Particle Simulation of CH₄/H₂ RF Glow Discharges for DLC Film Deposition

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ABSTRACT

Particle-in-cell/Monte Carlo (PIC/MC) simulations of capacitively coupled radio-frequency (RF) glow discharges were carried out for low pressure CH₄/H₂ plasmas. The present computational scheme considers the motions and collisions of both neutral and charged particles. The CH₄/H₂ plasma is modeled by combining a one-dimensional PIC/MC method with a polyatomic particle collision scheme. The model considers the motions of neutrals CH₄, CH₃, C₂H₅, H₂, and H, positive ions (CH₄⁺) and electrons. Space and time dependent results show that ionization rate is high at the sheath region. Deposition rate of carbon film is calculated by sampling impinging particles at the powered electrode. When CH₄ flow rate is decreased and the H₂ flow rate is increased, the gas density in the chamber and deposition rate decreased significantly for carbon containing radicals. On the other hand, when CH₄ flow rate is fixed and H₂ flow rate is increased, deposition rate again decreased, but the gas density in the chamber did not change much.

INTRODUCTION

Diamond like carbon (DLC) films deposited by various glow-discharge processes have properties much like those of diamond. DLC films are extremely hard, chemically inert, electrically insulating, and good thermal conductors. Many application areas have been suggested such as spacecrafts and heat sinks in electronic packaging. The role of hydrogen in vapor-activated deposition of diamond has been the focus of much attention because only after excess hydrogen was used in these processes, that mm/h growth rates were possible. The role of hydrogen is significant in both gas phase chemistry and surface chemistry for these deposition processes. In gas phase chemistry, atomic hydrogen promotes the gas phase production of growth precursors, and suppresses the formation of polyatomic hydrocarbon species (PAHs) by molecular hydrogen. PAHs may be precursors to unwanted sp² carbon during the vapor-deposited DLC growth. Regarding surface chemistry, several factors such as

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230
etching, covering of the dangling bonds of surface carbons, removing hydrogen from surface C-H bonds (to create active growth sites) are affected by atomic hydrogen.

The role of hydrogen in DLC deposition process in pure methane plasma is not clearly understood. Most of the reported models for DLC deposition process are for pure CH₄ plasma. These models focused on gas phase chemistry and surface chemistry rather than discharge kinetics. Rate equations with gas phase chemistry or plug flow model (simplified fluid model) were used to predict the number densities, etc. Electron energy, which determines ionization and dissociation rates, was obtained either by experimental data or via Monte Carlo simulation of electron kinetics. Depositions were predicted using sticking coefficients. A self-consistent fluid model for CH₄ plasma, using Boltzmann equation solver for DC field calculation of the electron energy distribution function was later developed. The radical densities for CH₃ and CH₂ were calculated, however, these profiles did not compare well with experimental data. Hybrid models have also been developed and applied to RF plasma with gas mixtures.

In this study, we applied the PIC/MC method to simulate CH₄/H₂ plasmas in a capacitively coupled RF reactor. The model considers the motions of CH₄, CH₄⁺, CH₃, C₂H₅, H₂, H and electrons. Both flow rates and gas compositions or pressure were varied. The results are analyzed by comparing the power consumed, current flow, and the electron energy and density (at the center of the plasma) as the gas compositions are varied. Ionization and dissociation rates and the species densities are computed as functions of the gas composition and flow rates. The energy of the impinging ions to the cathode, and deposition rates are also obtained. The developed computational model will allow us to predict the carbon film deposition rate and its quality when different CH₄/H₂ compositions are fed into low pressure plasma assisted CVD reactors.

MODEL DESCRIPTION

The models used here are an extension of the one dimensional self-consistent particle model for capacitively coupled RF glow discharge of pure CH₄. A parallel plate configuration of the reactor is considered where the two electrodes have large cross-sectional areas compared to their separation distance, so that a one-dimensional approximation is valid for characterizing the discharge. The model considers motion and collisions of neutrals as well as of charged particles. To simulate the CH₄/H₂ plasma, we combine the particle simulation model with neutral motion and a polyatomic particle collision model which was developed in the rarified gas dynamics area. For stable neutral/radical and radical/radical collisions, energy after collision is determined by the Borgnakke and Larsen model. In this model, both the relative transnational and the internal energies are assumed to be distributed according to the respective equilibrium distributions and, at each collision, new values are sampled at random from...
these distributions, subject to the condition that the total energy is conserved. Hence vibrational-vibrational and vibrational-translational energy exchanges are considered for the neutral/neutral collisions.

The model uses polyatomic particle collision scheme, which has been developed in the non-plasma area. Gas phase chemistry is considered by simplified reactions to reduce the number of species in the particle model. In our particle simulation, we simplified the chemistry model of Kline et al. Electron-electron, electron-ion, and ion-ion collisions are neglected in the present study, as the probability of such collisions are small in weakly ionized plasma. For neutral-electron collisions, elastic scattering, excitation, and ionization collisions are considered. In each collision process total momentum is conserved. Total energy of collision pairs in elastic collision is preserved, while energy is lost in excitation and ionization processes. For the discharge kinetics, elastic scattering between neutrals are considered and electron impact to CH₄ and H₂ are considered. Hydrogen ion is neglected because the density is negligible compared to that of CH₄⁺ in the simulated range of parameters. Following gas-phase reactions are considered for the plasma:

\[
\begin{align*}
\text{CH}_4 + e^- &\rightarrow \text{CH}_3 + H + e^- \\
\text{CH}_4 + e^- &\rightarrow \text{CH}_4^+ + e^- + e^- \\
\text{H}_2 + e^- &\rightarrow \text{H} + \text{H} + e^- \\
\text{CH}_3 + \text{H} &\rightarrow \text{CH}_4 \\
\text{CH}_3 + \text{CH}_3 &\rightarrow \text{C}_2\text{H}_5 + \text{H} \\
\text{H} + \text{H} &\rightarrow \text{H}_2
\end{align*}
\]

Surface reactions considered in the present analysis are as follows:

\[
\begin{align*}
\text{CH}_4^+ &\rightarrow \text{C} \text{ (deposit)} + 2\text{H}_2 \text{ (gas)} \\
\text{CH}_3 &\rightarrow \text{CH} \text{ (deposit)} + \text{H}_2 \text{ (gas)} \\
\text{C}_2\text{H}_5 &\rightarrow \text{C}_2\text{H} \text{ (deposit)} + 2\text{H}_2 \text{ (gas)} \\
\text{H} &\rightarrow \text{absorbed or H}_2 \text{ (gas)}
\end{align*}
\]

Further details of the gas-phase and surface reactions considered can be found in Nagayama et al. The depositing species are CH₄⁺ and CH₃ and C₂H₅ radicals. The deposition of hydrogen radical is neglected in this study. Film growth rate is predicted by sampling depositing particles on the surface using sticking probability. Sticking probabilities are assumed to be 1.0 for the ions and 0.1 for the radicals. Although the model does not consider a detailed surface model, it provides useful information for plasma physics and can identify major species impinging to the substrate.

For the present PIC/MC scheme, the reaction rates depend on the respective cross sections. In general, rate constant for any reaction is related to the cross section for that reaction as

\[
K = \int_0^\infty \left( \frac{2E}{m} \right)^{3/2} \sigma(E) dE
\]
where $E$ is the total energy of the collision pair, $f(E)$ is the energy distribution function, $m$ is the reduced mass of the collision pair and $\sigma(E)$ is the cross section. For electron impact ionization or dissociation, cross section area is expressed as a function of electron energy, which is directly used in PIC/MC simulations. No electron-impact excitation reactions were considered in this study. For neutral stable/radical and radical/radical reactions, rate constant must be transformed to cross section $\sigma$ as PIC/MC method requires cross section area as input data. Assuming hard sphere model, the above equation can be solved for $\sigma(E)$ as

$$\sigma(E) = K \sqrt{\frac{m}{2E}}$$

In order to get stable results with a relatively small number of particles (as used in this study), a time-averaging technique was used to determine the electric field. Based on the fact that RF plasma is a periodic phenomena, new electric field for a given time phase at the end of the $n^{th}$ cycle is calculated using averaged density data of the previous $n/2$ cycles at the same time phase. In addition weighting factors were used to represent the charged particles and the neutrals. Further details can be found in Nagayama et al.

**Calculation conditions for the CH$_4$/H$_2$ plasma**

The discharge is powered by RF source at 13.56 MHz. Eighty uniformly distributed grid points were used for the distance (2.5 cm) between the electrodes. 1,200 particles of each type are used. The gas is supplied from one electrode (anode). CH$_4$ and the neutral radicals produced by the reaction are partially eliminated under the condition that total pressure inside the chamber is held constant. The secondary electron emission coefficient was set to zero for all calculations reported here. In surface reactions, C-H or C$_2$H is absorbed to form film and hydrogen is released. Accordingly, the depositing particles are eliminated from the calculation and hydrogen particles are added. Anisotropic angular scattering is incorporated with the relative differential cross section for all electron and neutral collisions. Electron wall reflection ratio is set to 0.25. The calculations are carried out for 1200 RF cycles and the data are averaged between 600th - 1200th cycles for calculating the plasma properties. Time steps considered were between 0.001 and 1.0 ns for a charged particle depending on its velocity. Larger time steps were considered for the neutrals.

For all calculations, the driving voltage ($V_{RF}$) is set to 200 V, and the DC bias voltage ($V_{DC}$) is equal to zero. Flow rate and gas compositions or pressure were changed. Two cases of simulations were carried out.

**Case 1:** Total flow rate is fixed to 24 sccm, and supply gas composition CH$_4$/(CH$_4$ + H$_2$) ratio is varied keeping the total pressure at 400 mTorr.
Case 2: CH₄ flow rate is fixed to 24 sccm, and H₂ flow rate is changed keeping the CH₄ partial pressure to 100 mTorr.

RESULTS AND DISCUSSION

Case 1: Fixed total flow rate with varying composition

Simulations were carried out at different H₂ partial pressures (300, 200, and 0 mTorr), while total pressure is kept constant (400 mTorr). In other words, the gas composition is changed while total pressure is kept constant. The simulated power consumption and current in the plasma (as a function of the gas composition) are shown in Fig. 1-a.

![Figure 1-a. Power and displacement current as function of CH₄/(CH₄ + H₂)](image)

Figure 1-a. Power and displacement current as function of CH₄/(CH₄ + H₂)

![Figure 1-b. Electron energy and electron density (at the center of the discharge) as function of CH₄/(CH₄ + H₂)](image)

Figure 1-b. Electron energy and electron density (at the center of the discharge) as function of CH₄/(CH₄ + H₂)

Note that small values of CH₄/(CH₄ + H₂) value indicates that the gas composition is highly diluted by hydrogen. Power consumed in the reactor does not depend on the gas composition in the simulated range. Total current tends to increases as CH₄ ratio increases, which may be related to the increase of plasma density. Fig. 1-b shows the electron density and electron energy values at the center of the discharge as a function of the above ratio.

Electron density increase as CH₄ ratio increases because the CH₄ ionization is the major source of electrons. Electron energy is between 3.4 - 3.8 eV in the simulated range. The electron-impact ionization and dissociation rates are shown in Fig. 1-c as function of the inlet gas composition ratio.
CH₄ dissociation rate is about ten times higher than CH₄ ionization rate and the variations are small in the log scale. Although H₂ dissociation rate is negligible in pure CH₄ plasma, H₂ dissociation rises to the same level as CH₄ ionization rate at highly diluted condition. Although we neglected H₂ ionization process in this model, the assumption is reasonable because such rate will be lower than H₂ dissociation and will be negligible compared to CH₄ ionization and dissociation in the simulated range.

Fig. 2 shows the radical and neutral densities as functions of the CH₄/(CH₄ + H₂) ratio. CH₄ increases and H₂ decreases as the gas composition is changed. H density does not change much although H⁺ density increases significantly. The reason may be that H is generated from both CH₄ and H₂ dissociation. CH₃ density increases as CH₄ dissociation increases. C₂H₅ density also increases as CH₃ density increases.

The energy of ions impinging to the cathode tends to decrease as CH₄ density increases and charge exchange collisions increase. It is noted that the present model does not consider the interaction between CH₄ ion and H₂. Fig. 3 shows the deposition rates for the three depositing species as function of the CH₄/(CH₄ + H₂) ratio. CH₃ and C₂H₅ deposition rates increase as CH₄ density increases. C₂H₅ represents PAHs (polyatomic hydrocarbon) and high C₂H₅ may cause polymer like films. On the other hand CH₄⁺ deposition rate is constant because ionization rate does not change.
Figure 3. Deposition rates as function of functions of CH\textsubscript{4}/(CH\textsubscript{4} + H\textsubscript{2})

**Case 2: CH\textsubscript{4} flow rate is fixed while hydrogen is added**

Simulations were also carried out at different H\textsubscript{2} flow rates (0, 48, 96 sccm), while CH\textsubscript{4} flow rate is kept constant at 24 sccm. The CH\textsubscript{4} partial pressure is thus indirectly fixed at 100 mTorr. The power consumption and current are high for high H\textsubscript{2} addition. It means power is mostly consumed by electron-hydrogen collision. Although H\textsubscript{2} density increases as the dilution becomes high, the density levels of most species do not change as in the previous case. The ion energy is between 24 - 28 eV and does not show any variation with hydrogen addition. As noted before, no interactions between CH\textsubscript{4}\textsuperscript{+} and H\textsubscript{2}, were considered here.

Fig. 4 shows the spatial profiles of time averaged rate coefficients for different values of H\textsubscript{2} pressure as CH\textsubscript{4} pressure is held constant at 100 mTorr.

With pure CH\textsubscript{4}, dissociation rate is large and H\textsubscript{2} dissociation is negligible (Fig. 4-a). The CH\textsubscript{4} dissociation rate is high at the center of the plasma that is typical at low pressure (100 mTorr). As the H\textsubscript{2} pressure is increased (Fig. 4-b, c), H\textsubscript{2} dissociation is increased. It is interesting to note that by adding H\textsubscript{2}, the spatial profile of the rate coefficients become bow
shaped, which is similar to the case of pure gas discharges where pressure is increased. At \( H_2 \) pressure of 400 mTorr (80% of the total flow), \( H_2 \) dissociation rate is comparable to \( CH_4 \) ionization rate but still about ten times smaller than \( CH_4 \) dissociation rate. \( H_2 \) dissociation and \( CH_4 \) ionization rates are high in the sheath region while \( CH_4 \) dissociation rate is uniform in the plasma bulk at this pressure (Fig. 4-c). The reason may be due to the fact that in the former two processes, high energy (threshold energy is 13 eV for \( H_2 \) dissociation and 14 eV for \( CH_4 \) ionization) is needed compared to \( CH_4 \) dissociation (threshold energy is 10 eV).

CONCLUSIONS

Particle-in-cell/Monte Carlo simulations of capacitively coupled RF (radio-frequency) glow discharges were carried out for low pressure \( CH_4 / H_2 \) plasmas. The model employs a one-dimensional scheme and considers polyatomic particle motion and collision. Calculations were carried out for two cases: (a) total flow rate is fixed while gas composition or \( CH_4/(CH_4 + H_2) \) ratio is varied, and (b) \( CH_4 \) flow rate is fixed while \( H_2 \) flow rate is changed. When \( CH_4 \) flow rate is decreased, the gas density in the chamber and deposition rate decrease significantly for carbon containing radicals while \( CH_4^+ \) density does not change much. On the other hand, when \( CH_4 \) flow rate is fixed and \( H_2 \) flow rate is increased, and deposition rate decrease similarly, but the gas density in the chamber does not change much (for the range of parameters considered). For both cases, \( H_2 \) dissociation rate is comparable to \( CH_4 \) ionization rate when \( H_2 \) partial pressure is about 75 ~ 80% of the total gas pressure. However, \( H_2 \) dissociation rate is still very small compared to \( CH_4 \) dissociation rate. When \( H_2 \) flow rate increases with fixed \( CH_4 \) flow rate, lower \( CH_4 \) and \( C_2H_5 \) deposition rates occur, but the overall effect is not large (\( H_2 \) flow rates between 0 to 80% of the total flow). The major reason is that electron impact dissociation cross section of hydrogen is smaller than that of \( CH_4 \). With the addition of \( H_2 \), carbon-containing gas decreases significantly and deposition rate is decreased especially for \( C_2H_5 \) while that for \( CH_4^+ \) does not change much. This may improve the film quality suppressing the PAHs formation. Adding \( H_2 \) also changes the rate coefficient spatial profiles to bow shape, which is similar to the case of pure gas discharges when pressure is increased.

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