Numerical Simulation of a Single-Wafer Isothermal Plasma Etching Reactor

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ABSTRACT

A two-dimensional finite element simulation of the gas flow and reactive species distribution in a parallel-plate single-wafer isothermal reactor was conducted. The oxygen plasma etching of polymer under high pressure (~1 torr), high frequency (13.56 MHz) conditions was chosen as a model system for analysis with emphasis on chemical etching. Etching rate and uniformity were examined as a function of reactor operating parameters. The maximum in etching rate with flow rate was observed, and this maximum shifted to higher flow rates as the pressure increased. The pressure dependence of the etching rate was complex, but in general a broad maximum in etching rate with pressure existed, which shifted to higher pressures as the flow rate increased. Etching rate increased but etching uniformity degraded as the wafer reactivity increased. A shower radius at least equal to the wafer radius, and a plasma radius slightly greater than the wafer radius were found to give the best etching rate and uniformity. Two novel reactor designs were also studied, namely, a reactor with a graded gas velocity at the shower, and a pulsed-plasma reactor. When compared to the conventional reactor, the new designs can yield improved uniformity and etching rate (the etching rate of the pulsed-plasma reactor was prorated by the duty cycle).

Plasma-assisted etching and deposition of thin films using reactive gas flow discharges is currently in widespread use in the microelectronics industry. However, despite the importance of plasma processing, reactive gas flow discharges are not well understood. This may be due to the nonequilibrium nature of the plasma, and the complex interaction among potential field, transport phenomena, plasma chemistry, and surface reaction kinetics. The fact that plasma reactor design was still based largely on empirical approaches is not surprising. Recently, there has been an increased interest in developing mathematical models of the plasma process in an effort to better understand the process, and to assist in the rational design of plasma reactors (2-10). The modeling studies have been complemented by a host of plasma diagnostic techniques (11-13).

Important requirements of plasma-assisted etching include high etching rate, uniformity, anisotropy, and selectivity, and no radiation damage. However, as is often the case in complex engineering systems, it is very difficult to satisfy all of the above requirements simultaneously. For example, one may desire to operate at relatively high pressure in order to increase the etching rate. Nevertheless, under such condition one may have to sacrifice uniformity, because of low reactant diffusivity, and/or anisotropy because of low ion bombardment energy. Therefore, "optimum" parameter settings may be identified for which the etching rate, for instance, is maximized while uniformity and anisotropy are within acceptable limits.

As the wafer size continues to increase and stringent requirements are placed on reactor uniformity, the use of single-wafer reactors becomes increasingly compelling. In addition to improved uniformity, other advantages of single-wafer etchers, as compared to multi-wafer batch systems, are better process control and reproducibility. Although single-wafer etching reactors are used extensively in the semiconductor industry, there are very few published works on the transport and reaction phenomena occurring in such reactors.

A mathematical model for a single-wafer etcher was recently developed (2). Given information on reaction kinetics, the model predicted etching rate, uniformity, and anisotropy. Emphasis was placed on the effect of reactor operating conditions on etching uniformity. The oxygen plasma system was selected to test the model predictions. An experimental technique based on optical emission actinometry and the Abel transform was developed to obtain the three-dimensional etchant concentration profile. Experimental data were in good quantitative agreement with the model predictions over a wide range of operating conditions. The encouraging results of this earlier work prompted the authors to carry out a more detailed investigation of the single-wafer etcher.

In the present work, an extension of the previous mathematical model is presented. Specifically, a more practical reactor configuration was considered including part of the etching chamber downstream from the plasma region, and separate mass balances for the etchant species and for the parent gas molecules were written. The finite element method was used to calculate the fluid velocity distribution and in turn the concentration distribution of active species. A similar model was very recently reported by Kobayashi et al. (6) for the etching of aluminum. In the present work, the oxygen plasma etching of polymer was used as a model system because pertinent reaction constants are known, and because the electron density and energy can be estimated as a function of reactor geometry and operating parameters. The effect of reactor design on the etching rate and uniformity was studied assuming that chemical etching was the dominant mechanism (negligible ion-assisted etching). The effect of flow rate, pressure, power, etching rate constant, and radius of electrode, wafer, and shower was studied. Two novel reactor designs were also examined, namely, a reactor with a graded gas flow velocity at the showerhead, and a pulsed-plasma reactor.

Mathematical Model Formulation

The model was developed for the single-wafer etcher shown schematically in Fig. 1. The axisymmetric reactor has a showerhead upper electrode and a lower electrode where the wafer rests. Feedstock gas enters through the shower of the showerhead electrode and is pumped radially towards the reactor exit. The plasma was assumed to be confined between the equal area electrodes, and the gas temperature was assumed to be spatially uniform. Furthermore, the wafer was assumed to be in good thermal contact with the temperature-controlled lower electrode.

The reactor dimensions are shown in Fig. 2 where, owing to symmetry, only half of the reactor is shown. The two electrodes were assumed to have the same radius, r2. However, the wafer radius r1 as well as the shower radius r3 of the showerhead electrode could be smaller than the electrode radius. Radii r1, r2, and r3 were varied. Other reactor dimensions were kept constant at the values shown in Fig. 2. Basic parameter values used for calculations and the range of parameter values examined are shown in Table I. Other parameter values are shown in Table II.

As with any plasma etching reactor, modeling of the single-wafer etcher requires consideration of the plasma physical chemistry, the ion transport in the sheath, and the transport and reaction phenomena of important species and of heat in both the plasma region and the "downstream" region. The present investigation emphasizes ap-
Applications for which ion-assisted etching is of secondary importance. Hence, ion transport in the sheath was not considered. In the case of polymer etching in an oxygen discharge examined here, appropriate conditions for chemical etching to dominate would be relatively high pressure (~1 torr) and high excitation frequency (>10 MHz). Furthermore, a simplified treatment of the gas discharge was adopted, as was done in previous work (2, 3). Specifically, the effective electric field $E_{el}$ approximation was used, and the ratio $E/P$ was found as a function of $pA$, where $p$ is the gas pressure and $A$ is the electron diffusion length given by

$$\frac{1}{A^2} = \left( \frac{2.405 \times 10^3}{r_2} \right)^2 + \left( \frac{\pi}{H} \right)^2 \tag{1}$$

In addition, a Maxwellian electron energy distribution function was assumed with an electron temperature which is a unique function of $E/P$. The average electron density in the plasma region $n_e$ was found by

$$\frac{P}{n_e e^2 E_{el}} = \frac{n_e e^2 E_{el}}{v_p} \tag{2}$$

where $P$ is the power dissipated in the plasma, $v_p$ is the plasma volume ($v_p = \pi H r_2^2$), $e$ and $m$ are the electron charge and mass, respectively, and $v_e$ is the electron momentum transfer collision frequency. An electron density equal to zero was assumed outside the plasma. An important assumption was that the discharge is not significantly affected by the etching reaction products, i.e., the discharge was treated as if it were one in pure oxygen. This assumption is better for low etching rate and high gas flow rate, conditions which minimize the concentration of reaction products. The advantages of the above treatment of the discharge are simplicity of calculation and account of the variation of electron energy and density with reactor geometry and operating conditions. The disadvantages of the above treatment are that the model is not applicable in the low-pressure, low-frequency regime where secondary electron emission effects may be important, the electron energy distribution function which may well be non-Maxwellian is not found, and any effects of the etching reaction products on the plasma chemistry are not considered. Nevertheless, use of the simplified discharge model has been previously met with success (2, 3).

With the electron temperature $T_e$ known, the rate constant of reactions involving electrons may be calculated. For example, the rate constant $k_p$ of the electron impact dissociation reaction [R1], may be found using Eq. [3] below, where $r_o(e)$ is the reaction cross section as a function of electron energy $e$, and $k$ is the Boltzmann constant

$$k_p \propto \frac{kT_e}{e^{3/2}} \exp \left(-\frac{e}{kT_e}\right) \tag{3}$$

**Fluid velocity distribution**—Under the conditions examined, the pressure is high enough for the continuum approximation to be valid, and the flow is isothermal, laminar, and axisymmetric. Moreover, neglecting any change in the number of moles due to reaction, the momentum balance equations can be decoupled from the mass balance equations. The velocity field was obtained by solving the steady-state Navier-Stokes equations

$$\rho \frac{\partial v}{\partial t} = \nabla \cdot (\tau + \rho g) \tag{4}$$

where the tensor

$$\tau = -\rho I + \mu (\nabla v + (\nabla v)^T) \tag{5}$$

$I$ being the identity matrix, along with the continuity equation

$$\nabla \cdot v = 0 \tag{6}$$

Here $v = (U, W)$ is the fluid velocity vector, $U$ is the radial velocity, $W$ is the axial velocity, and $\rho$ and $\mu$ are the fluid density and viscosity, respectively. The following boundary conditions were applied on fluid velocity, where the boundary condition (BC) number refers to the corresponding surface as shown in Fig. 3

$$\frac{\partial W}{\partial n} = 0 \quad U = 0 \tag{7}$$

### Table I. Parameter values used for calculations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Basic value</th>
<th>Range examined</th>
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</thead>
<tbody>
<tr>
<td>$k_p$</td>
<td>Etching rate constant</td>
<td>50 cm/s</td>
<td>10-100 cm/s</td>
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<tr>
<td>$P$</td>
<td>Plasma power</td>
<td>100 W</td>
<td>25-200W</td>
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<tr>
<td>$p$</td>
<td>Gas pressure</td>
<td>1 torr</td>
<td>0.5-2 torr</td>
</tr>
<tr>
<td>$Q$</td>
<td>Inlet gas flow rate</td>
<td>100 sccm</td>
<td>10-500 sccm</td>
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<tr>
<td>$r_1$</td>
<td>Wafer radius</td>
<td>5 cm</td>
<td>1-6.5 cm</td>
</tr>
<tr>
<td>$r_2$</td>
<td>Electrode radius</td>
<td>6.5 cm</td>
<td>3-8 cm</td>
</tr>
<tr>
<td>$r_3$</td>
<td>Shower radius</td>
<td>6.5 cm</td>
<td>1-8 cm</td>
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### Table II. Other parameter values

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Value</th>
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</thead>
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<tr>
<td>$H$</td>
<td>Interelectrode spacing</td>
<td>2.2 cm</td>
</tr>
<tr>
<td>$f$</td>
<td>Plasma pulsing frequency</td>
<td>106 Hz</td>
</tr>
<tr>
<td>$T$</td>
<td>Gas temperature</td>
<td>298 K</td>
</tr>
<tr>
<td>$k_1$</td>
<td>Volume recombination rate constant</td>
<td>4.762 10$^{-14}$ cm$^3$/mol$^2$/s</td>
</tr>
<tr>
<td>$k_2$</td>
<td>Volume recombination rate constant</td>
<td>8.343 10$^{-14}$ cm$^3$/mol$^2$/s</td>
</tr>
<tr>
<td>$k_3$</td>
<td>Volume recombination rate constant</td>
<td>5.441 10$^{-15}$ cm$^3$/mol$^2$/s</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Wall recombination coefficient</td>
<td>1.6 10$^{-4}$</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic of the parallel-plate single-wafer etching reactor studied.

Fig. 2. Dimensions of the single-wafer etching reactor considered; $r_1$, $r_2$, and $r_3$ were varied.
Here \( n \) is the unit normal pointing outwards the computational domain, and \( W_w \) is the gas velocity at the shower of the showerhead electrode (reactor inlet velocity). Three cases were examined: (i) a uniform gas velocity at the shower

\[
W_w = \frac{Q}{\pi r_0^2} \quad [11]
\]

\( Q \) being the feedstock gas volumetric flow rate at plasma reactor conditions, (ii) a gas velocity which was zero at the shower center \( r = 0 \), and which increased linearly with radial position to its maximum value at the shower edge \( r = r_s \)

\[
W_w = \frac{2Qr}{\pi r_0^2} \quad [12]
\]

and (iii) a gas inlet velocity which was maximum at the shower center and which decreased to zero at the shower edge

\[
W_w = \frac{2Q}{\pi r_0^2} (r_0 - r) \quad [13]
\]

BC1 is a symmetry condition along the reactor centerline, BC2 is the boundary condition at the shower (along segment AB in Fig. 2), BC5 implies a fully developed gas flow at the reactor exit, and BC3, BC4, BC6-BC9 are the no-slip condition at solid surfaces.

**Mass transport and reaction.**—A variety of neutral and charged species in both the ground and excited states may be found in the oxygen discharge (14-16). Important neutral species are molecular and atomic oxygen and perhaps metastable oxygen and ozone. However, molecular oxygen at the ground state is the dominant gas-phase species. Atomic oxygen has been found to be the main etchant in relatively high pressure oxygen plasma etching of photoresist (17, 18). In order to simplify the analysis, only three neutral species were considered, namely, molecular and atomic oxygen, and etching reaction product. Constants \( k_1, k_2, \) and \( k_3 \) were obtained from the literature (14). Volume recombination reactions are strongly pressure dependent and are normally insignificant at pressures less than about 1 torr. In this work \( M \) was assumed to be \( O_2 \), the dominant gas-phase species. The etching reaction rate constant was assigned a basic value of \( k_n = 50 \) cm/s. However, the effect of changing the value of \( k_n \) was examined. Constant \( k_w \) was written as

\[
k_w = \frac{k_w}{\gamma_u} \quad [14]
\]

where \( \gamma \) is the wall recombination coefficient, and \( u_0 \) is the thermal velocity of the oxygen atoms given by

\[
u_0 = \sqrt{\frac{2kT_0}{\pi M_1}} \quad [15]
\]

where \( M_1 \) is the oxygen-atom mass and \( T \) is the gas temperature. The value of the wall recombination coefficient was assumed to be \( \gamma = 1.6 \times 10^{-4} \) (20).

Mass balance equations were written for both molecular and atomic oxygen, neglecting multicomponent diffusion effects and using a pseudo-binary diffusion coefficient

\[
\frac{\partial C_1}{\partial t} + \mathbf{v} \cdot \nabla C_1 = \nabla \cdot (D_1 \nabla C_1) + G_1 \quad [16]
\]

where \( C \) is the total gas concentration \( C = p/R_0T \), and \( C_1, C_2, \) and \( C_3 \), are molar concentration, mole fraction, diffusion, and net production rate of species i, respectively. Subscripts 1 and 2 refer to atomic and molecular oxygen, respectively. The net volumetric production rate of atomic oxygen was written as

\[
G_1 = 2k_1(t) n(t) C_2 - (k_1 C_1 C_2 + 2k_2 C_1^2 C_2 + 2k_3 C_1^3) \quad [17]
\]

and that of molecular oxygen was written as

\[
G_2 = -k_2(t) n(t) C_2 - k_3 C_1 C_2^2 + (k_2 C_1 C_2 + k_3 C_1^2) \quad [18]
\]

The first term on the right-hand side (rhs) of Eq. [17] is the production of O atoms according to reaction [R1]. The corresponding rate constant and the electron density are a function of time in the case of pulsed-plasma reactor considered later. The first, second, and third terms in parenthesis on the rhs of Eq. [17] correspond to O-atom eliminations according to reactions [R2], [R3], and [R4], respectively. Despite the fact that the production of etchant is localized in space and occurs in the discharge region only, etchant volumetric recombination occurs throughout the reactor volume. The mass balance for the reaction product \( P \) was not considered since its mole fraction can be found from the other two species mole fractions and the fact that the mole fractions must sum up to unity. The O\textsubscript{2}O\textsubscript{2} binary diffusion coefficient was estimated from experimental collision diameter data (21), and the O\textsubscript{2}O\textsubscript{2} self-diffusion coefficient was estimated using standard techniques (22). Etching and wall recombination reactions enter in the boundary conditions for Eq. [16] which are described below

\[
\begin{align*}
BC1 & : \quad \frac{\partial C_1}{\partial n} = 0 \quad [19] \\
BC2 & : \quad D_C \frac{\partial C_1}{\partial n} = W_w (C_{1o} - C_1) \quad [20] \\
BCC3, 4, 6-8 & : \quad \left\{ \begin{array}{l}
D_C \frac{\partial C_1}{\partial n} = -k_w C_1 \\
D_C \frac{\partial C_1}{\partial n} = 1 - k_w C_1
\end{array} \right. \quad [21, 22]
\end{align*}
\]

Here \( k_1, k_2, k_3 \) are the volume recombination rate constants, \( k_n \) is the etching reaction rate constant, and \( k_w \) is the wall recombination rate constant. \( M \) is a third body required to conserve both energy and momentum during collision, \( S \) is the polymer surface where etching occurs, \( W \) represents a wall, and \( P \) represents the etching reaction product. Constants \( k_1, k_w, \) and \( k_n \) were obtained from the literature (14). Volume recombination reactions are strongly pressure dependent and are normally insignificant at pressures less than about 1 torr. In this work \( M \) was assumed to be \( O_2 \), the dominant gas-phase species. The etching reaction rate constant was assigned a basic value of \( k_n = 50 \) cm/s. However, the effect of changing the value of \( k_n \) was examined. Constant \( k_w \) was written as

\[
k_w = \frac{k_w}{\gamma_u} \quad [14]
\]
was applied. This discharge was treated as if it were one in pure oxygen, i.e., product interference was neglected. (ii) Only neutral chemistry was considered, and atomic oxygen was taken to be the only etchant species of photoresist. (iii) Ion bombardment effects were neglected. (iv) Linear etching and wall recombination reactions were assumed. (v) The electron energy distribution function was assumed Maxwellian. (vi) The continuum approximation was made, and the gas was assumed to be a Newtonian incompressible fluid with constant physical properties (density, viscosity). (vii) Multicomponent transport effects were neglected and a constant diffusivity was used. (viii) Only neutral chemistry was considered, and atomic oxygen was taken to be the only etchant species of photoresist. (ix) Linear etching and wall recombination reactions were assumed. (x) The effective rate constant for etching at the wafer surface. Only chemical etching was considered, and simple linear kinetics was assumed (17, 23).

Before proceeding any further, the model assumptions are summarized below. (i) The discharge was treated as if it were one in pure oxygen, i.e., product interference was neglected. (ii) Only neutral chemistry was considered, and atomic oxygen was taken to be the only etchant species of photoresist. (iii) Ion bombardment effects were neglected. (iv) Linear etching and wall recombination reactions were assumed. (v) The electron energy distribution function was assumed Maxwellian. (vi) The continuum approximation was made, and the gas was assumed to be a Newtonian incompressible fluid with constant physical properties (density, viscosity). (vii) Multicomponent transport effects were neglected and a constant diffusivity was used. (viii) Only neutral chemistry was considered, and atomic oxygen was taken to be the only etchant species of photoresist. (ix) Linear etching and wall recombination reactions were assumed. (x) The effective rate constant for etching at the wafer surface. Only chemical etching was considered, and simple linear kinetics was assumed (17, 23).

The finite element method was used to solve the governing equations (24, 25). The computational domain and the finite element mesh used for most calculations are shown in Fig. 3. Owing to symmetry, only half of the reactor was considered. Figure 3 refers to the base case corresponding to the parameter values shown in the third column of Table I (i.e., \( \tau_3 = \tau_6 = 6.5 \) cm, and \( \tau_3 = 5 \) cm). The momentum balance and the mass balance equations were solved separately. Such decoupling of the equations is permissible in isothermal systems in which there is negligible change in the number of moles upon reaction. In the present case, the approximation is better at low power and pressure and high flow rate, conditions which result in small degree of dissociation of the parent gas. The decoupling of the equations resulted in substantial savings in computation time. The continuity and momentum balance Eq. [4]-[6] along with the associated boundary conditions Eq. [7]-[10] were solved first. The penalty function formulation (26, 27) was employed to eliminate pressure as one of the dependent variables. The penalty parameter was selected as \( 10^6 \) (27).

The convective diffusion Eq. [16] subject to boundary conditions Eq. [19]-[24] were solved next using the known velocity field. The streamline upwind Petrov-Galerkin finite element method (28, 29) was used with bilinear basis functions. The resulting set of nonlinear algebraic equations was solved using the skyline solver of gauss elimination (24). For all the results reported below the steady-state form of Eq. [16] was solved, except for the pulsed-plasma reactor.

For the pulsed-plasma reactor, it was assumed that the flow field is not affected by the pulse, and therefore the steady-state fluid velocity distribution was used. The finite element discretization of the convective diffusion Eq. [16] led to a set of ordinary differential equations of the form

\[
\dot{\mathbf{C}} + \mathbf{N}(\mathbf{C}) = \mathbf{F}
\]

where \( \mathbf{C} \) is the temporal derivative of vector \( \mathbf{C} = (C_1, C_2, \ldots, C_M) \), \( \mathbf{M} \) is the mass matrix, \( \mathbf{N}(\mathbf{C}) \) is a nonlinear vector-valued function, and \( \mathbf{F} \) is the force vector. A predictor/multi-corrector scheme with generalized trapezoidal method was employed to solve Eq. [25] (24). The following error norm was used to detect the periodic steady-state solution

\[
\varepsilon_{\text{res}} = \left( \sum_{i=1}^{N_b} \left( \frac{R_i}{R_{\text{avg}}} \left( \frac{R_i}{R_{\text{avg}}} \right)^{1/2} \right)^2 \right)^{1/2}
\]

where \( \varepsilon_{\text{res}} \) is a user-specified error tolerance, \( N_b \) is the number of nodes along the wafer radius (typically 15), \( R_i \) is the etching rate at node \( i \), \( R_{\text{avg}} \) is the average etching rate, \( I \) is an integer counter, and \( T_p \) is the pulse period. The number of pulse periods and (hence the computation time) required to achieve the periodic steady-state depended critically on the gas flow rate, and it was typically several hundred (using \( \varepsilon_{\text{res}} = 10^{-4} \) for low flow rates e.g., 20 sccm) decreasing at higher flow rates. The time integration step was chosen ten times smaller than the pulse period.

**Results and Discussion**

The effect of the parameters shown in Table I on etching rate and uniformity was studied. Basic parameter values are shown in the third column of Table I. The range of parameter values examined is shown in the fourth column of the same table. Parameter values shown in Table II were kept constant. In order to study the effect of a parameter, the value of that parameter was varied while keeping the other parameters at their basic value. In the following calculations all parameters were at their basic value unless noted otherwise.

Figure 4 is a velocity vector plot. The vectors show the magnitude and direction of the local fluid velocity. The axial velocity component has its maximum value at the reactor entrance (\( r = 0.0-6.5 \) cm, \( z = 2.2 \) cm) and decreases monotonically to become zero at the wafer surface. The ra-

![Fig. 3. Finite element mesh used for most calculations. BC number indicates the surface on which the corresponding boundary condition was applied.](image)

![Fig. 4. Fluid velocity vector plot. Parameters were at their basic value.](image)
The plasma volume above the relatively inert electrode to where a reactive surface (wafer) and a relatively inert surface meet. This is due to etchant diffusing from the plasma volume above the relatively inert electrode to react on the wafer. Since the etching rate is a monotonic function of etchant concentration, such gradient would result in nonuniform etching. In fact, the situation depicted in Fig. 5 would result in a “bullseye” film clearing pattern in which the film clears at the wafer edges first. Beyond the shower edge and up to the reactor corner region (around \( r = 10 \text{ cm} \)) the velocity profile is nearly parabolic with a zero axial component. Approximate analytic expressions for the velocity distribution in the plasma region were given before (2).

Figure 5 shows the etchant (O-atom) mole fraction distribution. The mole fraction varies between 5.3 and 8.4% under the conditions of Fig. 5. Since the wafer is a sink of reactant. Hence, a maximum etching rate exists. The maximum shifts slowly to higher flow rate as the power increases. One further observes that the etching rate is not as sensitive to flow rate at very high flow rates. The etching rate profiles will be identical to the concentration profiles shown in Fig. 6. The spatially averaged etch rate concentration first increases with flow rate, reaches a maximum, and then decreases monotonically with flow rate. The flow rate effect is examined in more detail below (Fig. 7).

Figure 6 shows the atomic oxygen concentration as a function of radial position along the wafer surface for different values of the gas flow rate. Other parameters were at their basic value. One observes large concentration gradients around the periphery of the wafer (\( r = 5 \text{ cm} \)) and around the plasma edge (\( r = 6.5 \text{ cm} \)), and the concentration reaches a maximum between these two locations. The maximum in concentration can be clearly seen in Fig. 5 as well. Moreover, since the etching rate was assumed proportional to the etchant concentration (Eq. [29] below), the etching rate profiles will be identical to the concentration profiles shown in Fig. 6. The spatially averaged etch rate concentration first increases with flow rate, reaches a maximum, and then decreases monotonically with flow rate. The flow rate effect is examined in more detail below (Fig. 7).

The etching rate \( R \) was calculated by

\[
R(A/\text{min}) = CF R(\text{mol O/cm}^2\text{-s}) \tag{27}
\]

where the conversion factor \( CF \) is given by

\[
CF = \frac{1}{q} \left( \frac{MWf}{\rho_t} \right) \left( \frac{60}{10^{-3}} \right) \tag{28}
\]

and \( R(\text{mol O/cm}^2\text{-s}) \) is given by

\[
R = \kappa_0 C_t \tag{29}
\]

Here \( C_t \) is the local O-atom concentration, \( q \) is the number of moles of atomic oxygen consumed by one mole of the monomeric unit of the polymer (photoresist) film, \( \rho_t \) and \( MWf \) are the film density and molecular weight of the monomer, respectively. The values used were \( q = 11 \), \( \rho_t = 1.28 \text{ g/cm}^3 \), \( MWf = 94 \). These values correspond to etching of a Novolac-type photoresist represented by the formula \((\text{C}_6\text{H}_6\text{O})_n\), assuming that half of the carbon is converted to \( \text{CO}_2 \) and the other half to \( \text{CO} \) (30). The above parameter values are arbitrary but reasonable, and are used here simply to give an idea of what the etching rate in a single-wafer reactor may be under the conditions examined. The average etching rate was calculated from the local etching rate by using

\[
R_{av} = \frac{2}{r_3^2} \int_0^{r_3} R r dr \tag{30}
\]

Figure 7 shows the average etching rate as a function of the flow rate for different values of power. At low flow rates etching is limited by reactant supply, and at high flow rates etching is limited by convective removal of the reactant. Hence, a maximum etching rate exists. The maximum shifts slowly to higher flow rate as the power increases. One further observes that the etching rate is not as sensitive to flow rate at very high flow rates. The etching
rate was found to increase almost linearly with power at low power values. This was the result of electron density increasing linearly with power. However, the power dependence of etching rate turned into sublinear at higher power values, especially at high pressure.

The effect of pressure is shown in Fig. 8. Over the pressure range examined, the etching rate is relatively insensitive to pressure at low flow rate, but increases rapidly with pressure at high flow rate. At very high pressure, the etching rate is expected to fall because volume recombination reactions become very important, and because the electron energy decreases with pressure resulting in lower dissociation rate. For a given flow rate, the pressure dependence of the etching rate appears to exhibit a broad maximum, and this maximum shifts to higher pressure as the flow rate increases. Similar behavior has been found in a plasma-assisted downstream etching reactor (31).

The local etching rate as a function of radius along the wafer is shown in Fig. 9, with the chemical etching rate constant $k_n$ as a parameter. Etching is fairly uniform when the reactivity of the wafer is low (small $k_n$). Under such condition, diffusion is rapid enough to replenish the reactant consumed on the wafer surface. This is not the case, however, when etching is rapid (large $k_n$), resulting in nonuniform etching. The value of $k_n$ above which etching becomes nonuniform depends on the reactivity of the electrode surrounding the wafer (2). The etching rate increases with $k_n$, as seen in Fig. 10, despite the fact that the etchant concentration decreases with $k_n$ (not shown here). As the chemical etching rate constant increases, the relative gain in etching rate diminishes. For very large values of $k_n$, the etching rate will be diffusion controlled, and hence insensitive to the value of $k_n$.

Figure 11 shows the etching rate along the wafer radius for different radii of the gas shower of the showerhead electrode, $r_3$. The pressure and the total flow rate $Q$ were kept constant at their basic value of 1 torr and 100 sccm, respectively, and therefore the nominal residence time ($\tau = \rho_r Q$) is independent of $r_3$. Nevertheless, both etching rate and uniformity depend on $r_3$. For small values of $r_3$, etching is highly nonuniform. Let us examine the case of $r_3 = 1$ cm as an example, remembering that the wafer radius was 5 cm and that the plasma radius was 6.5 cm. Beyond
The effect of electrode (and plasma) radius \( r_2 \) is shown in Fig. 12. The wafer radius was 5 cm, and the gas was uniformly distributed over the entire showerhead electrode surface (i.e., \( r_1 = r_2 \), see Fig. 2). Other parameters were at their basic value. As the electrode radius decreases, the power density in the plasma increases (power was kept constant), and this results in higher etching rate. For a plasma radius significantly greater than the wafer radius, etchant species generated beyond the wafer radius contribute to etching, yielding higher etching rate around the wafer periphery as compared to the wafer center (case of 6.5 cm and 8 cm electrode radius in Fig. 12). However, for plasma radius equal to the wafer radius (case of 5 cm), the etching profile changes dramatically. In such case, the etching rate decreases monotonically with decreasing wafer radius. Moreover, for wafer radius less than the plasma radius (the latter was 6.5 cm), the typical bullseye wafer clearing pattern would be observed. However, for wafer radius equal to the plasma radius, the reverse clearing pattern would be observed. This observation is similar to that of Fig. 12 for the case of equal wafer and plasma radii (5 cm in that case). The loading effect is further shown in Fig. 14 where the inverse of the average etching rate is plotted as a function of the square of the wafer radius (proportional to wafer area) (32). The squares are calculated points and the solid line is a fit to guide the eye. A nearly linear plot is obtained. The plot would have been strictly linear if concentrations were spatially uniform, if volume recombination reactions were neglected, and if the molecular oxygen mole fraction remained constant as the wafer radius changed. The behavior shown in Fig. 13 and 14 may be expected in the absence of reaction product interference. For example, if a product of the etching reaction participates in other reactions which produce etchant species, an inverse loading effect may be found, i.e., the etching rate may increase with increasing wafer area (35).

An advantage of mathematical modeling is that reactor design alternatives may be evaluated rapidly, before any costly experimentation. Promising designs may then be chosen for further examination including experimental verification of the model. In this context, the usefulness of the present mathematical model will be demonstrated by...
studying two novel reactor designs, namely, a reactor with a graded velocity profile at the shower, and a pulsed-plasma reactor.

**Plasma reactor with a graded inlet velocity profile.**—Figure 15 shows the etching rate along the wafer radius for three different gas velocity profiles at the shower. Parameters were at their basic value, except that the gas flow rate was 500 sccm. Case A corresponds to the basic reactor design of uniform shower velocity (Eq. [11]). Case B corresponds to a shower velocity which increases linearly from the center to the edge of the shower (Eq. [12]). One observes an improvement in etching uniformity by using the graded profile. This can be explained as follows: the typical situation is one in which the reactant concentration increases monotonically from the center to the edge of the wafer. Compared to the basic case, the graded velocity profile results in increased residence time close to the reactor center (increasing the chance for gas dissociation), and in faster etchant removal from the wafer edge. The final result is a milder etchant concentration gradient. The opposite is true for a shower velocity which is maximum at the center and decreases to zero at the shower edge (Eq. [13]). The latter case (curve C in Fig. 15), yields worse uniformity as compared to the basic case. It is conceivable that the etching rate can be made nearly uniform by choosing the appropriate flow rate. Alternatively, for a given flow rate, a velocity profile may be found (not necessarily linear) which would yield nearly uniform etching. Figure 15 also reveals that the etching rate is higher with the graded velocity profile (case B), as compared to the conventional case of uniform velocity profile (case A). The reason for this behavior is that the delay in the gas residence time distribution is important in determining the etching rate and uniformity. For example, in all three cases of Fig. 15 the nominal gas residence time was the same, yet different results were obtained for each case.

**Pulsed-plasma etching reactor.**—Another example of novel reactor design is that of a pulsed-plasma etching reactor (PPER). In the PPER to be examined, the plasma is modulated at a frequency much lower than the common radio frequencies. For instance, consider the case shown in Fig. 16. A square power waveform is applied with a frequency of 100 Hz and a duty cycle of 50%. During the 5 ms of power-on, the plasma may be operated at the usual frequency of 13.56 MHz in order to achieve higher efficiency of power-on, the plasma may be operated at the usual frequency of 13.56 MHz in order to achieve higher efficiency of gas dissociation and to avoid intense ion bombardment and/or charging of insulating surfaces. Although more complex situations can arise (33), it was assumed that the electron density and energy were modulated according to the applied power waveform. Therefore, the effective etchant production rate constant \( k_{\text{eff}} = k_p n_e \) was assumed to follow exactly the applied waveform shown in Fig. 16. Despite the fact that the plasma may be completely modulated by the applied power waveform, the response of the species concentration depends on the modulation frequency, the gas residence time, and the species reaction time.

Figure 17 shows the space-time dependence of the etching rate for the case of plasma modulation shown in Fig. 16. Other parameters were at their basic value except that the flow rate was 20 sccm. The plot of Fig. 17 corresponds to the periodic steady-state achieved after a number of cycles. The etching rate increases with time during the power-on portion of the cycle, reaches a maximum, and then decreases monotonically during the power-off portion of the cycle. The decay time depends on the time scale for etchant loss by gas flow and by reactions such as etching, wall and wall recombination. For a period of modulation which is long relative to the decay time (low modulation frequency), the etching rate would be very small throughout most of the power-off portion of the cycle. At the opposite extreme of high modulation frequency, the etching rate would be nearly time independent.

The dependence of the space- and time-average etching rate on gas flow rate is shown in Fig. 18 for the basic plasma reactor design (continuous-wave (cw) reactor, curve A; see also Fig. 7 for \( P = 100W \)) and the PPER (curve B). As before, the plasma was modulated according to the waveform shown in Fig. 16. One observes a similar behavior with flow rate for both the cw and pulsed-plasma reactors, i.e., the etching rate passes through a maximum. For high flow rates, for which the pulse period is much larger than the gas residence time, the etching rate in the PPER is that of the cw reactor pro-rated by the duty cycle.
Summary and Conclusions

A two-dimensional mathematical model for a parallel-plate isothermal single-wafer plasma etching reactor was developed. The etching chamber analyzed included both the plasma region and part of the downstream region. The oxygen plasma etching of polyimide was chosen as a model system for analysis. The finite element method was employed to calculate the fluid velocity profiles and the concentration distribution of reactive species. Emphasis was placed on conditions for which chemical etching was the dominant mechanism (negligible ion-assisted etching). Etching rate and uniformity were studied as a function of reactor geometry and operating conditions. The range of operating conditions studied was pressure 0.5-2 torr, power 25-200 W, and flow rate 10-500 sccm.

For given reactor pressure, a maximum etching rate with gas flow rate was observed. The maximum shifted to higher gas flow rates with increasing power. The pressure dependence of the etching rate was rather complex. At low flow rates (e.g., <20 sccm), the etching rate was relatively insensitive to pressure over the pressure range examined. At higher flow rates, the etching rate as a function of pressure seemed to exhibit a broad maximum, with the maximum shifting to higher pressures as the flow rate increased.

As the etching rate constant (wafer reactivity) increased ($k_e = 10-100$ cm/s), the etching rate increased but the etching uniformity degraded. The etching uniformity improved as the wafer reactivity became comparable to the reactivity of the surrounding electrode surface. The etching uniformity was also affected by the shower radius of the showerhead electrode and by the plasma radius. Uniformity was low for small shower radii and improved monotonically by increasing the shower radius. A shower radius at least equal to the wafer radius is recommended to avoid excessive nonuniformity. Uniformity of etching as a function of the plasma radius was examined for plasma radii equal to or larger than the wafer radius. A plasma radius slightly larger than the wafer radius (e.g., 15% larger) was found to give the best results under the conditions examined.

Two novel reactor designs were studied in an effort to improve reactor performance. A graded velocity at the shower (instead of a constant velocity) resulted in improvements in both etching rate and uniformity. A pulsed-plasma reactor can result in improved uniformity and
higher etching rate (when etching rate is prorated by the duty cycle) as compared to a continuous-wave plasma reactor.

Neglecting the effect of the reaction products on the discharge chemistry and physics is thought to be the most critical assumption of the present model. Hence, the model results will be more accurate under conditions of negligible product interference. An example is low power discharge systems where the reaction products have negligible product interference. An example is low power discharge systems where the reaction products have negligible product interference.

Plasma reactor systems are characterized by complex physical and chemical processes, and current understanding of reactive gas plasmas is incomplete. Even if all reaction channels and the corresponding rate constants were known, the state-of-the-art supercomputers are not sufficiently powerful to solve the equations of a model which includes details of all important plasma reactor phenomena. Plasma reactor engineering models based on transport and reaction principles and tested with experimental observations can be valuable reactor design tools. The power of such models will improve tremendously when they are integrated with models of discharge physics and chemistry.

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LIST OF SYMBOLS

C
C
C
C
F
D
f
G
H
k

C
C

conversion factor (Eq. [28])

diffusion coefficient of species i, cm²/s
effective electric field, V/cm

force vector (Eq. [25])

inlet concentration of species i, moles/cm³

total gas concentration, moles/cm³

inlet concentration of species i, moles/cm³

inlet concentration of species i, moles/cm³

inlet concentration of species i, moles/cm³

inlet concentration of species i, moles/cm³

inlet concentration of species i, moles/cm³

inlet concentration of species i, moles/cm³

inlet concentration of species i, moles/cm³

photoresist film density, g/cm³

gas density, g/cm³

electron temperature, K

gas temperature, K

electron density, cm⁻³

gas temperature, K

electron density, cm⁻³

electron density, cm⁻³

Greek

γ
ε
η

wall recombination coefficient
electron energy, eV

error tolerance for detection of periodic steady state

REFERENCES


Characterization of Silicon Surface Contamination and Near-Surface Damage Caused by C$_2$F$_6$/CHF$_3$ Reactive Ion Etching

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ABSTRACT

Silicon surface contamination and near-surface damage of the Si(100) substrate caused by reactive ion etching (RIE) of SiO$_2$ overlayer in C$_2$F$_6$/CHF$_3$ plasma were characterized by x-ray photoelectron spectroscopy (XPS), He-ion channeling technique and high-resolution transmission electron microscopy (HRTEM). XPS study indicates that a thin (<20Å thick) C,F polymeric layer was formed on the Si surface and underneath the polymer film a thin oxide layer (~10Å) was produced due to air exposure after RIE. These films were also characterized in terms of chemical composition and bonding state. The C,F film displays six bonding states of carbon, i.e., CF$_x$, CF$_y$, CF, C—CF$_z$, C—C—F, and C—Si. The variations of etchant gas composition and overetching time represent that the content of fluorine in residue film increase with increasing CHF$_3$ gas fraction and overetching time. The formation of residue film on SiO$_2$ surface were also investigated. The residue deposited on SiO$_2$ surface is thinner and contains less concentration of fluorine than the residue on Si surface. He ion scattering/channeling spectrum and cross-sectional high resolution transmission electron micrograph showed that the damaged layer contains displaced Si of about 1 x 10$^{15}$ atom/cm$^2$, and about 25Å thick amorphous layer is present on the Si surface.

Patterning by anisotropic dry etching technique is a necessary step for fabrication of very large scale integrated (VLSI) devices and reactive ion etching (RIE) has become the standard process to achieve anisotropic etching (1-3). The RIE anisotropy is mostly based on energetic ion bombardments to the surface of a film to be etched, and a direct exposure to reactive plasmas can lead to bombardment damage (4-7) and also deposition of involatile fluorocarbon residues and ion-induced damage (4-7) of the present work is to quantitatively analyze the surface and damage induced by C$_2$F$_6$/CHF$_3$ RIE process, using XPS, RBS, and HRTEM. The residue on the Si surface was also compared with that on the SiO$_2$ surface.

Experimental

The (100) p-type Si substrates with 3000Å thick thermally grown oxide film were used in order to simulate the real SiO$_2$ etching situation and subsequent overetching on the Si surface. Reactive ion etching experiments were performed in QUAD 484, Drytek RIE system using a C$_2$F$_6$/CHF$_3$ gas mixture. Etching conditions are RF power density of 1.215 W/cm$^2$ and the self-induced bias voltage ~ 80V, the total gas flow of 50 sccm, and the chamber pressure of 250 mtorr. The etch rate of SiO$_2$ was about 1500Å/min at 50% C$_2$F$_6$/50% CHF$_3$. The end point was determined by a change in the dc bias voltage, as it reaches the interface. In the study of the residue on SiO$_2$ surface, a SiO$_2$ film on Si substrate was exposed for 2 min under the same etching condition as described above and then the surface of SiO$_2$ overlayer partially remained after RIE process was analyzed by XPS. This was confirmed by the elemental Si 2p peak which was not detected on the remained SiO$_2$ layer. For the study of Si surface residue, the Si substrates remained in the plasma for 2 and 5 min after the end-point detection. The plasma gas composition, C$_2$F$_6$/CHF$_3$, was varied with the mixing ratios of 30%/70%, 50%/50%, 70%/30%, at the conditions of total gas flow 50 sccm and 2 min overetching. After removal from the RIE chamber, the etched specimens were studied without further treatment in the as-etched and air-exposed states.

X-ray photoelectron spectra were obtained with Perkin-Elmer PHI 5400 ESCA instrument using Mg K$_x$ (1253.6 eV) x-ray source. Survey spectra were recorded with 89.45 eV pass energy and narrow scan spectra of all regions of interest were recorded with 71.55 eV pass energy. The fine structures of narrow scan spectra were resolved to characteristic component peaks by a least squares fitting technique using gaussian and lorentzian functions. The backgrounds were nonlinearly subtracted by the integrated method (18, 19). Angle-resolved profiles were obtained by rotating the sample surface, i.e., varying the take-off angle.

The RBS were performed with the NEC 35DH RBS instrument. A 2.275 MeV He ion beam was aligned to the <100> axis of the Si sample. The data were obtained with a