Modeling Species and Energy Transport in Moderate Pressure Diamond Deposition H₂ Plasmas

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Abstract. — A one-dimensional diffusion model for H₂ plasma obtained under moderate pressure discharge conditions is presented. The transport equations resulting from this model are solved and enable the estimation of the axial profiles of the plasma species densities and of plasma temperatures on the axis of a diamond deposition microwave plasma reactor. The comparison between the calculated results and experimental measurements shows that the temperatures are well predicted by the model, while some discrepancy was observed for H-atom mole fraction. The analysis of the energy dissipation channels shows that, at low pressure, most of the power lost by the electron is dissipated in activating electron-impact H₂ dissociation reaction. The model is also used to investigate the effect of the microwave power density on the plasma composition and temperatures. It shows that the increase of the power density leads to a strong and non-linear increase of gas temperature and H-atom mole fraction. This result is also in a good agreement with measurements and is consistent with the high quality of the diamond films obtained at high power density discharge conditions.

1. Introduction

The understanding of diamond growth process in Microwave Plasma Assisted Chemical Vapor Deposition (MPACVD) devices requires the development of satisfactory H₂/CH₄ plasma transport models which provide an estimation of species and temperature spatial distributions in the deposition reactor. Such models must take into account the numerous physical phenomena and chemical processes which occur in the plasma and at the plasma/substrate interface.

The high frequency electric field and the plasma temperatures and species concentrations are strongly coupled in a microwave plasma reactor. In addition, they are linked to the heterogeneous gas-surface chemical kinetics at the reactor wall and at the substrate surface. As a consequence, the modeling of the deposition reactor requires the solution of the transport equations for chemical species and energy modes and of the electromagnetic field equations. Furthermore, a surface chemical kinetics model must specify the boundary conditions of the species equations. Therefore, a complete modeling of the deposition reactor may be very complex, especially when considering the large number of chemical species in H₂/CH₄ plasmas.

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Since hydrogen represents the major part of the deposition plasma feed gas, a modeling of the deposition reactor requires first a good description of H\textsubscript{2} plasmas obtained under diamond deposition discharge conditions. This will be the scope of the present article, where we will especially focus on the investigation of species and energy transport in MPACVD reactor which has been extensively used for diamond film deposition [1].

The physical model used here is mainly based on that of reference [2] for the computation of the different chemical species production and energy exchange rates. However, while reference [2] deals only with average values and makes use of macroscopic loss terms for describing the effect of the substrate surface (zero dimensional model), this work deals with a one-dimensional model which enables taking into account the strong non homogeneity of the plasma. Furthermore, the coupling between species chemical production, energy exchange sources, and species and energy transport is more accurately described here. Finally, the spatial distribution of the microwave power absorbed by the plasma is more accurately estimated in this paper.

2. Model Basis and Assumptions

The hydrogen plasma considered in this study is obtained under moderate pressure discharge conditions (2 500 Pa < \(P\) < 10 000 Pa) with an injected microwave power in the range [600 W, 2 000 W]. The plasma reactor is an asymmetrical 100 mm diameter quartz bell jar containing a 50 mm diameter deposition substrate (Fig. 1). The plasmas, obtained in this reactor, are thermally and chemically non equilibrium. The major chemical species are H\textsubscript{2}, H, H\textsuperscript{+}, H\textsubscript{3}\textsuperscript{+}, H\textsuperscript{−}, and electrons [1]. These species may exist in the electronic ground state or in electronically excited, radiative or metastable, states. Owing to their very short life-time and to the typical averaged electron energy in the considered discharge, the radiative states have very low concentration with respect to the ground state. The metastable state concentrations are also very low because of the relatively high discharge pressures which induce important quenching rates for these states. For the typical discharge conditions considered in this study (average electron energy < 3 eV and pressure > 10 mbar), an upper limit of the ratio between the electronically
excited states and the ground states concentrations is $10^{-4}$ [3]. Therefore, only the populations of the electronic ground states of the chemical species will be considered in this model.

As far as the thermal non-equilibrium is concerned, three energy modes may be: the rotational-translational mode of heavy species, the vibrational mode of the molecules and the translational mode of electrons [2]. For the conditions studied in this work, the translational-rotational and vibrational modes of heavy species are described by Maxwell-Boltzmann distribution functions characterized by two different temperatures $T_g$ and $T_v$. The Electron Energy Distribution Function (EEDF) presents non-Maxwellian behavior [4-6]. For the investigated discharge conditions, the EEDF is bimodal and characterized by a first Maxwellian part at low energy ($\varepsilon_e < 8$ eV) and a second Maxwellian for electron energy above 12 eV [4]. The description of a such behavior requires the solution of the two term expansion of the electron Boltzmann equation in the whole flow field [4]. From the practical point of view, the solution of this equation makes the numerical treatment of the transport equations very time consuming. We have then chosen, as a first approximation, to assume a Maxwellian EEDF characterized by an electron temperature $T_e$. With this assumption, the H$_2$ plasma may be described using a three temperature chemically non-equilibrium flow model.

In the reactor zone of interest, e.g. around the reactor axis and in the thermal and species boundary layer at the substrate surface, measurements [1] show that the radial fluxes divergence is much smaller than the axial one and that the transport mainly takes place along the axial direction. This enables an important simplification since on the reactor axis, where all the radial gradients are zero, the transport equations may be reduced and expressed in one-dimension. This simplification leads to an important reduction of the numerical complexity of the transport equations, but prevents the study of the transport along the radial coordinate.

For the deposition setup considered in this work, the feed gas flow rate is usually very low, in the range of [100 sccm, 300 sccm] [1]. We have then assumed that convection fluxes are negligible with respect to diffusion. If the convection transport is mainly forced, this assumption is valid near the substrate surface where species and temperatures gradients are very high. However, for high power density plasmas, the thermal gradients in the boundary layer may be high enough to induce an important free convection. In this case the assumption of negligible convection fluxes would no longer be valid even in the high gradient region.

3. Mathematical Formulation

3.1. Model Equations. — Under the assumption of a three temperature thermo-chemically non-equilibrium flow, the full description of the plasma requires the knowledge of the spatial distribution of the species mole fraction and of the translation-rotation, vibration and electron temperatures. The transport equations which govern these parameters have been already reported by Lee [7] and Scott et al. [8] for two-dimensional non-equilibrium flow, their adaptation to purely diffusive flow and one-dimensional geometry leads to the following governing equations ($^1$):

Species continuity equations for each chemical species $s$:

$$\frac{d}{dz} \left[ \rho D_s \frac{dx_s}{dz} \right] = W_s \quad (s = 1, 7) \quad (1)$$

$D_s$, $x_s$ and $W_s$ are the diffusion coefficient, the mole fraction and the chemical production source term of species $s$. $\rho$ is the plasma total mass density. In the chemical-kinetics model used in this

$^1$Since the convection fluxes are neglected and since we are only interested in species and energy transport, the momentum equations need not be considered.
work, the plasma is described as a mixture of seven chemical species, \(H_2, H, H_3^+, H_2^+, H^+, H^-\) and \(e^-\), which undergo 27 chemical reactions [2]. These reactions may be divided in two groups. The first one consists of reactions involving electron which are activated by the electron temperature. The second one involves only heavy species reactions which are activated by the gas temperature. The list of the reactions and the rate constants used in the present model may be found in reference [2]. Because of the relatively high discharge pressure, the Debye length is small compared with the plasma dimension [3]. As a consequence, the transport of the charged species may be described under the assumption of an ambipolar diffusion [2]. However, anticipating on the results, one could distinguish two groups of ions. The first group consists of \(H_3^+\) and \(H^-\), the densities of which are mainly governed by chemistry. The second one consists of \(H^+\) and \(H_2^+\) which densities are governed by both transport and chemistry. The ambipolar diffusion coefficients for a plasma containing several ionic species depend on the mobility and on the free diffusion coefficients of the ions and the electron [9]. An expression of these coefficients may be found in reference [9].

Electron energy equation:

\[
\frac{d}{dz} \left[ \lambda_e \frac{dT_e}{dz} \right] - \frac{d}{dz} \left[ \rho D_e h_e \frac{dx_e}{dz} \right] = \text{MWPD}_{\text{abs}} - Q_{e-v} - Q_{e-t} - Q_{e-\text{chem}} \tag{2}
\]

The Left Hand Side (LHS) of this equation accounts for the energy fluxes due to conduction transport and electron diffusion. \(\lambda_e\) is the electron heat conduction coefficient and \(h_e\) is the electron enthalpy. \(Q_{e-v}\) accounts for the energy transfer from electrons to \(H_2\) vibration mode, and involves two mechanisms [2, 10, 11]. The first one consists of the direct vibrational excitation and deexcitation of \(H_2\), \(H_2(v) + e^- \rightarrow H_2(w) + e^-\), the corresponding rate of \(e-v\) energy exchange may be computed from a modified Landau Teller relaxation equation [12]. This mechanism includes both of elastic \((w > v)\) and superelastic \((w < v)\) collisions with excited vibrational states of \(H_2\). The second mechanism for \(e-v\) energy exchange consists of reactions involving a radiative triplet state: \(e^- + H_2(v) \rightarrow H_2(B^1\Sigma) \rightarrow H_2(w) + e^- + h\nu\), the corresponding rate of energy exchange is given in reference [2]. \(Q_{e-t}\) accounts for the energy transfer from electrons to heavy species translation-rotation mode, it may be estimated from classical kinetic theory [2, 7]. \(Q_{e-\text{chem}}\) is a source term accounting for the energy lost by electrons for the activation of \(H_2\) dissociation and \(H_2\) and \(H\) ionization. It depends on the energy threshold and on the rates of these reactions [2]. \(\text{MWPD}_{\text{abs}}\) is the Microwave Power Density absorbed by the electrons, its spatial distribution is a model parameter whose choice will be discussed in a next section. As a rule, an additional term accounting for electron heating by superelastic collisions from electronic excited states should be taken into account. However, Capitelli et al. [4] showed that the effect of such collisions on the electron average energy (or temperature) is very weak. The superelastic collisions from electronically excited states only affect the high energy part of the EEDF \((\varepsilon_e > 8 \text{ eV})\).

\(H_2\) vibration energy equation:

\[
\frac{d}{dz} \left[ \lambda_v \frac{dT_v}{dz} \right] - \frac{d}{dz} \left[ \rho D_{H_2} E_{v-H_2} \frac{dx_{H_2}}{dz} \right] = -Q_{v-e} - Q_{v-t} \tag{3}
\]

The two derivatives appearing in the (LHS) of equation (3) are flux terms corresponding to the vibration energy conduction and to the diffusion of vibrationally excited \(H_2\). \(\lambda_v\) is the vibration energy conduction coefficient and \(E_{v-H_2}\) is the \(H_2\) vibrational energy per unit mass. \(Q_{v-e}\) is a source term accounting for the energy gained from the electrons by the \(H_2\) vibration mode, its estimation may be performed in a similar way to that of \(Q_{e-v}\). \(Q_{v-t}\) is the source term corresponding to the energy exchange between the translation-rotation mode and \(H_2\) vibration mode, it may be estimated from a Landau-Teller relaxation equation [2, 7].
The fluxes term appearing in the LHS of equation (4) correspond to the conduction of the three energy modes and to the diffusion of the enthalpic species. $\lambda_{t-r}$ is the translation-rotation mode conduction coefficient and $h_s$ the mass enthalpy of $s$ species. The source terms correspond to the microwave power absorbed by the electrons, $\text{MWPD}_{\text{abs}}$, and to the energy loss by radiation, $Q_{\text{rad}}$, which will be neglected in this model.

The detailed expressions of all the transport coefficients and energy transfer source terms involved in the present model may be found in references [2] and [3].

The use of this set of equations to describe the plasma diffusion in the one-dimensional domain of Figure 2, requires the specification of the boundary conditions at the substrate surface and at the discharge inlet and of the absorbed microwave power spatial distribution.

### 3.2. Boundary Conditions.

The visible region of the plasma volume usually obtained in the typical deposition discharge conditions is a 5 cm diameter hemisphere located just above the deposition substrate. The 1D simulation domain length was chosen larger than the plasma radius (Fig. 2). In this way, the computation domain inlet is out of the discharge region, and reasonable inlet boundary conditions may be easily specified.

- At the computation domain inlet: $z = z_{\text{inlet}}$

As far as the gas and H$_2$ vibrational temperatures are concerned, Coherent Anti-Stokes Raman Spectroscopy (CARS) measurements previously carried out on the studied reactor [1], showed that the gradients of these temperatures are very weak at $z \approx 2.5$ cm. We have then used zero gradient boundary conditions at $z_{\text{inlet}}$ for gas and H$_2$ vibration temperatures. Due to the absence of any electric field and to the high pressure, the electron temperature may be expected to be in quasi-equilibrium with the gas temperature in the post-discharge region. As a consequence, zero gradient boundary condition may also be used for $T_e$.

In the post-discharge region ($z > 3$ cm), where the electron temperature is low, most of the electron-heavy species collisions lead to recombination reactions. The ionic species involved in
the model may be divided in two groups:

- $H^+_2$ and $H^+_3$ which rapidly recombine in the post-discharge;
- $H^+$ and $H^-$ which slowly recombine in the post-discharge.

For the first two species, the concentration far from the discharge may be expected to be very low and almost constant. For the second, two species the very low recombination kinetics may result in low concentration gradients far from the discharge area. It seems reasonable to specify zero concentration gradient boundary conditions for the charged species.

For $H$-atom and $H_2$-molecule the chemical kinetics outside the discharge region consists of the thermal recombination and dissociation reactions which depend on the gas temperature. If this latter is low enough to insure very slow dissociation and recombination rates of $H_2$ and $H$, the concentrations of these species may be expected to be approximately constant, which leads to approximately zero concentration gradient outside the discharge area ($z > 3$).

From the above analysis the boundary conditions at the computation domain inlet will be of the form:

$$
\left(\frac{d\phi}{dz}\right)_{z=z_{inlet}} = 0, \quad (\phi = x_1, x_2, \ldots, x_7, T_g, T_v, T_e). \quad (5)
$$

- At the substrate surface: $z = 0$

For the pressure conditions considered here, the gas temperature at the substrate surface is in equilibrium with the substrate temperature. This leads to the following boundary condition:

$$
T_g|_{\text{substrate}} = T_{\text{substrate}} \quad (6)
$$

The $H_2$ vibrational temperature at the substrate surface may be different from the gas temperature. For the investigated reactor, CARS measurements showed that, at 1 mm from the substrate surface, $T_v$ is slightly higher than $T_g$, the difference $T_v - T_g$ being of approximately 200 K for a pressure of 2500 Pa [1]. We have then used:

$$
T_v|_{\text{substrate}} = T_{\text{substrate}} + 200 \quad (7)
$$

For the boundary condition on $T_e$, we have to consider the existence of an electrical sheath near the substrate surface. For the discharge conditions considered in this work, the sheath thickness is typically between 5 and 30 $\mu$m and is much smaller than the spatial step dimension used in the discretized form of the conservation equations, e.g. $\delta = 1 - 10$ mm. As a consequence, the boundary condition for $T_e$ may be derived by assuming that the electrical sheath boundary coincides with the substrate surface. In the investigated reactor, the substrate surface is insulated and the net electrical current normal to the wall vanishes. In this case, a boundary condition which is widely used for $T_e$ is that of zero gradient at the substrate surface [13].

$$
\frac{dT_e}{dz}|_{\text{substrate}} = 0 \quad (8)
$$

The chemical species concentration at the substrate are governed by a balance between the species arriving at the surface by diffusion and that produced at the substrate surface by heterogeneous reactions. The heterogeneous chemical model for the seven species $H_2$ plasma was reported by Scott et al. [2]. It consists of the following reactions, where $S$ denotes a surface site:

- $H + H - S \rightarrow \frac{1}{2}H_2 + S \quad (R1)$
- $H^+ + e^- - S \rightarrow H + S \quad (R2)$
- $H^+_3 + e^- - S \rightarrow H + H_2 + S \quad (R3)$
- $H^+_2 + e^- - S \rightarrow H_2 + S \quad (R4)$
- $H^- + S \rightarrow H + e^- + S \quad (R5)$
The boundary conditions for the chemical species are of the form:

\[- \rho D_s \frac{dx_s}{dz} = W_{s-surf} \tag{9}\]

where \(W_{s-surf}\) is the surface chemical production source term of the species \(s\). The charged species totally recombine at a surface and a value of 1 can be adopted for the recombination coefficients of reactions (R2)-(R5). For H-atom, the catalytic recombination is partial and we have used the value of 0.1 measured by Harris [14].

3.3. Spatial Distribution of the Absorbed Microwave Power Density. — The Spatial Distribution of the absorbed Microwave Power Density (SDMWPD) depends on the plasma composition. Its exact determination requires the solution of the Maxwell equations which have to be coupled to the plasma transport equations. Since in this study, we mainly focus on the investigation of the plasma transport, we have simply estimated the behavior of the SDMWPD along the reactor axis from the solution of the one-dimensional wave equation, where the wave is assumed to be injected at the top of the reactor and reflected back on a plate located at the bottom end of the reactor. The plasma electrical permittivity was assumed constant over all the plasma volume. We have also assumed that the radial behavior of the SDMWPD is similar to the axial distribution. The absorbed microwave power density is then given by the following expressions:

for \(0 < z < z_0 + \lambda/4\) and \(0 < r < (\lambda^2/16 - (z - z_0)^2)^{1/2}\)

\[\text{MWPD}(z,r) = \text{MWPD}_0 \cos^2 \left( \frac{2\pi(z - z_0)}{\lambda} \right) \cos^2 \left( \frac{2\pi r}{\sqrt{\lambda^2/16 - (z - z_0)^2}} \right) \tag{10}\]

and for \(z > z_0 + \lambda/4\) or \(r > (\lambda^2/16 - (z - z_0)^2)^{1/2}\)

\[\text{MWPD}(z,r) = 0 \tag{11}\]

\(\lambda\) is the wavelength of the high frequency electric field \((\lambda = 12.24 \text{ cm})\) and \(z_0\) is the position of the maximum power density. The parameter \(\text{MWPD}_0\) is directly linked to the total absorbed microwave power by the following energy balance equation:

\[\text{MWP}_{\text{total}} = \int \int _{\text{hemisphere}} \text{MWPD}(z,r) 2\pi r dr dz \tag{12}\]

For given discharge conditions, the exact determination of the absorbed microwave power density in the whole plasma volume is now equivalent to the estimation of its maximum location \((z_0)\) and of the total absorbed power \(\text{MWP}_{\text{total}}\) which gives the parameter \(\text{MWPD}_0\). Both of these parameters were estimated by the use of optical emission spectroscopy and heat flux measurements [3].

4. Results and Discussions

Using a one-dimensional grid of 30 mesh points, the set of governing equations (1)-(4) was expressed in finite difference form at each grid point. The resulting non-linear algebraic system was solved using a Gauss-Siedel relaxation technique, for several discharge conditions.
4.1. **Comparison with Experimental Measurements.** — Extensive experimental investigations have been already performed on the H$_2$ plasma obtained in the reactor under discharge conditions corresponding to: MW$_{\text{input}}$ = 600 W, P = 25 mbar, $T_{\text{substrate}}$ = 1173 K and Flw = 300 sccm [1,15]. Therefore, we have chosen to validate the model for these discharge conditions. The heat flux and OES measurements performed on the H$_2$ plasmas obtained at this discharge conditions show that the corresponding SDMWPD, which is presented in Figure 3, is characterized by MW$_{\text{total}}$ = 530 W and $z_0$ = 0 mm [3]. The computed gas and H$_2$ vibration temperatures are nearly in equilibrium in the plasma bulk (Fig. 4), the small non-equilibrium observed in the boundary layer near the substrate surface is mainly due to the boundary condition used in this calculation. The calculated axial profiles are in good agreement with those determined by CARS ($T_{{g,\text{med}}} - T_{{g,\text{exp}}}$ < 150 K) even though the small vibrational non-equilibrium ($T_v - T_g$ ≈ 100 – 200 K) observed experimentally [1] is not predicted by the model (Fig. 4). The calculations show a sharp decrease of $T_g$ from a value of 2250 K in the plasma bulk ($z > 2$ cm) to 1173 K at the substrate surface. The values of the thickness of the high gradient layer obtained from the experiment and from the model are in good agreements (2 cm).

For the investigated discharge conditions, the calculated H-atom mole fraction in the plasma bulk is $6.1 \times 10^{-2}$. The calculated axial profile of the H-atom molar fraction is given in Figure 5, where we have also reported the normalized ratio ($I_H/I_{Ar})_{\text{norm}}$ given by the following equation:

$$
\left( \frac{I_H}{I_{Ar}} \right)_{\text{norm}} = \frac{(I_H/I_{Ar})}{(I_H/I_{Ar})_{\text{max}}} [H]_{\text{bulk}}
$$

(13)

where $I_H$ and $I_{Ar}$ are the H$_\alpha$ and Ar(750 nm) emission lines intensities, and $[H]_{\text{bulk}}$ denotes the calculated H-atom molar fraction in the plasma bulk. The ratio $I_H/I_{Ar}$ is a linear function of the H-atom mole fraction [3]. The comparison between the measured and calculated profiles shows that the thickness of the high H-atom mole fraction gradient layer is well predicted by the model ($\delta = 2$ cm). The calculated values of $[H]/[H]_{\text{bulk}}$ near the substrate ($0.1 \text{ cm} < z < 1 \text{ cm}$) are however much higher than those measured by actinometry (Fig. 5). This discrepancy may be due to the assumption of a Maxwellian EEDF, which leads to an overestimation of the rate constants of high energy electron-heavy species collisions (dissociation and ionization) [4,6].

![Fig. 3. — Axial profile of the microwave power density on the reactor axis.](image-url)
Fig. 4. — Calculated and measured axial profile of gas and vibration temperatures.

Fig. 5. — Calculated axial profile of H-atom mole fraction and measured axial profiles of the normalized $I_{H}/I_{Ar}$. 
The calculated electron temperature (Fig. 6) is about 18 000 K in the plasma bulk (0.5 cm < z < 2 cm) and increases in the vicinity of the substrate surface where it reaches a value of 19 500 K (0 < z < 0.3 cm).

The major ionic species are the electrons, $H_3^+$ and $H^+$. Their mole fraction axial distributions are presented in Figure 7. In the high power density discharge zone (z < 2 cm), the major ion is $H_3^+$. Its mole fraction profile shows a maximum value of $1.7 \times 10^{-5}$ at 8 mm from the substrate surface. This ion rapidly recombines out of the discharge zone where the major ion is $H^+$. The axial profile of $H^+$ mole fraction shows a maximum value of $1.2 \times 10^{-5}$ at 16 mm from the substrate surface. The electron mole fraction may be deduced by summing those of $H^+$ and $H_3^+$. Its axial profile shows a maximum value of $2.8 \times 10^{-5}$, $n_e \approx 3 \times 10^{12}$ cm$^{-3}$, at 11 mm from the substrate surface.

Although the $H_2^+$ and $H^-$ ions mole fractions are very low, they are very important for the kinetic modeling of this kind of plasma [1]. Their maximum values are $5 \times 10^{-9}$ for $H_2^+$ and $2 \times 10^{-8}$ for $H^-$. 

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**Fig. 6.** Calculated axial profile of electron temperature.

**Fig. 7.** Calculated axial profiles of the mole fraction of the major charged species $H^+, H_3^+$ and $e^-$.
4.2. **Energy Dissipation in the Discharge.** — It may be very interesting to investigate the relative magnitudes of the different energy transfer channels. In Figure 8 we have reported the axial profiles of the source terms corresponding to the power densities gained and lost by electrons, those transferred from electrons to the other modes, and those lost by electrons for the activation of the dissociation and ionization processes. The total power densities gained and lost by electrons are approximately equal; the slight difference between these densities is due to the electron enthalpic flux gradient which also participates in the electron energy equation (2). This weak difference shows that the electron energy transport may be well described by neglecting the enthalpic diffusion. This simplification should lead to an important simplification of the mathematical problem, since the resulting electron energy equation is algebraic and not differential. Figure 8 shows that most of the energy gained by electrons from the electromagnetic field is lost by activation of the e\(^{-}\) – \(\text{H}_2\) dissociation reaction which constitutes 58% of the total lost power at 1 cm from the substrate surface. The second channel for the electron energy dissipation consists of the transfer to the translational and vibration modes of the heavy particles. It represents 40% of the total lost power at 1 cm from the substrate surface. The power dissipated for the ionization of H and \(\text{H}_2\) is very weak compared to the other dissipation channels (2%).

4.3. **Effect of the Averaged Microwave Power Density.** — Deposition experiments have previously shown that an increase of the averaged power density, MWPD\(_{av}\), from 9 W cm\(^{-3}\) to 30 W cm\(^{-3}\), while keeping the plasma volume constant, has a strong effect on the diamond growth rate and quality [15]. To investigate the effect of such a parameter on the plasma composition and temperatures, the transport equations were solved for four couples (MWP\(_{total}\), P) corresponding to a constant discharge volume \(V \approx 32.7\) cm\(^3\) and to MWPD\(_{av}\) = MWP\(_{total}\)/V = 9 W cm\(^{-3}\), 15 W cm\(^{-3}\), 22.5 W cm\(^{-3}\) and 30 W cm\(^{-3}\).

The increase of the averaged power density from 9 W cm\(^{-3}\) to 30 W cm\(^{-3}\) leads to a strong increase of the gas temperature which varies from 2250 K to 3100 K in the bulk of the plasma \((z > 2.5\) cm\) (Fig. 9). The variation of \(T_g\) with MWPD\(_{av}\) is non-linear and decreases at high power density \((\Delta T_g/\Delta PMW \text{ decreases with MWPD}_{av})\).
The increase of \( T_g \) with MWPD\textsubscript{av} results in a sharp increase of H-atom mole fraction which varies from 0.06 to 0.21 in the investigated domain of the averaged power density (Fig. 10). The variation of H-atom mole fraction with the power density is also non-linear and is more important at high power density. At low MWPD\textsubscript{av} values the H-atom is mainly produced by electron-H\(_2\) collision which is controlled by electron temperature. This is not the case at high MWPD\textsubscript{av}, where the dissociation of H\(_2\) is mainly due to H\(_2\) – H\(_2\) and H\(_2\) – H collisions which are controlled by gas temperature (thermal dissociation).
These results show that at high power density the energy transferred to the heavy species is dissipated in the activation of the $\text{H}_2$ thermal dissociation which leads to a higher increase of H-atom molar fraction and slower increase of $T_e$. They are in a good qualitative agreement with CARS and actinometry measurements [3]. They also explain the high quality of the diamond films obtained under high power density discharge conditions, since the high H-atom concentration obtained for these conditions insures a high etching rate of the non-diamond phase [15].

In the discharge zone ($z < 3 \text{ cm}$), the electron temperature decreases when increasing the averaged microwave power density. It varies from 19 500 K to 17 000 K in the investigated absorbed power domain (Fig. 11). This behavior is due to the increase of the pressure which leads to higher energy transfer rates from the electron kinetic mode to the other modes.

As far as the major charged species are concerned, lower values of the ionization degree are obtained at high microwave power density (Fig. 12). Furthermore, the increase of the power density leads to a sharp decrease of the charged species concentrations out of the discharge zone. This is due to recombination reactions which are accelerated at the high pressures that characterize the high power density discharge conditions.

5. Conclusion

The one-dimensional transport model presented here enables the estimation of some key parameters for $\text{H}_2$ plasmas obtained under diamond deposition discharge conditions. The comparison of the model results and experimental measurements shows that the gas and $\text{H}_2$ vibration temperatures are well predicted by the model. The discrepancy between the calculated and measured H-atom molar fraction show that the chemical kinetic modeling of the discharge must be improved by taking the non-Maxwellian behavior of the EEDF into account. Such improvement should especially enable a better estimation of high energy threshold electron-heavy particle reactions rate constants. The analysis of the energy dissipation channel shows that most of the energy gained by the electrons from the electromagnetic fields is dissipated, at low pressure, for activating the dissociation of $\text{H}_2$ and for heating the translation-rotation mode of heavy species. Finally, the investigation of the effect of the absorbed microwave power
density on the plasma composition and temperatures shows that the increase of this density leads to a strong increase of the gas temperature and of the H-atom mole fraction. This result is in good qualitative agreement with those of the deposition experiment which show a strong increase of the film quality when increasing the absorbed microwave power density. This model may be also improved by taking into account the convection flux, especially for high power density discharge conditions, where the high temperature gradients near the substrate surface may induce an important free convection effect on species and energy transport.

References


