

Theoretical analysis of the diffusive ion in biased plasma enhanced diamond chemical vapor deposition

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The role of the bias pretreatment for the enhanced nucleation of the diamond nuclei in the chemical vapor deposition of diamond is theoretically investigated. We obtain the kinetic energy of ions impinging on the surface of the substrate as a function of bias voltage. The experimentally obtained optimum bias voltage of -100 V for the enhanced nucleation of diamond nuclei corresponds to the C ion energy of ~ 5 eV at the surface of the substrate. The reduction of the ion energy is caused by the scattering in the ion sheath region of the plasma. The ion sheath width and the ion energy on the surface of the substrate are given as functions of the gas pressure and the bias voltage. The results are compared with the experimental results. © 2001 American Institute of Physics.
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I. INTRODUCTION

A bias pretreatment as an initial process prior to the crystal growth of diamond is known to be very effective for the enhanced nuclei formation in the plasma chemical vapor deposition (PCVD) of diamond.¹⁻³ The bias voltage of around -100 V applied to the substrate relative to a countermetal electrode in the plasma is known to form diamond nuclei on the substrate at a density of $10^{10}/\text{cm}^2$, which is six orders larger than that obtained without bias pretreatment. In addition, the bias pretreatment is effective for the aligned nucleation of nuclei on the substrate.⁴⁻⁹

In spite of the significant enhancement of the nucleation, the role of the bias pretreatment is not clearly understood. For example, it is speculated that the energetic carbon ions may form C-C sp^3 bonds as diamond nuclei or amorphous carbon on Si substrate where the number of diamond nuclei increases with increasing the ion energy.¹⁰ However, the bond energy of C-C sp^3 is in several eV, and we do not know why such a high bias voltage (-100 V) is needed for the enhanced nucleation of diamond nuclei. It is considered qualitatively that ions are strongly decelerated due to scattering in the ion sheath region of plasma and that the energy of ions impinging upon the substrate surface may become much lower than that expected directly from the applied bias voltage.

In this article, we make a theoretical analysis of the biased plasma and calculate the relationship between a carbon ion energy impinging on the substrate surface and the applied bias voltage in the plasma as a function of plasma parameters. We compare the results with experiments and discuss the role of bias pretreatment on the enhanced nucleation of diamond nuclei.

Microscopically, Sternberg *et al.* have performed the theoretical treatment of molecular dynamics of the diamond/silicon interface and show an essential role of the internal strain of carbon chemical bonds for the formation of the

heteroepitaxial growth.^{11,12} A variety of the interface structures between the Si substrate and diamond layers formed during the bias pretreatment, such as SiC,^{13,14} amorphous carbon,¹⁵ and nanographite,¹⁶ are directly observed by high-resolution transmission electron microscopy (HRTEM).¹⁷ The formed structures may essentially depend on the kinetic energy of the ions on the substrate surface which is dependent on the plasma parameters. In a recent CVD experiment of carbon nanotube^{18,19} and cubic boron nitride,²⁰ the bias enhancement of the nucleation is observed.

In order to get a clear understanding of the effect of bias pretreatment and reproducible results for the nucleation of diamond nuclei or other materials, we need a simple but a universal relationship between the kinetic energy of ions and plasma parameters, for example, gas pressure, distance between the substrate and the counterelectrode, etc. The present theoretical analysis is useful for understanding the nuclei formation and crystal growth in the plasma.

In the bias pretreatment, the bias is applied between a tungsten needle counterelectrode and a substrate in the plasma as shown in Fig. 1(a). A typical value of the bias voltage on the substrate for the enhanced nucleation of the diamond nuclei is -100 V.¹ At a pressure of about 20–40 Torr of the mixture gas with a ratio of $\text{CH}_4/\text{H}_2=7\%$, the mean free path of molecules is estimated much smaller than the width of the ion sheath. For example, the mean free path of a H_2 molecule at a pressure of 30 Torr at 900°C is estimated to be $10\ \mu\text{m}$, while the width of the ion sheath is calculated to be $300\text{--}500\ \mu\text{m}$ ^{21,22} when the degree of ionization of the molecules at the temperature of 1000°C is estimated to be 10^{-3} . Due to such a low ionization rate, the plasma is considered to consist mainly of neutral molecules with a small portion of ions and electrons. The kinetic energy of ions obtained by the bias voltage is limited by the energy loss due to scattering mostly by neutral molecules.

The main part of the plasma is electrically neutral due to the equal density of electrons and ions, and the bias voltage is applied only in the ion sheath region and a quasineutral (QN) region near the negatively biased substrate [see Fig.

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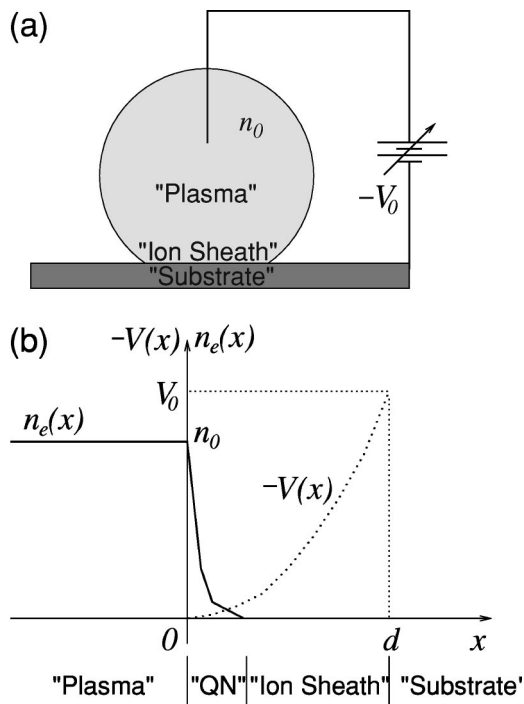


FIG. 1. (a) Schematic view of the bias pretreatment. A bias voltage is applied between needle and substrate. (b) The electrostatic potential $-V(x)$ and electron density $n_e(x)$ is plotted as a function of the distance from the edge of the neutral plasma region. "QN" denotes quasineutral region and d is the depth of the ion sheath.

1(b)]. The ion sheath which appears between the neutral plasma and the negatively biased substrate is composed of neutral molecules and ions. The ion sheath is formed even in the unbiased plasma due to a large difference of mobility between electrons and ions.

In the biased plasma, ions are accelerated in the direction of the substrate by the electric potential in the ion sheath region, but the ions lose the kinetic energy given by scattering with other neutral molecules and ions in the sheath. On the other hand, electrons can hardly enter the ion sheath region because of the electric potential. Since the average thermal energy of electrons^{23,24} [$k_B T_e/2$ (0.5–1 eV), T_e : electron temperature] is much smaller than the electric potential ($3.7k_B T_e/e \sim 4\text{--}8\text{ V}$)²¹ of the ion sheath under no bias voltage, electrons exist only in a narrow region of the sheath, known as the QN region [see Fig. 1(b)], between the ion sheath and the neutral plasma. In the QN region, both electrons and ions distribute inhomogeneously and make a potential. This quasineutral region is found to be essential to determine the electric potential in the sheath.

In this article, we present a theoretical formulation of ion energy and ion current versus bias voltage with the plasma conditions as parameters. We calculate the electric potential in the ion sheath of the biased plasma, taking the quasineutral region into consideration. We show that the average kinetic energy of ions impinging on the substrate surface is proportional to the bias voltage, whose factor is expressed in terms of the plasma parameters.

In Sec. II we introduce a Poisson's equation for the ion sheath in the diffusive gas pressure. In Sec. III we compare

the calculated results with our experimental ones, and show a consistent relation between them. In Sec. IV a summary is given.

II. POISSON'S EQUATION FOR THE ION SHEATH

The electric potential of the plasma is calculated by solving the Poisson's equation for the ion sheath. The width of the ion sheath, d , is a function of the bias voltage, $-V_0 < 0$, and an additional equation is necessary for determining the electric potential, $V(x)$, and d simultaneously. As is discussed in Sec. I, we consider the case that the mean free path of ions in the ion sheath is much smaller than the width of the ion sheath. The average velocity of ions which is known as a drift velocity, is a function of the position, x , in the ion sheath. Here we define the position in the ion sheath, x , from the end of the plasma neutral region $x=0$ to the substrate $x=d$, where $V(x)$ changes from $V(0)=0$ to $V(d)=-V_0$ as shown in Fig. 1(b). Here we assume that the plasma potential without bias voltage can be neglected compared with that in applied bias voltage. Further we consider the ion sheath shown in Fig. 1(a) as a one-dimensional system for simplicity. In fact electrostatic potential of the plasma is constant in the plasma since plasma is a good conductor consisting of free ions and electrons. Further, we can assume that the electrostatic potential of Si substrate is constant, too, since the voltage is mainly applied in the ion sheath. Thus a one-dimensional model is a good model for describing the potential over the touching area of plasma on the substrate [see Fig. 1(a)].

First we define the drift velocity of ions, $v_i(x)$, in a gas mixture of H_2 and CH_4 . $v_i(x)$ is proportional to the electric field, $E(x)$, as

$$v_i(x) = \mu_i E(x), \quad (1)$$

in which μ_i is the mobility of ions. When we neglect three body scattering or ion-ion reactions, the mobility of ions in the gas mixture is estimated by

$$\frac{1}{\mu_i} = \frac{f(\text{H}_2)}{\mu(\text{H}_2)} + \frac{f(\text{CH}_4)}{\mu(\text{CH}_4)}, \quad (2)$$

where $f(\text{H}_2)$ and $\mu(\text{H}_2)$ [$f(\text{CH}_4)$ and $\mu(\text{CH}_4)$] are the partial pressure and the mobility of H_2 (CH_4) molecules, respectively. Here we assume that mobility of an ion is approximated by that of a neutral molecule at a low ionization rate, as discussed in Sec. I. In addition since the partial pressure of H_2 is dominant in this system, the mobility of the gas mixture is close to that of a hydrogen molecule. In fact when we perform an experiment with only H_2 molecules, the electric current as a function of the bias voltage shows similar behavior to that for the case of $\text{CH}_4/\text{H}_2 = 7\%$. Since the kinetic energies obtained by the bias voltage are the same for the H_2 and CH_4 ions, we assume for simplicity that the kinetic energies of the H_2 and CH_4 ions at the substrate are the same as each other, too, even after many scattering processes in the mixed gas. In the following the ions means H_2 or CH_4 ions. The electric current density, J , consists of the ionic and the electronic contributions denoted by

$$J = q\{n_i(x)\mu_i + n_e(x)\mu_e\}E(x), \quad (3)$$

in which q , $n_i(x)$, $n_e(x)$, and μ_e are the charge of ions (or $-q$ for electron), the number density of ions and electrons, and the mobility of electrons, respectively. It is clear from the time-independent equation of continuity for the current ($\text{div } J=0$) that the one-dimensional current density J is constant for any position in the sheath. Since the electron mobility is much larger than that of ions, we assume that the voltage drop in the electron sheath at the positive needle can be neglected and that the bias voltage V_0 is applied only to the ion sheath.

Further we assume that the density of electron $n_e(x)$ in the electric potential $V(x) < 0$ is in thermal equilibrium and that $n_e(x)$ is given by the Boltzmann distribution as

$$n_e(x) = n_0 e^{qV(x)/k_b T_e}, \quad (4)$$

where n_0 , k_b , and T_e are the density of electrons (or ions) in the plasma, the Boltzmann constant, and the electron temperature, respectively. This assumption is valid when $k_b T_e$ is much larger than $qE(x)\lambda_D$, where $\lambda_D = \sqrt{\epsilon_0 k_b T_e / n_e q^2}$ is the Debye length. Here ϵ_0 is the dielectric constant of vacuum. At a high temperature of 900 °C and in a low pressure of 30 Torr compared with the ambient pressure, the dielectric constant of vacuum can be used as that of the gas, ϵ . A typical value of the Debye shielding length for $T_e = 2 \times 10^4$ K and $n_e = 1.0 \times 10^{20} / \text{m}^3$ is 1.0 μm , which is much smaller than the width of the ion sheath.

The Poisson's equation for the electric field $E(x)$ is given by

$$\frac{dE(x)}{dx} = \frac{q}{\epsilon} \{n_i(x) - n_e(x)\}. \quad (5)$$

When we put Eqs. (3) and (4) into Eq. (5) we get

$$\frac{dE(x)}{dx} = \frac{1}{\epsilon} \left\{ \frac{J}{\mu_i E(x)} - \left(1 + \frac{\mu_e}{\mu_i} \right) q n_0 e^{qV(x)/k_b T_e} \right\}. \quad (6)$$

We solve Eq. (6) with $V'(x) = -E(x)$ and the boundary conditions at $x=0$: $V(0)=0$, $n_i(0)=n_e(0)=n_0$, and $E(0) = J / [qn_0(\mu_i + \mu_e)]$. We integrate Eq. (6) from $x=0$ to $x=d$ such that $V(d) = -V_0$ for a given V_0 . The constants in the calculation are q , k_b , T_e , μ_i , μ_e , J , and V_0 .

In Fig. 2 we plot (a) the density of ion, $n_i(x)$, (b) the density of electron, $n_e(x)$, (c) the electric field, $E(x)$, and (d) the electric potential for electrons, $-V(x)$ as functions of position x . The physical parameters²⁵ used in Fig. 2 are as follows: the temperature of electrons $T_e = 2 \times 10^4$ K, the mobility of ions $\mu_i = 0.5 \text{ m}^2/\text{V s}$ estimated for 1 Torr, 1173 K, the mobility of electrons $\mu_e = 17.5 \text{ m}^2/\text{V s}$ (1 Torr, 2×10^4 K), the pressure $P = 30$ Torr, and the density of plasma $n_0 = 1 \times 10^{16} \text{ m}^{-3}$. It is noted here that the mobility of ions and electrons do not depend on the pressure much for pressures lower than 50 Torr. Thus we simply use the known values of mobility at 1 Torr. Several lines in each figure correspond to the different current densities, $J = 20, 40, 60, 80,$ and 100 A/m^2 , respectively, from the bottom to the top of Figs. 2(a), 2(c), and 2(d), and from the top to the bottom in Fig. 2(b).

When the electric potential $|-qV(x)|$ is larger than the kinetic energy of electrons ($k_b T_e / 2 = 1 \text{ eV}$), $n_e(x)$ decreases quickly from the value n_0 as shown in Fig. 2(b). As is ex-

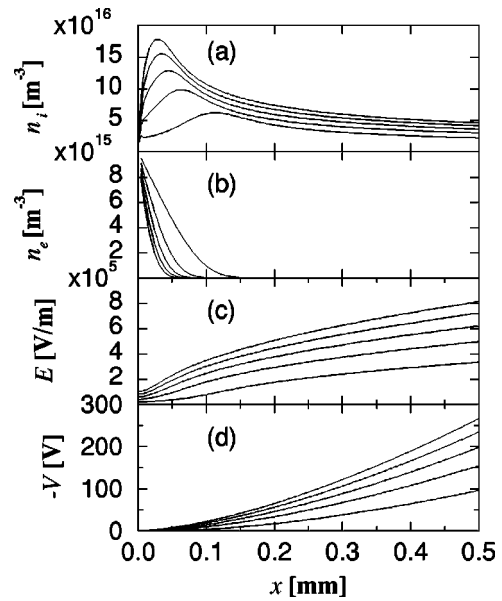


FIG. 2. (a) Density of ion, $n_i(x)$, (b) density of electron, $n_e(x)$, (c) electric field, $E(x)$, and (d) electric potential for electron, $-V(x)$. The parameters used are as follows: the temperature of electrons $T_e = 20\,000$ K, the mobility of ions $\mu_i = 0.5 \text{ m}^2/\text{V s}$ estimated by the condition of (1 Torr, 1173 K), the mobility of electrons $\mu_e = 17.5 \text{ m}^2/\text{V s}$ (1 Torr, 20 000 K), pressure $P = 30$ Torr, and density of plasma $1 \times 10^{16} \text{ m}^{-3}$. Several lines in each figures corresponds to the different densities of current, $J = 20, 40, 60, 80,$ and 100 A/m^2 , respectively, from the bottom to the top line of (a), (c), and (d), and from the top to the bottom in (b).

plained in Sec. I, the region in which $n_e(x)$ has a finite value is called the quasineutral region. $n_i(x)$ has a maximum in the quasineutral region of the plasma in order to keep the total electric current constant, as shown in Fig. 2(a). The maximum value of $n_i(x)$ increases with increasing J . With an increase in J , $n_e(x)$ decreases in the region of small x where ions are not yet accelerated, as shown in Figs. 2(b) and 2(d). Thus a larger value of $n_i(x)$ is needed in order to keep J constant.

The maximum value of $n_i(x)$ for a given J is important for determining the width of the ion sheath, which is shown below. Here we define that the ion sheath starts at the point at which $n_e(x)$ becomes 1% of n_0 . In the ion sheath region, the second term of the Poisson equation of Eq. (6) can be neglected by putting $n_e(x) = 0$, and then the equation can be solved as

$$E(x) = \left(\frac{2JP}{\epsilon \mu_{i1}} \right)^{1/2} x^{1/2}. \quad (7)$$

Here the ionic mobility is scaled by the pressure of the gas, P , $\mu_i = \mu_{i1} / P$, which will be used when the theoretical results are compared with the experiment. We can see $E(x) \propto x^{1/2}$ in Fig. 2(c). Strictly speaking, $x=0$ of Eq. (7) should be different from that of Eq. (6). However, we can put the same position for $x=0$. This assumption is justified since the quasineutral region is much smaller than the ion sheath. In the quasineutral region we can see a deviation from $E(x) \propto x^{1/2}$ at small x as shown in Fig. 2(c).

Using Eqs. (1), (3), and (7), the density of ions, $n_i(x)$, is given by

$$n_i(x) = \frac{J}{q\mu_i E(x)} = \frac{1}{q} \left(\frac{\varepsilon J P}{2\mu_{i1}} \right)^{1/2} x^{-1/2}. \quad (8)$$

This relation of $n_i(x) \propto x^{-1/2}$ is seen in Fig. 2(a) for large x . This expression shows that $n_i(x)$ diverges at $x=0$ if we do not consider the electron contribution to the Poisson's equation [Eq. (6)].

Integrating Eq. (7) on x with $V(0)=0$, the electric potential $V(x)$ is given by

$$V(x) = - \left(\frac{8PJ}{9\varepsilon\mu_{i1}} \right)^{1/2} x^{3/2}. \quad (9)$$

The width of the ion sheath, d , is defined by $V(d) = -V_0$, which is a function of V_0 and J . When we put $V(d) = -V_0$ we get the following relationship between J and V_0 :

$$J = \frac{9\varepsilon\mu_{i1}}{8} \frac{V_0^2}{P d^3}. \quad (10)$$

In the following we will show $d \propto V_0^{1/2}$ and thus we get $J \propto V_0^{1/2}$ from Eq. (10). An essential difference of the present result of $J \propto V_0^{1/2}$ from the well-known result of the space charge limited current in a vacuum tube of $J \propto V_0^{3/2}$ comes from the fact that (1) ions are scattered by other molecules and that (2) d in the present case is variable while the distance between the cathode and the anode of the vacuum tube is constant.

Since $V(x) \propto x^{3/2}$, the electric field at the substrate $x = d$, $E(d)$, is given by

$$E(d) = - \left. \frac{dV}{dx} \right|_{x=d} = \frac{3V_0}{2d}. \quad (11)$$

When we put $x=d$ and $n_e(d)=0$ in Eqs. (1) and (3) and eliminate J in Eq. (10), we obtain

$$d = \left(\frac{3}{4} \frac{\varepsilon}{qn_i(d)} \right)^{1/2} V_0^{1/2}. \quad (12)$$

Thus $d \propto V_0^{1/2}$ if the density of ions at the substrate, $n_i(d)$, does not depend on V_0 which will be further given below.

Although $E(x)$, $V(x)$, and d are calculated by Eq. (6) for given values of J and V_0 , the relations between J and V_0 cannot be determined, since d is a variable. In other words, the values of J , V_0 , and d are not determined simultaneously only by Eqs. (6) and (10).

In order to get d numerically, we connect the microscopic loss of the ion energy to the macroscopic dissipation. The macroscopic dissipation is the Joule heat which is given by JV_0 in the unit of energy per unit area and per unit time. The microscopic dissipation of energy is the loss of the kinetic energy of ions, W_{loss} , by scattering with the neutral molecules of the gas which is given in the same unit of energy per unit area and per unit time, by

$$W_{\text{loss}} = [qV_0 - \frac{1}{2}mv_i^2(d)]n_i(d)v_i(d), \quad (13)$$

where $v_i(d)$ is the velocity of ions at the substrate which is defined by Eq. (1). We get d from $JV_0 = W_{\text{loss}}$ numerically.

In Fig. 3 we plot (a) J , (b) d , and (c) kinetic energy of ions, $E_{\text{ion}}(d) = mv_i^2(d)/2$, as functions of V_0 . As seen in Fig. 3(a), J has a finite value at $V_0=0$. This corresponds to the

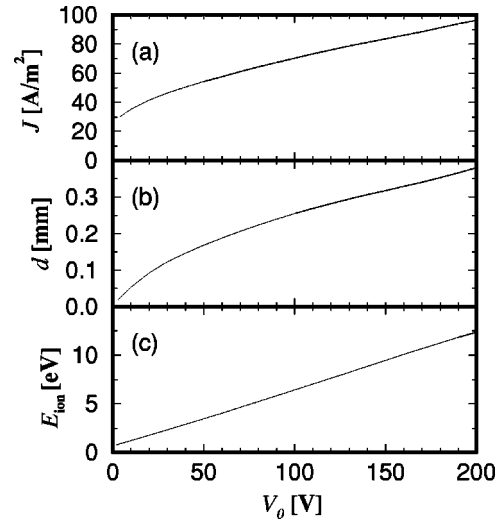


FIG. 3. (a) The electric current density, J , (b) ion sheath width, d , and (c) the kinetic energy of the ion at the substrate, $E_{\text{ion}}(d)$ as functions of the bias voltage V_0 . The parameters used are the same as that in Fig. 2.

fact that the current flows from the plasma to the substrate without a bias voltage, which is observed in the experiment, too. The plasma generates the electric voltage between the center and the edge of the plasma as is known the plasma potential whose value is estimated 5–10 V for the present case. Since the present system has two electrodes, one at the center of the plasma and the other at the substrate, the electric current flows without a bias voltage if the two electrodes are connected electrically outside the plasma. Thus we can understand that the calculated value of $-V_0$ is a sum of the self-generated voltage of the plasma and the bias voltage.

Finally let us discuss a scaling law for the properties of the plasma. When we see the calculated results of Fig. 2, all physical parameters except $n_e(x)$ obey power laws of x for large values of x , which are given by the analytical expressions of Eqs. (7), (8), and (9). Thus it is reasonable to consider a scaling law for such properties. When we assume that the width of the ion sheath is proportional to V_0^α ,

$$d \propto V_0^\alpha, \quad (14)$$

where α is a constant, all the other physical values show similar power law dependence;

$$J \propto V_0^{2-3\alpha}, \quad E(d) \propto V_0^{1-\alpha}, \quad v_i(d) \propto V_0^{1-\alpha},$$

and

$$n_i(d) \propto V_0^{1-2\alpha}, \quad (15)$$

whose relations are given, respectively, by Eqs. (10), (11), (1), and (3). From Eq. (15) the Joule heat JV_0 is proportional to $V_0^{3-3\alpha}$. When we see W_{loss} of Eq. (13), the first term is proportional to $V_0^{3-3\alpha}$ but the second term gives $mv_i^2(d)n_i(d)v_i(d)/2 \propto V_0^{4-5\alpha}$. In order to satisfy the power law dependence for any value of V_0 , we get $3-3\alpha=4-5\alpha$, which gives $\alpha=1/2$.

The result of $\alpha=1/2$ provides a fundamental property of biased CVD plasma. First, the density of ions at the substrate $n_i(d) \propto V_0^{1-2\alpha}$ does not depend on the bias voltage V_0 , which is assumed in Eq. (12). Second, the kinetic energy of ions at the substrate, $mv_i^2(d)/2$, is proportional to V_0 . Al-

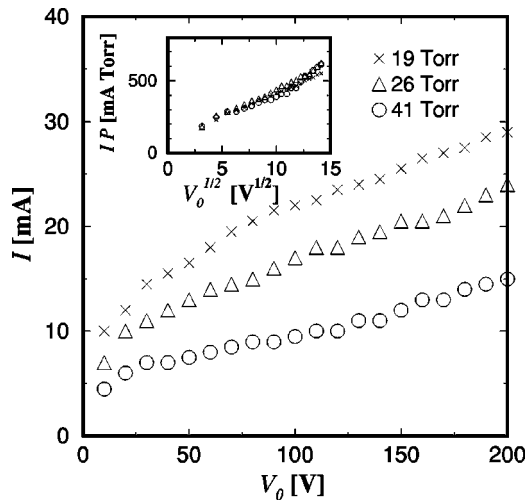


FIG. 4. The observed bias current for the gas pressures of 19, 26, and 41 Torr, as a function of the bias voltage V_0 . The inset shows the bias current multiplied by the gas pressure, IP , as a function of $V_0^{1/2}$.

though the plasma gas is diffusive, the bias pretreatment is effective for giving the kinetic energy of molecules which is proportional to the bias voltage. Third, the ion sheath width d is proportional to $V_0^{1/2}$.

The width of the ions sheath d and the kinetic energy of ions at the substrate $E_{ion}(d)$ seem to satisfy the scaling law as shown in Figs. 3(b) and 3(c) since no ion sheath is formed for the positive substrate ($V_0 > 0$). When we use the experimental value of the bias voltage $-V_0 = -70$ to -100 V, the kinetic energy of ions becomes 5–7 eV, which is the same order of energy for the carbon ions to break C–C or Si–Si covalent bondings and to form sp^3 bonds in the semiempirical calculation of the dynamic reaction coordinate(DRC),²⁶ which will be reported elsewhere.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In order to check the validity of the present theory we have observed the current I in the plasma as a function of the bias voltage V_0 . Here we adopt three different pressures, $P = 19, 26,$ and 41 Torr, of the mixture gas with a volume ratio of $CH_4/H_2 = 7\%$. The 2.45 GHz microwave power is 500 W. The distance between the top of the needle and the substrate is set to be 40 mm. We did the experiments for different distances of 20 and 30 mm but we could not find any substantial differences of the phenomena. The contact area of the plasma on the substrate is almost constant for the three pressures which is checked from the spatial distribution of the synthesized diamond nuclei. The top of the needle is set in the center of the plasma which is checked by eye. The relative position of the substrate to the plasma position is important to discuss the appropriate condition of the temperature of the plasma which determines the density and the velocity of ions in the plasma.

In Fig. 4 we plot the observed bias current I as a function of the bias voltage, V_0 , for $P = 19, 26,$ and 41 Torr. In the inset, the bias current multiplied by the gas pressure, PI , is plotted as a function of $V_0^{1/2}$. It is clear from the figure that the current I is proportional to $V_0^{1/2}$ and inversely propor-

tional to P , which is consistent with Eq. (10). At large V_0 in Fig. 4 we can see a small upshift of the I vs V_0 curves from a linear relation at $V_0 = 60, 90,$ and 130 V for 19, 26, and 41 Torr, respectively. The upshift is relevant to the secondary electron emission, whose threshold bias voltage increases with increasing the pressure.²⁷ When the pressure of the gas increases, the higher V_0 are needed for the secondary electron emission. When ions have larger kinetic energy than the energy gap of diamond, 5.5 eV, at the substrate, the valence electrons of diamond can be excited to the conduction band whose electron affinity is known to be negative.²⁸ Thus the threshold energy of the kinetic energy of ions for the secondary electron emission is nearly equal to the energy gap.

Here we estimate the kinetic energy of ions at the substrate $E_{ion}(d)$ for the given values of the bias voltage for the upshift as above. Using the formula in the previous section we get the following relationship for the kinetic energy

$$E_{ion}(d) = AV_0/P. \tag{16}$$

The fitting parameter A depends on the power of the microwave and other plasma parameters. Under the present experimental conditions we obtain $A = 1.95$ from the values of $E_{ion}(d) = 5$ eV, $V_0 = 77$ V, and $P = 30$ Torr in Fig. 3(c). The corresponding kinetic energies of ions for the secondary electron emission are $E_k(d) = 6.2, 6.8,$ and 6.3 eV for 19, 26, and 41 Torr for $V_0 = 60, 90,$ and 130 V, respectively. These three $E_k(d)$ values are nearly the same and close to 5.5 eV, the band gap of diamond. The deviation from the band-gap value might be due to the hydrogen coverage effect of the surface.²⁸

It is important that the kinetic energy is proportional to the bias voltage and inversely proportional to the pressure. The bias enhancement is observed for those selections of bias voltage and pressure that give ion energies of 1–5 eV. Similar values of V_0/P will give similar ion energies, thus similar enhancement of nucleation. A larger V_0 value at a fixed value of V_0/P may lead to faster crystal growth.

Using Eq. (10) and the observed values of I and V_0 for each pressure, the width of the ion sheath d is plotted as a function of V_0 and $V_0^{1/2}$, respectively, in Fig. 5 and the inset of Fig. 5. Here the area of the plasma for converting I to J is taken as 5 cm² measured from the diamond nuclei distribution of the substrate. We have used the value of the mobility of the CH_4^+ ion, 0.5 m²/V s for the gas pressure of 1 Torr and 900 °C. The calculated ion sheath clearly shows that the width of the ion sheath does not depend on the gas pressure but only on the bias voltage. Although the effect of secondary electron emission is included in the observed values of I and V_0 , d is proportional to $V_0^{1/2}$ for higher values of V_0 . This result suggests that the secondary electrons do not affect the width of the ion sheath very much.

It is desirable to measure $V(x)$ experimentally. Yugo *et al.* measured a floating potential of the plasma by inserting a probe needle.²⁹ However, they did not measure the electric potential as a function of x . Since the electronic temperature is relevant to the electric potential of the quasineutral region and the ion sheath, the measurement of $V(x)$ will give important information on T_e , too.

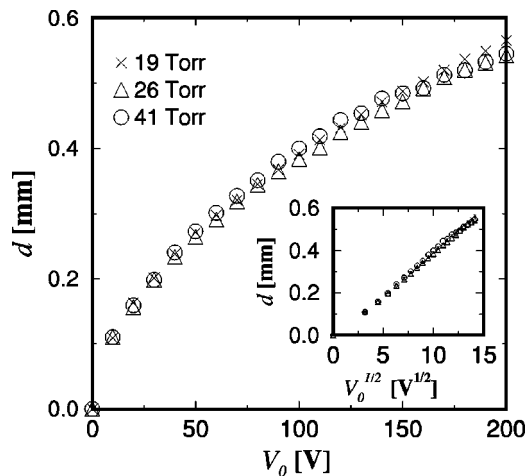


FIG. 5. The width of the ion sheath, d , for the gas pressures of 19, 26, and 41 Torr, is plotted as a function of the bias voltage V_0 . The inset shows the same plot as a function of $V_0^{1/2}$. Here we used the observed values of I and V_0 and Eq. (10) for obtaining d .

The kinetic energy of ions affects the diamond nucleation process in several aspects in the bias pretreatment.³⁰ First, the accelerated ions hit the substrate atoms and form sp^3 covalent bondings which might occur at the kinetic energy of CH_4^+ ions of about 4 to 5 eV.²⁶ For relatively lower ion energies of about 2 to 3 eV, we expect a hydrogen ion irradiation of the substrate, which makes sites for nucleation. We further expect a migration of carbon ions on the substrate for finding nucleation sites at relatively low ion energies. Since hydrogen ions dominate in the plasma, we consider that hydrogen ions with kinetic energies above a threshold energy might remove the sp^2 species of amorphous carbons and help to form diamond nuclei. This speculation will be shown in the experiments carried out for different gas pressures or clarified by a more sophisticated theory in the future. Thus the voltage bias is effective for reactions between carbon and hydrogen or between carbon and carbon.^{11,12,31} A detailed calculation of the dynamical chemical reaction for various kinetic energies of hydrogen ions is required for the further discussion of nucleus formation of diamond in the microwave CVD process.

IV. SUMMARY

In conclusion, we solve the Poisson's equation for the electric current of ions in the ion sheath. Although the quasineutral region of the plasma is small, this region is essential to determine the width of the ion sheath. The electric current is proportional to the square root of the bias voltage, $I \propto V^{1/2}$, while the kinetic energy of ions impinging on the substrate is proportional to the bias voltage and inversely proportional to the pressure, $E_{\text{ion}}(d) = AV_0/P$. The width of the ion sheath is proportional to the square root of the bias voltage and does not depend on the gas pressure, $d \propto V^{1/2}$.

These theoretical results are consistent with the bias pretreatment experiments with reasonable values of plasma parameters.

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- ¹S. Yugo, T. Kanai, T. Kimura, and T. Muto, *Appl. Phys. Lett.* **58**, 1036 (1991).
- ²A. A. Morish and P. E. Pehrsson, *Appl. Phys. Lett.* **59**, 417 (1991).
- ³B. R. Stoner, G. H. Ma, S. D. Wolter, and J. T. Glass, *Phys. Rev. B* **45**, 11067 (1992).
- ⁴X. Jiang, C.-P. Klages, R. Zachai, M. Hartweg, and H.-I. Uüsser, *Appl. Phys. Lett.* **62**, 3438 (1993).
- ⁵B. R. Stoner, G. H. Ma, S. D. Wolter, W. Zhu, Y.-C. Wang, R. F. Davis, and J. T. Glass, *Diamond Relat. Mater.* **2**, 142 (1993).
- ⁶T. Suesada, H. Nakamura, H. Nagasawa, and H. Kawarada, *Jpn. J. Appl. Phys., Part 1* **34**, 4898 (1995).
- ⁷A. Flöter, H. Güttler, G. Shulz, D. Steinbach, C. Lutz-Elsner, R. Zachai, A. Bergmaier, and G. Dollinger, *Diamond Relat. Mater.* **7**, 283 (1998).
- ⁸R. Stockel, M. Stammer, K. Janischowsky, and L. Ley, *J. Appl. Phys.* **83**, 531 (1998).
- ⁹See a special issue of CVD diamond, in *Diamond Films: Recent Developments*, edited by D. M. Gruen and I. Buckley-Golder (*Mater. Res. Soc. Bull.* **23**, No. 9, 1998).
- ¹⁰S. Yugo, K. Semoto, K. Hoshina, H. Nakai, and T. Kimura, *Diamond Relat. Mater.* **4**, 903 (1995).
- ¹¹M. Sternberg and W. R. L. Lambrecht, *Phys. Rev. B* **56**, 1568 (1997).
- ¹²P. Mahalingam, H. Liu, and D. S. Dandy, *J. Appl. Phys.* **81**, 1966 (1997).
- ¹³E. Maillard-Schaller, M. Kuettel O, and L. Schlapbach, *Phys. Status Solidi A* **153**, 415 (1996).
- ¹⁴W. Zhou, X. H. Wang, B. R. Stoner, M. Ma, H. S. Kong, M. Braun, and J. T. Glass, *Appl. Phys. Lett.* **60**, 698 (1992).
- ¹⁵P. Reinke and P. Oelhafen, *Phys. Rev. B* **56**, 2183 (1997).
- ¹⁶J. Robertson, J. Gerber, S. Sattel, M. Weiler, K. Jung, and H. Erhardt, *Appl. Phys. Lett.* **66**, 3287 (1995).
- ¹⁷S. T. Lee, H. Y. Peng, X. T. Zhou, N. Wang, C. S. Lee, I. Bello, and Y. Lifshitz, *Science* **287**, 104 (2000).
- ¹⁸M. Okai, T. Muneyoshi, T. Yaguchi, and S. Sasaki, *Extended Abstracts of the 20th Fullerene General Symposium*, Okazaki, Japan (2001), p. 103.
- ¹⁹S. Huang, A. W. H. Mau, T. W. Turnet, P. A. White, and L. Dai, *J. Phys. Chem. B* **104**, 2193 (2000), and a related paper therein.
- ²⁰W. J. Zhang and S. Matsumoto, *Appl. Phys. A: Mater. Sci. Process.* **71**, 469 (2000).
- ²¹A. Hatta, *New Diamond* **37**, 7 (1995) (in Japanese).
- ²²S. Katsumata and S. Yugo, *Diamond Films Technol.* **3**, 199 (1994).
- ²³E. Sevillano and B. Williams, *Diamond Films Technol.* **8**, 73 (1998).
- ²⁴K. Hassouni, C. D. Scott, and S. Farhat, in *Handbook of Industrial Diamonds and Diamond Films*, edited by M. Prelas, G. Popovici, and L. K. Bigelow (Marcel Dekker, New York, 1998), p. 697.
- ²⁵J. S. Chang, R. M. Hobson, Y. Ichikawa, and T. Kaneda, in *Atomic and Molecular Processes in the Ionized Gas* (Tokyo Denki University Press, Tokyo, 1982). Title and text are written in Japanese.
- ²⁶K. Hirahara *et al.* (unpublished).
- ²⁷S. Barrat, S. Saada, I. Dieguez, and E. Bauer-Grosse, *J. Appl. Phys.* **84**, 1870 (1998).
- ²⁸R. E. Thomas, T. P. Humphreys, D. P. Malta, J. B. Posthill, M. J. Mantini, R. A. Rudder, G. C. Hudson, R. J. Markunas, and C. Pettenkofer, *Appl. Phys. Lett.* **70**, 1257 (1997).
- ²⁹S. Yugo, N. Ishigaki, K. Hirahara, J. Sano, T. Sone, and T. Kimura, *Diamond Relat. Mater.* **8**, 1406 (1997).
- ³⁰S. Yugo, K. Semoto, N. Nakamura, H. Nakai, T. Kimura, and M. Hashimoto, *Diamond Relat. Mater.* **6**, 1047 (1997).
- ³¹I. Gouzman, B. Fiskeer, Y. Avigal, R. Kalish, and A. Hoffman, *Diamond Relat. Mater.* **6**, 526 (1997).