Modeling of RF Plasma Discharges of Polyatomic Gases for Carbon Film Deposition

K. Nagayama, B. Farouk and Y.H. Lee*

Department of Mechanical Engineering and Mechanics
*Department of Chemical Engineering
Drexel University
Philadelphia, Pennsylvania 19104

Abstract

Particle-in-cell Monte Carlo simulations of capacitively coupled glow discharges were carried out for low pressure Ar and CH_4 plasmas. The present scheme includes the motions and collisions of both neutrals and charged particles. In Ar plasma, neutral density is found to be almost uniform between the electrode and the neutrals are at room temperature. CH_4 plasma is modeled combining PIC/MC method with a polyatomic gas collision scheme. For CH_4 the PIC/MC model considers the motions of CH_4, CH_4^+, CH_4^* (which represents dissociated species such as CH_3 + H, $CH_2 + H_2$ or CH + H + H_2), and electrons. Space and time dependent results show ionization rate is high at sheath edge while dissociation rate is also high in the plasma bulk for the CH_4 glow discharge.

Introduction

Low pressure radio-frequency (RF) discharges are used for a wide variety of thin film fabrication processes. These discharges are inherently complex, hence there is considerable interest in understanding the discharge structure. Weakly ionized gas discharges are widely used in sputtering, etching and plasma-assisted chemical vapor deposition (PACVD), which are all important processes in integrated circuit manufacturing. PACVD processes have been used for diamond-like-carbon (DLC) film deposition in CH_4 plasmas at room temperature. DLC films primary deposited by glow discharges are hard carbonaceous films having properties much like those of diamond. DLC films have broad applications such as protective coatings and heat sinks.

Particle-in-cell/Monte Carlo methods have been used extensively in the past for the study of plasmas, and the method is well documented by Birdsall [1]. PIC/MC technique have recently been applied with considerable success in modeling the monatomic gas discharge. PIC/MC methods have been applied to monatomic gas discharges such as atomic hydrogen, helium, and argon by Boswell and Morney [2], Surendra and Graves [3] and others. Etching species are usually the monatomic ions while depositing species are polyatomic radicals and ions. To simulate deposition, PIC methods must be hybridized with fluid models or extended to modeling of discharges of polyatomic feed gases. Modeling of neutral polyatomic gas particle collisions has been developed in rarefied gas dynamics area, however, such techniques have not been applied to RF glow discharges. Borgnakke and Larsen [4] proposed polyatomic particle collision modeling as a phenomenological model for binary collisions in a low pressure mixture of polyatomic gases. Nanbu et al. [5] applied this model to simulate a SiH_4 thermal CVD process.

In this work we introduce a self-consistent particle model which considers motions and collisions of charged particles as well as of neutrals. We applied this model to an Ar plasma in a capacitively coupled RF reactor and studied the effect of neutral collision and motion. Next we combined the particle simulation technique in an RF plasma with a polyatomic particle collision scheme. We applied this technique to simulate a CH_4 RF plasma discharge (that can be eventually used for carbon film deposition studies).

Model Description

Simulation of a one-dimensional RF glow discharge reactor is carried out based on a PIC/MC method with the neutral and charged particles motions and collisions. The model comprises of elastic and ionizing electron-neutral collisions, ion-neutral and neutral-neutral collisions. Electron-electron and electron-ion collisions are neglected in the present study because the probability of such collisions are small. Electron-neutral collisions used in the simulations include elastic scattering, ionization and excitation. The neutral-ion collisions consider charge exchange only. The electron impact cross section data for Ar are summarized by Trombley et al.[6], while electron impact cross section for CH_4 is summarized by Gogolides et al.[7]. The cross-section data for neutral-neutral (Ar-Ar or CH_4-CH_4) collision is derived from Nanbu's model [5].

A simulation of an RF glow discharge begins with an equal number of electrons, ions and neutral particles, uniformly distributed in space between conducting electrodes and with a random Maxwellian velocity distribution. For the present calculations, 80 uniformly distributed grid points are used. Depending on the species being considered, 1 to 4000 time steps for each RF cycle was used. To start the simulations, 1,000 particles of each type are used. However, great numbers of charged (10^9 - 10^{12} cm^{-3}) and neutral particles (10^{14} - 10^{16}) are contained in a low pressure (50 - 250 mTorr) RF glow discharge. The weighting factor for each species depends on the respective number densities. The cell volumes are calculated such that the above number of particles considered represent the number densities of the charged and neutral particles. At the start of each time step, the positions of the charged particles are used to determine the charge density of the plasma for each cell. The potential across the plasma is given by Gauss's law. The potential across the plasma is calculated from the charge density and the boundary conditions. The electric field is given by the negative gradient of the electric potential. The electric field is updated only after a discrete number of particle motion time steps.

Results

a. Ar plasma discharge simulation

Ar (a monatomic gas) plasma simulation is carried out for a given set of parameters as given in Trombley et al.[6]. The discharge is powered by a 250 volt (peak-to-peak) source at 13.56 MHz. The gas pressure is 250 mTorr. the spacing between the electrodes is 2 cm. The secondary electron emission coefficient (γ)was set to 0. Anisotropic angular scattering is incorporated with the relative differential cross section for all electron and neutral collisions (Surendra and Graves [2]). Electron wall reflection ratio is 0.25 (Surendra and Graves [2]). The calculations are carried out for 1000 RF cycles and data are averaged between 500-1000 cycles.

One of the merits of the present model is that neutral motion is also considered, which broadens the application area of PIC/MC schemes. Instantaneous density profiles at time phase $\theta = 0$ are shown in Figure 1. Neutral density is almost uniform but slightly high at the electrodes due to the neutralization of the ions at the wall. Electron and ion densities are high (and equal) at the center of the plasma and low at the sheath regions due to the diffusion to the wall. Figure 2 shows instantaneous energy profiles at time phase $\theta = 0$. Neutral energy is uniform and is at room temperature (0.04 eV). Electron energy is high due to the heating by the electric field, ions are accelerated and have high energies at the sheath region. The energy probability distribution of impinging ions at the cathode are shown in Figure 3. The distribution has some peaks which means that the energies of ions are affected by the wave of the electric field in the sheath region. The electric field profiles at different time phases are shown in Figure 4. As expected, there is a large modulating field in the sheaths, while in the bulk, the field is negligible. Electron energy contours (Figure 5) and ionization rate contours (Figure 6) are shown as functions of space and time. The position of high ionization rate corresponds to the position of high electron energy.

b. CH_4 plasma discharge simulation

To simulate CH_4 plasma we combined the above particle simulation technique for RF plasma and a polyatomic molecule collision model. The total energy for polyatomic particles is expressed as the sum of the translational energy and the internal energies (such as rotation and vibration). The degrees of freedom for translational motion is 3. The internal degrees of freedom are zero for monatomic particles and electrons, and 12 for CH_4 ion assuming fully excited state. But for CH_4 neutral, (at room temperature), internal degrees of freedom is assumed to be 3 which can be obtained from specific heat data. For ionization and dissociation collisions, energy after collision is determined by the Borgnakke and Larsen [4] model. In this model, both the relative translational and the internal energies are assumed to be distributed according to their 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.

The species considered here are CH_4 neutral, CH_4^+, CH_4^*, and electron. CH_4^* is an excited molecule which will dissociate to CH_3 + H, CH_2 + H_2 or CH + H + H_2. For simplicity in the calculation procedure, the effect of dissociated species is represented by CH_4^*. The collisions considered here are CH_4-electron, neutral-radical and neutral-neutral collisions. The calculation conditions considered are different from that of Ar plasma (presented earlier) so that plasma could be sustained. A possible reason is that most of the supplied energy is lost by the dissociation process. The discharge is powered by a 500 voltage source at 13.56 MHz. The gas pressure is 250 mTorr and the spacing between the electrodes is 4 cm. The secondary electron emission coefficient γ was set to 0.05. Deposition probability rates are assumed to be 0.1 for radicals and 1.0 for ions. After deposition, the particle is eliminated from the calculation. The calculation is carried out for 1000 RF cycles and data are averaged between 500-1000 cycles. The neutral and radical densities were not in stable state even after 1000 RF cycles, hence further calculations are in progress now.

Instantaneous density profiles for the CH_4 plasma at time phase $\theta = 0$ are shown in Figure 7. Neutral density is almost uniform, while radical density is low at the wall due to deposition. Electron and ion densities are high (and equal) at the center of plasma and low at the sheath regions due to the diffusion to the wall. Figure 8 shows instantaneous energy profiles at time phase $\theta = 0$. Neutral and radical energies are uniform and at room temperature. The energy is higher than that of Ar neutrals (Figure 2), because energy is proportional to the total degrees of freedom of the particle. Secondary electrons emitted from electrode are accelerated by the strong electric field in the sheath region and have energy of several hundred eV. Electron energy in the sheath region is not continuous where sampled data number is small.

The energy probability distribution of impinging ions for the CH_4 plasma at the cathode are shown in Figure 9. This distribution is very important in studying the effect of ion bombardment in etching and deposition process. The electric field profiles at different time phase are shown in Figure 10. As expected, there is a large modulating field in the sheaths, while in the bulk the field is negligible. Ionization rate contours (Figure 11) and dissociation rate contours (Figure 12) are shown as functions of space and time. Dissociation rate is higher than ionization rate due to the large cross sections and low threshold energies (10 eV for dissociation, 14 eV for ionization). Ionization rate is high at sheath edge due to the heating by large modulating field in the sheaths, while dissociation rate is also high in the plasma bulk.

Conclusions and future work

Particle-in-cell Monte Carlo simulations of capacitively coupled glow discharges were developed and applied to Ar and CH_4 plasmas. This model includes the motions and collisions of both neutrals and charged particles. In Ar plasma, neutral density is found to be almost uniform between the electrodes and neutral energy is at room temperature. CH_4 plasma is modeled combining PIC/MC method and collision modeling of polyatomic gas particles. The model considers the motions and reactions CH_4, CH_4^+, CH_4^*(which represents dissociated species such as $CH_3 + H$, $CH_2 + H_2$ or $CH + H + H_2$), and electron. Space and time dependent results show, ionization rate is high at sheath edge while dissociation rate is also high in the plasma bulk.

In future, the calculations for CH_4 plasma will be continued until the neutral and radical densities reach quasi-steady state conditions. For CH_4 plasma the effects of dissociation to $CH_3 + H$, $CH_2 + H_2$ or $CH + H + H_2$ will be studied in detail. The feed gas mixture of CH_4/H_2 will also be studied. The deposition rates will be studied as a function of operating conditions such as pressure in the reactor, applied RF and DC voltages.

Acknowledgments

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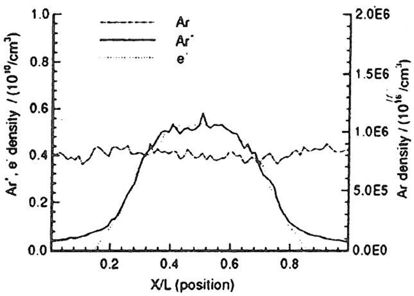

Fig. 1. Instantaneous density profiles for Ar plasma, at $\theta = 0$.

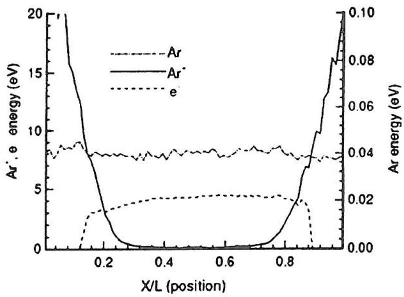

Fig. 2. Instantaneous energy Ar profiles for Ar plasma

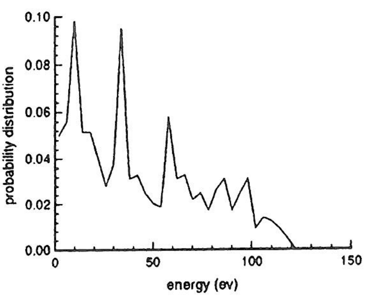

Fig. 3. Energy distribution of impinging ion at the cathode

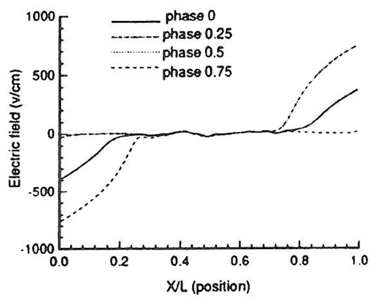

Fig. 4. Electric field profiles at different time phases

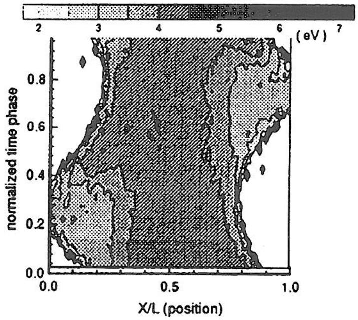

Fig. 5. Electron energy contours

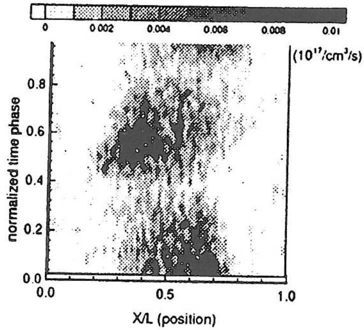

Fig. 6. Ionization rate contours

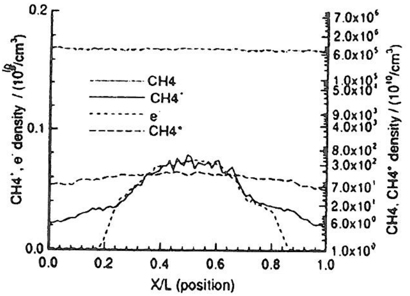

Fig. 7. Instantaneous density profiles for CH_4 plasma, at $\theta = 0$.

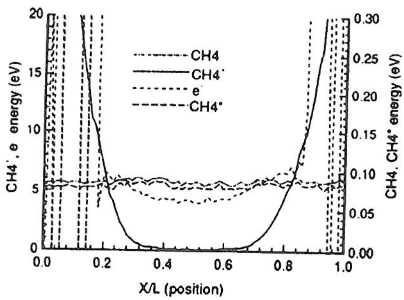

Fig. 8. Instantaneous energy profiles for CH_4 plasma

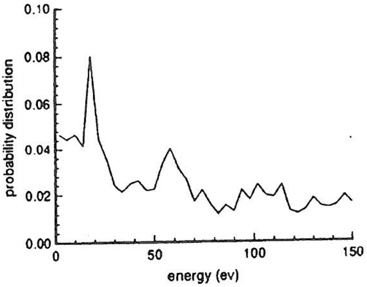

Fig. 9. Energy distribution of impinging ion at the cathode

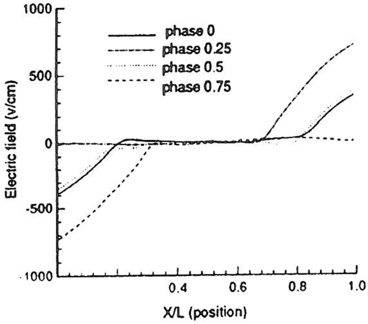

Fig. 10. Electric field profiles at different time phases

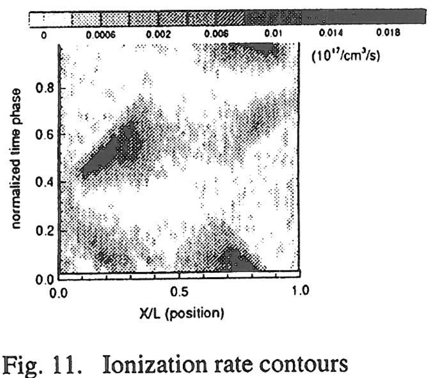

Fig. 11. Ionization rate contours for CH_4 plasma

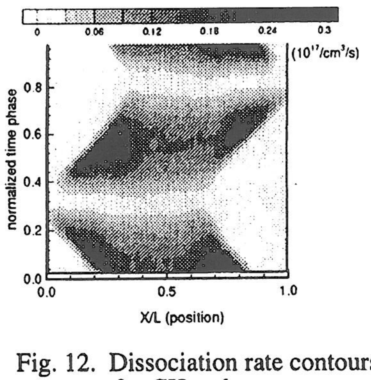

Fig. 12. Dissociation rate contours for CH_4 plasma