changing electric field. In the

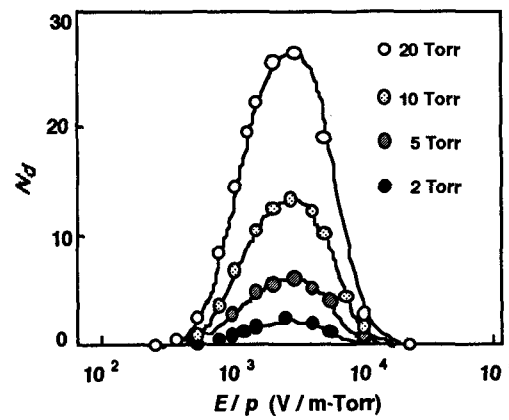

FIG. 3. Number of dissociative collisions occurred while one electron flies from the hot filament to the anode, N_d as a function of the ratio of electric field to gas pressure, E/p.

case of increasing applied bias voltage, the electric field is increased without changing the anode to hot filament distance. Therefore the electrons can be accelerated to higher energy. Consequently kinetic energy of electron is described to be proportional to the ratio of electric field to gas pressure, E/p.

Figure 3 shows N_d as a function of E/p. This result suggests that the N_d(max) can be obtained at E/p of approximately 4 kV/m.Torr and N_d(max) increases with increasing gas pressure. The changes of N_d and N_d(max) are explained using the relationship between the cross section of H_2 and electron energy for inelastic collisions. If the electrons are accelerated up to approximately 15 eV under suitable E/p condition, the cross section for H_2 dissociation becomes maximum. With relative low energy collision, H_2 can not be dissociated and vibrational excitation is dominant among the inelastic collisions. When the major electrons possess energy of >20 eV, ionization collision becomes dominant instead of dissociation. Furthermore, it should be noted that the reducing gas pressure increases electron energy. Therefore the number of collisions, *i.e.*, N_d(max) is decreased with reducing gas pressure.

3.2. Mass spectroscopy

In general, sampled H_2 molecules are dissociated in the ionization chamber in the QMS. In case the sample gas includes atomic H, m/e=1 signal intensity is consisted with the signals of dissociated H in the QMS and of sampled H. Threshold ionization technique is applied to separate sampled H signal intensity from total amounts. The ionization of atomic H requires energies of ≥ 19.9 eV for the reaction,

$$H_2+e \rightarrow H^+ + H + e, \quad (3)$$

and ≥13.5 eV for

$$H+e \rightarrow H^+ + e. \quad (4)$$

The ionization energy of sampled gas can be measured by changing the electron energy in the ionization chamber. The results are shown in Fig. 4. Let us remark the threshold energy for intensity of m/e=1. Without hot filament in the CVD camber, the threshold energy positioned relative high region. It is similar to energy when the hot filament was heated up to 1800°C. The filament temperature of 1800°C is expected to be too low to dissociate H_2 by

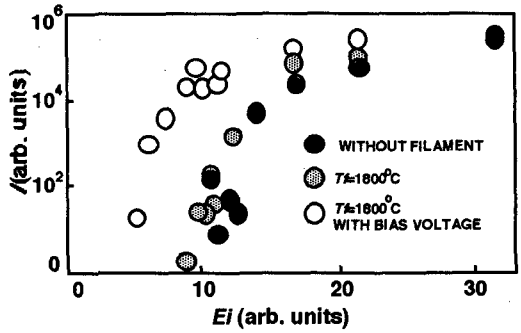

FIG. 4. Intensity of m/e=1 signal as a function of ionization energy (E_i).

surface dissociation. By applying bias voltage to the substrate, the threshold energy shifted toward lower energy. This implies that reaction (4) is dominant, *i.e.*, the sample gas includes atomic H generated by electron impacts in the CVD chamber without plasma excitement.

4. CONCLUSIONS

H_2 dissociation in the diamond deposition process was described and discussed using the results of Monte Carlo computer simulation and mass spectroscopy. By electron impacts to H_2 gas, spatial distribution of atomic H exists in the separation between the hot filament and the substrate. It is expected that the electron impact technique becomes the diamond synthesis method without using plasma state.

ACKNOWLEDGMENT

The authors are grateful to Mr. K. Katagiri for his collaboration.

REFERENCES

1. W. A. Yarbrough and R. Messier, Science, **247** (1990) 688.
2. S. Matsumoto, Y. Sato, M. Tsutsumi and N. Setaka, J. Mater. Sci., **17** (1982) 3106.
3. A. Sawabe and T. Inuzuka, Appl. Phys. Lett., **46** (1985) 146.
4. H. Saitoh, M. Klimkiewicz and W. A. Yarbrough (unpublished).
5. O. Matsumoto, H. Toshima and Y. Kanzaki, Thin Solid Films, **28** (1985) 341.
6. M. J. Kushnar, J. Appl. Phys.,**63** (1988) 2532.
7. H. Saitoh, T. Mochida, B. Tsuchiya and R. Urao (submitted to J. Mater. Res.).
8. H. T. Saelee and J. Lucas, J. Phys. D, **10** (1977) 343.