Kinetic Modeling of Rarefied Plasmas and Gases in Materials Processing

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Abstract. Plasma etching is the most important process in fabricating semiconductors. Production of plasma and radicals by electron-molecule collisions is strongly coupled with not only electromagnetic field but also rarefied flows of radicals, etch by-products, and gas molecules. A total simulation method to estimate the etch rate in inductively coupled plasmas is proposed. The etch rate obtained using the method showed a good agreement with measured data.

INTRODUCTION

Inductively-coupled plasma (ICP) is one of the key plasma sources for materials processing. The trend of the processing is toward high plasma density and low gas pressure (< 20mTorr). That is, plasma and gas are rarefied and hence the particle modeling based on the Boltzmann equation makes sense [1]. Economou et al. [2], carried out DSMC to examine the flow field of radicals and ions in an ICP reactor. Nanbu et al. [3] employed PIC/MC together with DSMC to predict etch rate of poly-Si in an ICP reactor. These works are not enough because the plasma production is decoupled from the gas flow. Here we consider the coupling and propose a more reliable particle modeling for predicting etch rate in ICPs.

GOVERNING EQUATIONS

We are doing experiments using the ICP reactor shown in Fig. 1. The 8-turned coils are wound around the quartz cylinder. The source gas Cl₂ is fed from the top of the quartz cylinder. Gases are pumped out from the bottom of the diffusion chamber. The wafer of poly-crystalline silicon with diameter of 6 inch is on the substrate holder at z = 0.

The goal of this study is to predict the optimum condition for uniform and high rate etching by modeling physical and chemical phenomena in the reactor. The optimum condition is found by adjusting such input parameters as the reactor size, mass flow rate of source gas, gas pressure in the reactor, coil current, and wafer biasing (power and frequency). The objective of the present work is to propose a total simulation method for predicting the etch rate. Here we consider the etching of Si-wafer by chlorine plasma. We try, however, to make a proposed method general as far as possible.

Figures 2 and 3 show the sets of e-Cl₂ and e-Cl collision cross sections, where e denotes electron. Radical atom Cl is produced by dissociation and dissociative attachment:

\[ e + Cl_2 \rightarrow e + 2Cl \] (1)
\[ e + Cl_2 \rightarrow Cl + Cl^- \] (2)

Reaction (2) yields also negative ion Cl⁻. Positive ions are produced by ionizations:

\[ e + Cl_2 \rightarrow 2e + Cl^+_2 \] (3)
\[ e + Cl \rightarrow 2e + Cl^+ \] (4)

The real reaction on Si-wafer is very complicated and still not clarified. We introduce a simplest model:

\[ Cl + \frac{1}{4}Si \rightarrow \frac{1}{4}SiCl_4 \] (5)
SiCl$_4$ is a volatile molecule. We see from reactions (1) to (5) that there exist 7 species in the reactor; electron (1), positive ions Cl$^+_2$(2) and Cl$^+(3)$, negative ion Cl$^-(4)$, and neutral species Cl$_2$ (5), Cl (6), and SiCl$_4$(7), where the numbers in the parentheses denote species hereafter. The Boltzmann equation for charged particles is 

$$\frac{\partial f_i}{\partial t} + c \cdot \frac{\partial f_i}{\partial x} + \frac{q_i}{m_i} (E + c \times B) \cdot \frac{\partial f_i}{\partial E} = \sum_{j=1}^{N} J_{ci}(f_i, f_j),$$

where $f_i$ is the velocity distribution function, $t$ is the time, $x$ is the position, $q_i$ and $m_i$ are the charge and mass of a particle, $E$ and $B$ are the electric and magnetic field, $N (= 7)$ is the number of species, and $J_{ci}(f_i, f_j)$ is the collision term for $i-j$ collision. In case of $i = 1$, the term $J_{ci}(f_i, f_j)$ for $j = 1-4$ denote Coulomb collisions, which may be disregarded when the plasma density is less than $10^{10}$ cm$^{-3}$. The Boltzmann equations for neutral species are also given by eq. (6) if we set $q_i = 0$ for $i = 5-7$.

Etching reaction (5) is usually ion-assisted. That is, in order to predict etch rate we require not only the flux of radical Cl onto the wafer but also the flux of ions. The flux $F_i$ for $i = 2, 3, 4, 6$ are obtained from 

$$F_i(r) = \int_{(c_z<0)} |c_z| f_i(e, r, z) de,$$

where $z = 0$ on the wafer and $r$ is the radial distance on the wafer. If $F_i(r)$ is constant, a uniform etching is realized.

Equation (6) shows that $f_i$ for charged species is directly influenced by the $E$- and $B$-field. On the other hand, $f_i$ for neutral species is also influenced by the fields through production and consumption of neutral species by energetic electrons. Anyway, we need the $E$- and $B$-field when we solve the Boltzmann equations. The fields are governed by the Maxwell equations:

$$\nabla \times E(x,t) = -\frac{\partial B(x,t)}{\partial t}$$

$$\nabla \times B(x,t) = \mu_0 J(x,t) + \frac{1}{c^2} \frac{\partial E(x,t)}{\partial t}$$

$$\nabla \cdot E(x,t) = \frac{\rho(x,t)}{\epsilon_0}$$

$$\nabla \cdot B(x,t) = 0$$

where $\mu_0$ and $\epsilon_0$ are the permittivity and dielectric constant of vacuum, respectively, $c$ is the speed of light, $J$ is the current density, and $\rho$ is the charge density. The second term of the right-hand side of eq.(9) is the displacement current.
which can be neglected in ICPs using a driving frequency of 13.56 MHz. Hereafter we neglect the displacement current. The solution of eqs.(8)-(11) can be found once $q$ and $J$ are given. The charge density $q$ is given by

$$q(x,t) = \sum_{i=1}^{4} q_i n_i(x,t)$$

where $n_i$ is the number density calculated from $f_i$:

$$n_i(x,t) = \int f_i(e,x,t)de$$

The current density is given by

$$J(x,t) = \sum_{i=1}^{4} q_i \int e f_i(e,x,t)de$$

We have already seen that when we solve the Boltzmann equations for charged species we need the $E$- and $B$- field. Now we see that when we solve the Maxwell equations we need the solutions of the Boltzmann equations for charged species. That is, the fields and the motion and collision of charged particles are coupled. This coupling makes the problem difficult to solve.

If the solutions $f_i$ are obtained, they may be employed to calculate various properties such as the density $n_i(x,t)$, flow velocity

$$V_i(x,t) = \frac{1}{n_i} \int e f_i(e,x,t)de$$

and temperature

$$T_i(x,t) = \frac{m_i}{3k_B} \left( \frac{1}{n_i} \int e^2 f_i(e,x,t)de - [V_i(x,t)]^2 \right)$$

where $k_B$ is the Boltzmann constant. The electron energy distribution function $\xi(e)$ is important because the dissociation rate constant $k_d$ is calculated from $\xi(e)$, where $\varepsilon = m_i c^2/2$ is the kinetic energy of electron. The function $\xi(e)$
is obtained from \( f_1(c_z, c_y, c_z, x, t) \):

\[
\xi(e) = \frac{\sqrt{2\varepsilon_e}}{m_1 m_1^{3/2}} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi F_1(c, \theta, \varphi, x, t)
\]

where \( F_1(c, \theta, \varphi, x, t) = f_1(c \sin \theta \cos \varphi, c \sin \theta \sin \varphi, c \cos \theta, x, t) \) and \( c = \sqrt{2\varepsilon_e / m_1} \). The rate constant \( k_d \) is given by

\[
k_d = \int_{\varepsilon_{th}}^{\infty} \sqrt{2\varepsilon / m_1} \sigma_d(e) \xi(e) d\varepsilon
\]

where \( \sigma_d(e) \) is the cross section for reaction (1) and \( \varepsilon_{th} \) is its threshold energy.

**DECOUPLING OF MAXWELL AND BOLTZMANN EQUATIONS**

An iterative procedure is used to decouple the Maxwell equations from the Boltzmann equations. We start from assumed distributions of \( \varrho \) and \( J \), e.g., \( \varrho = 0 \) and \( J = 0 \), and obtain the first approximation of \( E \) and \( B \). Then we solve the Boltzmann equations for charged particles and hence have an improved \( \varrho \) and \( J \) from eqs. (12) and (14). Using these renewed \( \varrho \) and \( J \), we solve the Maxwell equations and have the second approximation of \( E \) and \( B \). These \( E \) and \( B \) are used to find the solutions of the Boltzmann equations. These solutions are used to have a better approximation of \( \varrho \) and \( J \), which are used in obtaining the third approximation of \( E \) and \( B \). Repetition of these procedures may result in a convergence of \( E, B \), and \( f_i \).

**SOLUTION OF THE MAXWELL EQUATIONS**

We introduce the vector potential \( A \) and the scalar potential \( \phi \) by

\[
E = -\frac{\partial A}{\partial t} \cdot \nabla \phi \quad (15)
\]
\[
B = \nabla \times A \quad (16)
\]

Then the Maxwell equations without the displacement current take the form

\[
\nabla (\nabla \cdot A) - \nabla^2 A = \mu_0 J \quad (17)
\]
\[
\frac{\partial}{\partial t}(\nabla \cdot A) + \nabla^2 \phi = -\frac{\varrho}{\varepsilon_0} \quad (18)
\]

In ICPs with axisymmetrical discharge like the reactor in Fig. 1, we can set \( J_r = J_z = 0 \) and \( A_r = A_z = 0 \). Then we have \( \nabla \cdot A = 0 \) since \( \partial A_\theta / \partial \theta = 0 \). Now eqs. (17) and (18) become

\[
\left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} - \frac{1}{r^2} \right) A_\theta = -\mu_0 J_\theta \quad (19)
\]
\[
\nabla^2 \phi = -\frac{\varrho}{\varepsilon_0} \quad (20)
\]

Once \( A_\theta \) and \( \phi \) are obtained, we have, from eqs. (15) and (16)

\[
E_r = -\frac{\partial \phi}{\partial r}, \quad E_\theta = -\frac{\partial A_\theta}{\partial t}, \quad E_z = -\frac{\partial \phi}{\partial z}
\]
\[
B_r = -\frac{\partial A_\theta}{\partial z}, \quad B_\theta = 0, \quad B_z = \frac{1}{r \partial r}(r A_\theta)
\]

where we assumed \( \partial \phi / \partial \theta = 0 \), i.e., wafer biasing is also axisymmetrical. Usually the biasing angular frequency \( \omega_b \) is lower than the driving angular frequency \( \omega \) of the coils. It is probable, however, that the biasing has little effect on the plasma current \( J_\theta \) (\( \varrho \) and hence \( \phi \) is affected by both \( \omega \) and \( \omega_b \)). In this case we can write \( J_\theta = J_\theta(r, z)e^{j\omega t} \) and
The Boltzmann equation is solved in a particle image as in the case of PIC/MC or DSMC method. First, flow field is divided into small cells. The cell size should be the order of the Debye length for charged species and the order of mean free path for neutral species. We trace a time development of a system of plasma and gas. The time step \( \Delta t \) changes from species to species. The electron time step is chosen one order smaller than electron plasma oscillation period. The ion time step \( \Delta t_i \) and neutral time step \( \Delta t_n \) are divided into small cells. The cell size should be the order of the Debye length for charged species and the order of the particle mean free path for neutral species. We have to introduce the following iterative procedure. We assume a distribution function. Coulomb collisions are treated in the next section. The probability of ion–neutral and electron–neutral collisions may affect the electron energy distribution function. Coulomb collisions are treated in the next section. The probability of electron–neutral collision is given by

\[
P_{ni} = n_i c \sigma^T_b (\varepsilon) \Delta t
\]  

(23)
where $i = 5, 6, \text{ and } 7$ denote Cl$_2$, Cl, and SiCl$_4$, respectively, $c$ and $\varepsilon$ are the velocity and energy of electron, and $\sigma^T_i$ is the total collision cross section for $1-i$ collision. It is given by

$$\sigma^T_i = \sum_{k=1}^{K_i} \sigma_{ik}$$

(24)

where $\sigma_{ik}$ is the integrated cross section for collisional event $k$ of species $i$ and $K_i$ is the number of collisional events. For $e-Cl_2$ and $e-\text{Cl}$ collisions, $\sigma_{ik}$’s are in Figs. 2 and 3. For $e-\text{SiCl}_4$ collision, $\sigma_{ik}$’s appear not to be published. Equation (23) shows that electron collision is coupled with the flow fields of neutral species through $n_i$ ($i = 5-7$).

The total probability $P_1$ is $P_{15} + P_{16} + P_{17}$, i.e.,

$$P_1 = \sum_{i=5}^{7} \sum_{k=1}^{K_i} P_{1i,k}$$

where $P_{1i,k} = n_i \sigma_{ik}(\varepsilon) \Delta t$. The total number of collisional events is $K_5 + K_6 + K_7$. There is no need to obtain time-consuming $P_1$. Using only one random number, we can determine both whether electron collides or not in $\Delta t$ and which event out of $K_5 + K_6 + K_7$ events occurs in case of collision [5]. The post-collision velocity can be determined by use of the differential collision cross section [1]. If the data of the differential cross section is unknown, the scattering is assumed to be isotropic.

**Coulomb collision**

Coulomb collisions relevant to electron are treated based on Bobylev and Nanbu’s theory [6]. We consider all collisions $1-1, 1-2, \cdots, 1-N$, where 1 denotes electron and $N(=7)$ denotes SiCl$_4$ as before. The collisions are treated in two stages. In the first stage, the probability of $1-i$ collision $Q_{1i}$ is chosen to be

$$Q_{1i} = \frac{n_i}{n}$$

(25)

where $n(= n_1 + n_2 + \cdots + n_N)$ is the total number density. Of course, $Q_{11} + Q_{12} + \cdots + Q_{1N} = 1$. It is convenient to treat all simulated electrons in a cell together. Let $N_1$ be the number of simulated electrons in a cell. We divide $N_1$ electrons into $N(=7)$ groups: Electrons in group $i$ that consists of $N_1 Q_{1i}$ electrons make $1-i$ collision. Now we go to the second stage. Let electrons in group $i$ of $i \geq 5$ make a short-range collision with probability $P_{1i}/Q_{1i}$, where $P_{1i}$ is given by eq. (23). Note that the true probability of $1-i$ collision is $Q_{1i} \times (P_{1i}/Q_{1i})$, i.e., $P_{1i}$ as it should be. Next we consider groups of $i = 1-4$. Electrons in these groups make a Coulomb collision. First we consider group 1. The

**FIGURE 4.** Flow chart of total simulation.
number of 1−1 collisions in group 1 is \( N_1 Q_{11} / 2 \). We make \( N_1 Q_{11} / 2 \) electron pairs randomly and let two electrons of each pair collide. Let \( (e, e_2) \) be the pre-collision velocities of a pair. The post-collision velocities \( (e'_1, e'_2) \) are given by [7]

\[
\begin{align*}
    e'_1 &= c_1 - |g(1 - \cos \chi) + h \sin \chi| / 2 \\
    e'_2 &= c_2 + |g(1 - \cos \chi) + h \sin \chi| / 2
\end{align*}
\]

where \( g = c_1 - c_2 \) and the Cartesian components of \( h \) are

\[
\begin{align*}
    h_x &= g_x \cos \varepsilon \\
    h_y &= -(g_y g_x \cos \varepsilon + g g_x \sin \varepsilon) / g \perp \\
    h_z &= -(g_z g_x \cos \varepsilon - g y \sin \varepsilon) / g \perp
\end{align*}
\]  

(26a)

(26b)

(26c)

Here \( g \perp = (g_x^2 + g_y^2)^{1/2} \). The angle \( \varepsilon \) is given by \( 2 \pi U \), where \( U (0 < U < 1) \) is a uniform random number. The property of Coulomb collision is reflected on the scattering angle \( \chi (0 < \chi < \pi) \). It is given by [8]

\[
\cos \chi = A^{-1} \ln(e^{-A} + 2U \sinh A)
\]

where \( U \) is another random number and \( A \) is a solution of the equation

\[
\coth A - A^{-1} = e^{-s}
\]  

(27)

where

\[
s = (\ln \Lambda_{11} / \pi)(q_1^2 / \epsilon_0 m_1)^2 n_{11} g^{-3} \Delta t / Q_{11}
\]

Here \( \Lambda_{11} = 12 \pi n_1 \lambda_{\text{De}}^3 \), \( \lambda_{\text{De}} \) is the electron Debye length, and \( q_1 \) and \( m_1 \) are the charge and mass of electron.

Electrons in group \( i \) of \( i=2, 3, \) or 4 make \( N_i Q_{11} \), collisions with ions. Let \( e \) be the pre-collision velocity of a simulated electron. The post-collision velocity \( e' \) is given by

\[
e' = e \cos \chi - h \sin \chi
\]

where the components of \( h \) are given by eq. (26) by replacing all \( g' \)’s by \( v' \)’s. This time \( s \) in eq.(27) is given by

\[
s = (\ln \Lambda_{11} / 4\pi)(q_1^2 / \epsilon_0 m_1)^2 n_1 e^{-3} \Delta t / Q_{11}
\]

where \( \Lambda_{11} = \Lambda_{11} \).

Collision of ion

Even if we neglect ion-ion collisions, ion-neutral species collision should always be considered because the density of neutral species is one order larger than ion density. Let \( i=(2, 3, 4) \) denote ion and \( j=(5, 6, 7) \) denote neutral species. The collision probability of an ion is given by

\[
P_i = \sum_{j=5}^{7} \sum_{k=1}^{N_j} P_{ik}
\]  

(28)

where \( N_j \) is the number of simulated particles of species \( j \) in a cell and

\[
P_{ik} = \frac{n_j}{N_j} g_{ik} \sigma \tau (g_{ik}) \Delta t
\]

with \( g_{ik} = |e_k - e_i| \). \( P_{ik} \) is the collision probability that ion \( i \) collides with a neutral particle \( k \) of species \( j \). Since \( P_i \) depends on \( n_j \) and the velocities of neutral species, ion collisions are coupled with the flow field of neutral species. \( P_i \) consists of \( N_5 + N_6 + N_7 (\equiv N_n) \) probabilities. If we chose \( \Delta t \) in such a way that the maximum of \( P_{ik} \)’s is less than \( 1 / N_n \), we can apply the method [5] to determine whether ion \( i \) collides or not and which neutral particle is a collision partner. The post-collision velocity of ion is determined by use of hard-sphere model or dipole-interaction potential. If the data on ion drift velocity are known, charge exchange collision can be modeled [9].

Collision of neutral particle

Number densities of source gas, radicals, and etch by-product are usually one order larger than the densities of charged particles. So we can treat that collisions among neutral species separately from charged species. Let \( i=(5, 6, 7) \) denote neutral species. Unlike collisions are \( 5 - 6, 5 - 7, \) and \( 6 - 7 \) and like collisions are \( 5 - 5, 6 - 6, \) and \( 7 - 7 \). The maximum collision number method [11] used in DSMC is computationally most efficient.
COMPARISON OF SIMULATION AND EXPERIMENT

Simulated etch rate is compared with measured one in Fig. 5. The Si-wafer is biased with 13.56 MHz in our experiment. Ion-assisting effect of biasing on promoting etching is expressed by the probability $P_r$ of reaction (5) in the simulation. That is, eq. (20) was not solved under the condition of wafer biasing; we introduced a static sheath model to all solid walls instead. For a choice of $P_r = 0.16$ the simulation data showed a good agreement with the measurements. Computational conditions are as follows. Total gas pressure is 1 Pa. Mass flow rate of the source gas Cl$_2$ is 50 sccm. Probability of recombination ($\text{Cl} \rightarrow \frac{1}{2}\text{Cl}_2$) on all chamber walls is set 0.03. The driving frequency of the coil current is 13.56 MHz. The rf amplitude of the coil current is chosen in such a way that the total power deposition into plasma is 500 W. Figure 6 shows the electric field $|E_\theta|$ at gas pressure of 1 Pa. The field is strong only in the skin depth near the wall of the quartz cylinder. For a fixed power deposition of 500 W we examined the effect of gas pressure on the skin depth in the range of 0.5 Pa to 2.0 Pa. The skin depth becomes thinner as pressure decreases. This is because the electron density in the skin depth increases with decreasing gas pressure.

REFERENCES