Positive Ion/Molecule Reactions in Tetrafluoroethylene

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Gas-phase ion/molecule reactions in tetrafluoroethylene (C_2F_4) were studied with a pulsed electron beam mass spectrometer. When a few Torr of major gas, N_2, containing 1–10 mTorr C_2F_4, was ionized by 2 keV electrons, CF_3^+ and C_2F_4^+ were formed as major ions. CF_3^+ reacted with C_2F_4 rapidly to form C_3F_5+. The rate constant of reaction C_2F_4^+ + CF_3 → C_3F_5^+ + CF_2 was measured to be (1.5±0.5)×10^{-11} cm^3/molecule·s and found to be temperature-independent in the range of 180–310 K.

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1. Introduction

Fluorocarbon plasma is an indispensable tool for SiO_2 etching in ultra large scale integration (ULSI) manufacturing. In the selective etching of SiO_2, fluorocarbon plasma plays a key role in preferential formation of protective fluorocarbon polymer film on Si and Si3N_4 surfaces. In addition, fluorocarbon film prepared by plasma-enhanced chemical vapor deposition (PECVD) has attracted increasing interest as one of the most promising materials for interlayer dielectrics because of its low dielectric constant. These plasma process technologies with fluorocarbon gases require a deeper understanding of the chemical reactivities of these fluorocarbons. In our previous work, gas-phase ion/molecule reactions in CF_4, C_2F_6, c-C_4F_8, etc. were studied in detail. The interactions between positive ions and C_2F_6 or C_3F_8 are weak and mainly electrostatic.

C_2F_4 has attracted deep interest as an alternative for the plasma etching of SiO_2 as it dissociates readily to form the etching fragments. SiO_2 etching has been performed using CF_4, C_2F_6, c-C_4F_8, etc. These molecules have extremely high global warming potentials (GWP). In contrast, the atmospheric lifetime of C_2F_4 was calculated to be only 1.9 day due to the high reactivity of C_2F_4 with the OH radical.

Samukawa et al.7 proposed a new radical control (selective radical generation) method for high-performance SiO_2 patterning using non-perfluorocarbon gases (CF_4 and C_2F_6) in ultrahigh frequency (UHF) plasma. This method enables independent control of polymerization and etching through the selective generation of CF_3 and CF_4 radicals in CF_4/C_2F_4 gas mixture plasma. Thus it could accomplish both a high etching rate and also high etching selectivity during SiO_2 contact hole formation. Despite the importance of C_2F_4 for the semiconductor fabrications, investigation on the ion/molecule reactions in C_2F_4 was relatively scarce. The present paper provides important data for the reactivities of C_2F_4 in the positive and negative ion/molecule reactions.

2. Experimental

The experiments were made with a pulsed electron beam high-pressure mass spectrometer.7,9 The major gas, N_2, at a few Torr was purified by passing it through a dry ice acetone cooled 5A molecular sieve trap. The reagent gas C_2F_4 (5% in N_2, Daikan Industries, Ltd.) was introduced into the major gas through stainless steel capillaries (1 m long×0.1 mm inner diameter). The sample gas was ionized by a pulsed 2 keV electron beam. The ions produced in the field-free ion source were sampled through a slit made of razor blades and were mass analyzed by a quadrupole mass spectrometer (ULVAC, MSQ-400, m/z=1–550). The width and the length of the slit were 10 μm and 1 mm, respectively.

3. Results and Discussion

The ions CF_3^+ and C_2F_4^+ were formed when a few Torr N_2 major gas containing 1–10 mTorr C_2F_4 was ionized by a 2 keV electron irradiation. These ions were formed by the charge transfer reactions (2) and (3):

\[ \text{N}_2^+ + \text{N}_2 + \text{M} \rightarrow \text{N}_4^+ + \text{M} \]  \quad (M: third body) \quad (1)

\[ \text{N}_4^+ + \text{C}_2\text{F}_4 \rightarrow \text{C}_2\text{F}_4^+ + 2\text{N}_2 \]  \quad (2)

\[ \text{N}_4^+ + \text{C}_2\text{F}_4 \rightarrow \text{C}_3\text{F}_5^+ + \text{CF}_2 \]  \quad (3)

The ratio of the intensities of ions [C_2F_4^+]/[CF_3^+] right after the electron pulse was about 7/3. The formation of CF_3^+ as one of the major ions is a very important information in the plasma chemistry because this ion is known to act as a very efficient etchant in the semiconductor fabrication.

Figure 1 displays the temporal profiles of ions observed after the electron pulse in 3.5 Torr N_2 containing 10 mTorr C_2F_4 at 301 K. The primary ions CF_3^+ and C_2F_4^+ are found to react with C_2F_4 and converted to C_3F_5^+ and C_3F_5^+, respectively.
reactions (4) and (5) are highly exothermic.

Unfortunately, the ion intensities became too weak to measure the rate constants for reaction (4) by decreasing the partial pressure of C2F4. The measurement of rate constants for reaction (5) were independent on the change of the C2F4 pressure in the range of 1 to 13 mTorr, i.e., reaction (5) is first-order with the C2F4 pressure. The average value of the rate constants in the range of 180–310 K in Fig. 2, 1.5 × 10^{-11} cm^3/molecule·s, is in excellent agreement with that of 1.5 × 10^{-11} cm^3/molecule·s determined by Anicich and Bowers. \(^{11}\) It is worth noting that the obtained rate constant for reaction (5) is 50 times smaller than for reaction, C2Hs^+ + C2H4→products (reaction (6)), of 7.3 × 10^{-10} cm^3/molecule·s.

\[
\begin{align*}
CF_3^+ + C_2F_4 & \rightarrow C_2F_5^+ \\
C_2F_5^+ + C_2F_4 & \rightarrow C_3F_5^+ + CF_3
\end{align*}
\]

Reliable experimental data for the heats of formation of fluorinated molecules and ions are rather scarce. Bauschlicher and Ricca calculated the heats of formation for C3Fm, C2Fm^+, CHFm, and CHFm^++ \(^{10}\). By using computed heats of formation at 298 K (kcal/mol) of CFS (−111.99), CF3^+ (101.98), C2F4 (−161.69), C2F2^+ (75.25), C3F5^+ (10.63), C2F4^+ (isomer: CF2CF2CF2^+) (−99.19), C2F6^+ (isomer: CF3CF2CF2^+) (−85.58), the enthalpy changes of reaction (4) is calculated as −38.78 kcal/mol for the product ion, C2F4^+ (CF2CF2CF2^+), and −25.17 kcal/mol for the product ion, C3F5^+ (CF3CF2CF2^+), and −14.92 kcal/mol for reaction (5). That is, reactions (4) and (5) are highly exothermic.

The decay rate of CF3^+ in reaction (4) is much faster than that of C2F4^+ in Fig. 1. We have made some effort to measure the rate constants for reaction (4) by decreasing the partial pressure of C2F4. Unfortunately, however, the ion intensities became too weak to measure the reliable rate constants with the pressure of C2F4 lower than 1 mTorr. Thus, the measurement of the rate constants for reaction (4) could not be made.

The measurement of the rate constants for reaction (5) was straightforward because of the slow decay of C2F4^+ as shown in Fig. 1. Figure 2 shows the temperature dependence of the rate constants for reaction (5) measured in the temperature range of 180–310 K. Although the data points are rather scattered due to the difficulty in maintaining the steady-state experimental conditions (charging of the ion source), the rate constants for reaction (5) are found to be independent on the ion source temperature in the range of 180–310 K. It was confirmed that the second-order rate constants for reaction (5) were independent on the change of the C2F4 pressure in the range of 1 to 13 mTorr, i.e., reaction (5) is first-order with the C2F4 pressure.

![Fig. 1. Temporal profiles of ions observed after the electron pulse in 3.5 Torr N2 containing 10 mTorr C2F4 at 301 K.](image1)

![Fig. 2. Temperature dependence of the rate constants for reaction (5) measured in the temperature range 180–310 K. The measurement of rate constants were made under the similar experimental conditions to those for Fig. 1 except for the ion source temperature.](image2)

That is, fluorine substitution of ethylene leads to a marked decrease of the rate constant.

In our previous work, \(^{1}\) the C2F4^+ ion was found to be unreactive and only formed cluster ions with C3F6. In contrast, C2F4^+ reacts with C2F4 to form C3F5^+ as shown in Fig. 1. The substitution of CF3 with F in C2F4 apparently decreases the reactivity for C3F6 due to the inductive and hyperconjugation effects.

4. Conclusion

Positive ion/molecule reactions in C2F4 have been studied in detail. CF2^+ and CF3^+ were formed as major ions from the 2 keV electron impact on a few Torr N2 major gas containing 1–10 mTorr C2F4. The rapid association reaction of CF2^+ with C2F4 to form C3F5^+ was observed. The rate constant for reaction, C2F4^+ + C2F4→C3F5^+ + CF3, was measured to be \((1.5±0.5)×10^{-11}\) cm^3/molecule·s and found to be temperature-independent in the range of 180–310 K. The abundant formation of CF2^+, which acts as an important etchant in the plasma fabrication, indicates that the F atom migration takes place efficiently in the excited ion, C2F4^+. The theoretical investigation on the mechanisms of reactions of C2F4^+ and CF3^+ with C2F4 is in progress in our laboratory.

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References


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