Global Model of Inductively coupled CH₄/H₂ Plasmas 誘導性結合型CH₄/H₂プラズマのグローバルモデル

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A global model for electropositive plasma is used in order to understand the plasma chemistry in CH₄/H₂ plasmas assuming the Maxwellian electron energy distribution. Most of CH₄ molecules are easily dissociated, so that the dominant neutral species are hydrogen molecules, CH₄ molecules and hydrogen atoms, followed by the hydrocarbons such as C₂H₃₈ (m=1,2 and 4). The dominant ions are CH₅⁺, C₂H⁺, C₂H₃⁺, C₂H₅⁺, and C₃H₅⁺ at low hydrogen fractions, whereas the density of H₃⁺ becomes dominant ion species as hydrogen fraction increases. Some measurable parameters such as electron density and its temperature are compared with the model results, obtaining reasonably good agreement.

1. Introduction
Theoretical studies of the plasmas in hydrocarbon-based feedstock for the PECVD of diamond-like, graphite-like and amorphous carbon films [1-5] have been reported. The global model is one of the methods that have been used in order to treat the physical and chemical processes in the plasmas. On the other hand, the models, in which the plasma chemistry and surface chemistry are combined, have been developed for thin-film deposition and etching purposes.[4,5] Mantzaris et al [4] combined plasma chemistry and surface chemistry models to study the diamond-like-carbon film deposition process for an rf capacitively coupled CH₄ discharge and showed that the surface reaction can greatly affect on the composition of neutral radicals in the plasma. The objectives of this research are to investigate the effect of hydrogen addition on plasma parameters in inductively coupled rf (13.56MHz) CH₄/H₂ plasmas and to understand the plasma chemistry of such plasmas using the global model.

2. Description of Model
A global model for electropositive plasma is applied to the CH₄/H₂ plasmas in a cylindrical chamber of radius \( R (\approx 80\,\text{mm}) \) and length \( L (\approx 75\,\text{mm}) \), since the ratio of negative ion to electron density should be assumed to be very low. 27 neutral species (CH\(_n\) (j=1-4), C\(_2\)H\(_j\) (j=1-6), C\(_3\)H\(_j\) (j=1-8), C\(_4\)H\(_j\) (j=1-9), C, C\(_2\), H\(_2\), H(1s), H(2s), and H(2p)) and 27 charged species (electrons, CH\(_n^+\) (j=1-5), C\(_2\)H\(_j^+\) (j=1-6), C\(_3\)H\(_j^+\) (j=1-8), C\(_4\)H\(_j^+\) (j=1-9), C\(^+\), H\(^+\), H\(_2^+\), and H\(_3^+\)) are considered in the model. All neutral species are assumed to be uniform over the chamber. Electrons, which have a Maxwellian energy distribution with electron temperature \( T_e \), are also assumed to be uniform over the chamber. All positive ion species, which are assumed to have the same profile, must satisfy the quasineutrality, \( n_e = n_+ \), where \( n_+ \) is the sum of the positive ion densities. The gas temperature in the discharge space is assumed to be 600 K. The surface processes for hydrogen atoms, CH\(_3\), and CH\(_2\), are incorporated in the model. The adsorption and desorption processes, and the adsorbed layer processes, in which the adsorbed species can react with the atomic hydrogen from the plasma yielding the gas-phase products, are mainly considered using same parameters [4,5]. The ions are directly incorporated in the growing film. Therefore, the sticking coefficient for ions can be assumed to be unity. The incorporation of ions is considered to occur on the whole surface, whereas the reactions between the adsorbed layer and the ions are not considered in this model.

The equations for each particle and power balance are then solved by the Runge-Kutta numerical method to obtain equilibrium.

3. Results and Discussion
In Figs. 1(a)-1(b), the electron density and its temperature are shown as a function of hydrogen fraction \( X_{\text{H}_2} \), together with the experimental results. The measured and calculated \( n_e \) gradually decrease with increasing \( X_{\text{H}_2} \). On the other hand, the measured and calculated temperatures slightly increase with the increase in \( X_{\text{H}_2} \). Since the ionization rates of hydrocarbons by electron impact are much larger than those of hydrogens, the electron temperature increases with the decrease in the density ratio in order to satisfy the balance of
the charged species productions and loss to the wall. The increase in electron temperature should contribute to the increase in the collisional energy loss between electrons and neutral species, such as hydrogens and hydrocarbons, resulting in the decrease in electron density with increase in $X_{\text{H}_2}$ under the same power injected into plasmas.

The densities of neutral species calculated at 25 mTorr are shown in Fig. 2. Most of CH$_4$ molecules are easily dissociated, so that the dominant neutral species are always hydrogen molecules, CH$_4$ molecules and hydrogen atoms, followed by the hydrocarbons such as C$_2$H$_m$ (m=1, 2 and 4). The increase in net production rate is roughly proportional to the product [CH$_x$][CH$_y$] of the densities of light hydrocarbons, resulting in the increase in densities of C$_2$H$_m$ larger than the increase in densities of light hydrocarbons.

The positive ion densities calculated at 25 mTorr is shown in Fig. 3. The dominant ions at $X_{\text{H}_2}$ lower than 50% are CH$_5^+$, C$_2$H$^+$, C$_3$H$^+$, C$_2$H$_3^+$, and C$_3$H$_5^+$, whereas the density of H$_3^+$ increases with the increase in $X_{\text{H}_2}$ and H$_3^+$ becomes dominant ion species at $X_{\text{H}_2}$ higher than 60-70%. Most of dominant hydrocarbon ions except C$_2$H$^+$ are mainly produced by the reactions between the hydrocarbon ions and CH$_4$ (or H$_2$), rather than direct ionization and dissociative ionization processes by the electron impact.

References