FREE RADICAL CHEMISTRY IN THE PLASMA ETCHING PROCESS

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ABSTRACT

Measurements are presented for gas phase free radical reactions relevant to the plasma etching of semiconductors. The association reactions for P atoms with both CF$_2$ and CF$_3$ have been studied over an extended pressure range including that appropriate to the etching process. Contrary to earlier measurements, the rate coefficient determined here for CF$_2$+P is an order of magnitude lower than that for CF$_3$+P. The rate coefficients for reactions of SF$_2$, SF$_2$ and SOF with O atoms are also reported and comparisons are drawn between the chemistry occurring in CF$_4$/O$_2$ and SF$_6$/O$_2$ plasmas.

1. INTRODUCTION

Because of the importance of CF$_4$ in semiconductor processing, significant efforts have been made to explain mechanisms occurring in plasmas of CF$_4$ alone or in mixtures with either hydrogen or oxygen (1-5). In our work (6-9) we have concentrated on the neutral gas phase chemical reactions since these can control the nature of the reactive species which ultimately take part in the ion-stimulated processes on the surface. Furthermore, free radical processes will inevitably play a major role in the laser-driven photochemical etching of semiconductors.

CF$_4$ Chemistry

Measurements from this laboratory have shown that reactions of O atoms with both CF$_2$ and CF$_3$ are sources of P atoms (6,9). Also required are rate coefficients for the combination of P atoms with CF$_2$ and CF$_3$

\[ P + CF_2 \rightarrow CF_3 \]  \hfill (1)

\[ P + CF_3 \rightarrow CF_4 \]  \hfill (2)

since these reactions will have an important effect on the concentrations of P, CF$_2$ and CF$_3$. The measurements which exist for the rate coefficients for reactions (1) and (2) are puzzling (10). They were performed over a limited pressure range and the rate coefficient determined for reaction (1) was approximately the same high value reported for reaction (2). Intuitively one would expect that, at the low gas number densities which applied in those measurements and also in the plasma etching environment, the rate coefficient for reaction (1) would be significantly less than that for reaction (2). As part of the content of this paper we report measurements of the rate coefficients for reactions (1) and (2) and compare these with current theories of chemical kinetics.
SF₆ Chemistry

It was pointed out by d'Agostino and Flamm (11) that SF₆/O₂ mixtures may represent an attractive alternative to CF₄/O₂ for the plasma etching of silicon and SiO₂. These authors observed a broad chemical analogy with CF₄/O₂ plasmas and speculated on the nature of the major gas phase processes. In the present paper we report measurements for reactions of SF₅ and SF₂ with atomic and molecular oxygen and compare these results with our earlier measurements for the chemistry of CF₄/O₂ mixtures.

2. EXPERIMENTAL

The apparatus used here has been described in detail (12) and its configuration for the present experiment was as described most recently (9). CF₂ radicals were produced by pyrolysis of CF₃H at 1100°C and CF₃ by reaction of CF₃I with excess F atoms. The degree of pyrolysis of CF₃H and the initial [CF₃I] were chosen such that the initial radical concentration was \( 1 \times 10^{11} \text{ cm}^{-3} \). Given typical reaction times of \( 2 \times 10^{-2} \text{s} \) these conditions ensured that loss of radicals due to self combination had no effect on the measured loss due to reaction with F atoms. Fluorine atoms were obtained by passing a suitably diluted mixture of 1% F₂ in He through a microwave discharge. SF₅ and SF₂ were produced by the microwave discharge of SF₆ in helium. The concentration of these species was kept below \( 10^{11} \text{ cm}^{-3} \) as determined by O atom consumption and the amount of SF₆ consumed in the discharge. In the case of SF₂ production, molecular hydrogen was added immediately downstream of the discharge in order to consume F atoms thereby preventing reaction between SF₂ and F. Atomic oxygen was produced and its concentration determined as described previously (9). For reactions between F atoms and either CF₂ or CF₃ and between O atoms and either SF₅ or SF₂ the atomic species was always greatly in excess.

3. RESULTS

(a) F atom reactions with CF₂ and CF₃

For both systems the minor constituent was found to decay in a pseudo-first-order manner with a rate coefficient \( \psi \)

\[
\psi = k[F]
\]

where \( k \) is the rate coefficient under the prevailing conditions. As expected for association reactions of this type \( k \) was dependent on bath gas number density. Figure 1 shows the dependence of \( k \) upon the helium gas number density for reactions between CF₂ and F while Figure 2 gives the corresponding results for CF₃ and F. It is evident that the two reaction systems behave differently at the bath gas number densities used for the results in Figures 1 and 2. The rate coefficient for CF₂ appears to increase linearly with gas number density while that for CF₃ is about an order of magnitude higher but is much less dependent on gas number density.

The experimental results given in Figures 1 and 2 have been examined in terms of chemical kinetic theories for association reactions of this type. The simple Gorin theory as modified by Benson (13) has been used to predict the high pressure limit for these reactions and the geometry of the transition state. An RRKM calculation has been performed to predict the dependence of the rate coefficients on bath gas number density (14). This approach has been further refined by taking account of the nature of the energy exchange on collision of the excited adduct with the bath gas (15).
Figure 1. Dependence of $k$ for $F + CF_2$ on bath gas concentration.

Figure 2. Dependence of $k$ for $F + CF_3$ on bath gas concentration.
Considerations of this kind lead to agreement between calculated and measured rate coefficients within a factor of 2.

The experimental results obtained here for the rate coefficient for reaction (1) are more than an order of magnitude lower than those obtained previously (10). Use of the present results in models designed to predict gas phase concentrations would result in a very significant increase in the estimated values for [CF₂] and [F].

Reactions of SF₅ with O and O₂

The rate coefficient for the reaction between O and SF₅ with [O] within the range (1.7 to 9.4) x 10⁻¹² cm⁻³ s⁻¹ was (2.4 ± 0.6) x 10⁻¹¹ cm³ s⁻¹. No reaction could be detected between SF₅ and O₂. Analysis of the measurements gave an upper limit of 4.5 x 10⁻¹⁶ cm³ s⁻¹.

Reactions of SF₂ with O and O₂

Measurements of the rate coefficient for the reaction between SF₂ and O atoms determined with [O] in the range (0.34 to 2.43) x 10⁻¹² cm⁻³ gave a value of (1.1 ± 0.2) x 10⁻¹⁰ cm³ s⁻¹. As for SF₅ no reaction could be detected between SF₂ and molecular oxygen and an upper limit of 3.4 x 10⁻¹⁶ cm³ s⁻¹ was found for the rate coefficient for this process.

Figure 3 shows more detailed information concerning the SF₂+O reaction system. Here is seen the exponential decay of the SF₂ radical, the production and removal of the SOP intermediate and the formation of the stable products SO₂ and SO. In seeking to explain the sources of SO and SO₂ the following reactions have been considered:

\[ \Delta H^0_{298} \text{ kJ/mol} \]

\[
\begin{align*}
\text{SF}_2 + O & \rightarrow \text{SOF} + F & -134 \pm 125 \\
\text{SF}_2 + O & \rightarrow \text{SO} + F_2 & 52.8 \pm 17.1 \\
\text{SOF} + O & \rightarrow \text{SO} + PO & 126 \pm 131 \\
\text{SOF} + O & \rightarrow \text{SO}_2 + F & -206 \pm 124
\end{align*}
\]

For all entities other than SOP the heats of formation have been taken from JANAF (16). For SOP the heat of formation has been deduced from the heat of formation of SOF² listed in JANAF and the bond energy for the reaction

\[ \text{SOF}_2 \rightarrow \text{SOF} + F \]  

reported by Kiang and Zare (17). It can be seen that reaction (4) is endothermic even allowing for the uncertainty and will not proceed under our conditions. In the case of reaction (5) there is a very large uncertainty in the heat of reaction which, while nominally endothermic, may be exothermic. The experimental observation that SO is produced shows that indeed this is the case and therefore the heat of formation of SOP₂ is considerably higher than the value listed in JANAF.

Having determined the rate coefficient for the reaction of SF₂ with O atoms it is then possible to determine the combined rate coefficient for reactions (5) and (6). The curve fitting method employed has been described earlier (9) and the fit obtained is shown as a smooth curve through the SOP points. The results of several measurements such as those

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shown in Fig. 3 led to a value for this rate coefficient of $(7.9 \pm 2.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

![Graph showing signal versus reaction length for SO2, SO, SFO, and SF2.]

Figure 3. Reactants and products for $\text{SF}_2 + \text{O}$ versus reaction length.

Comparison of reactions occurring in $\text{CF}_4/\text{O}_2$ and $\text{SF}_6/\text{O}_2$ mixtures.

Table I summarises measurements from this laboratory for these two systems. As is evident from Table I there are in fact marked similarities in the chemistry occurring in $\text{CF}_4/\text{O}_2$ and $\text{SF}_6/\text{O}_2$ plasmas. In both systems reactions involving molecular oxygen appear to play unimportant roles under plasma etching conditions. $\text{CF}_3$ has been found to react with $\text{O}_2$ but the rate coefficient at gas number densities typical for plasma etching means that this reaction is about two orders of magnitude slower than the reaction between $\text{CF}_3$ and O atoms. In the case of $\text{SF}_5$ no reaction with molecular oxygen could be detected and thus in oxygen rich mixtures $\text{SF}_5$ will be consumed entirely by O atoms. Neither $\text{CF}_2$ nor $\text{SF}_2$ were found to react with $\text{O}_2$ and a strong parallel was observed in their reactions with O. In both cases the very active intermediate $\text{XOF}(\text{X}=\text{C, S})$ was formed which on further reaction with O atoms produced $\text{XO}$ and $\text{XO}_2$. For both systems ($\text{CF}_4/\text{O}_2$ and $\text{SF}_6/\text{O}_2$) the reactions listed in Table I are important sources of the increased F atom concentration which is known to occur when $\text{O}_2$ is added to plasmas of $\text{CF}_4$ or $\text{SF}_6$. 

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TABLE I

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient (10^{-11} cm^3 s^{-1})</th>
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<tbody>
<tr>
<td>CF_3 + O → COF_2 + F</td>
<td>3.2 ± 0.8</td>
</tr>
<tr>
<td>SF_5 + O → SOF_4 + F</td>
<td>2.4 ± 0.6</td>
</tr>
<tr>
<td>CF_2 + O → COF + F; CO + F_2</td>
<td>1.8 ± 0.4</td>
</tr>
<tr>
<td>SF_2 + O → SOF + F</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>COF + O → CO_2 + F; CO + FO</td>
<td>9.3 ± 2.1</td>
</tr>
<tr>
<td>SOF + O → SO_2 + F; SO + FO</td>
<td>7.9 ± 1.0</td>
</tr>
<tr>
<td>CF_3 + O_2 → CF_3O_2</td>
<td>depends on bath gas concentration.</td>
</tr>
<tr>
<td>SF_5 + O_2 → Products</td>
<td>&lt;4.5 x 10^{-5}</td>
</tr>
<tr>
<td>CF_2 + O_2 → Products</td>
<td>&lt;10^{-6}</td>
</tr>
<tr>
<td>SP_2 + O_2 → Products</td>
<td>&lt;3.4 x 10^{-5}</td>
</tr>
</tbody>
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REFERENCES