

THE CHEMISTRY OF HALOCARBON RF PLASMAS STUDIED BY INFRARED ABSORPTION SPECTROSCOPY

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Abstract

The chemistry of stable molecules and radicals has been studied in low pressure halocarbon rf discharges. Various particle densities have been measured and modeled. The densities of stable molecules are measured by Fourier transform absorption spectroscopy. The density of the CF_2 radical is measured by means of absorption spectroscopy with a tunable diode laser. Other radicals, like Cl, F and CH are detected optically. It appears that gases like CHF_3 and CCl_2F_2 are substantially dissociated in the discharge (30 and 80%, respectively). Based on the obtained data the dissociation rates of several molecules (CCl_2F_2 , CClF_3 , CF_4 , $\text{C}_2\text{Cl}_2\text{F}_4$) have been estimated. Furthermore, the presence of a silicon wafer strongly affects the plasma chemistry. The densities of halogen radicals and halocarbon molecules are significantly depleted in presence of Si. Space resolved density measurements show that the CF_2 radical is produced near the electrode, probably in an ion-induced reaction. The same is valid for the CH radical in a CHF_3 plasma.

Introduction

The widespread use of radio frequency (rf) plasmas for industrial surface modification requires a detailed study of the chemical nature of the active process gases under discharge conditions. In this work we show that in a low pressure weakly ionized plasma efficient dissociation and conversion of the feed gas takes place. There is little literature data on the electron induced dissociation rates of halocarbon molecules. Therefore we have developed a simple model, allowing to determine these rates by fitting the measured molecule densities and their dependencies on plasma parameters. The electron density, needed as an input parameter for this model, is measured using the microwave cavity method. Measured total dissociation rates can be compared with known dissociative attachment rates, in order to estimate the contribution of the electron impact dissociation. A comparison is made between etching conditions (in presence of a Si wafer on the electrode) and a "pure" CCl_2F_2 plasma, without the Si substrate. Further-

more, place resolved measurements of radical densities (CF_2 , CH) give insight in production mechanisms of these species.

Experimental

The measurements have been carried out in a 13.56 MHz capacitively coupled plasma in a parallel plate configuration with 12 cm plate diameter and a variable distance between the plates (3 or 5 cm). A 10 cm silicon wafer is placed on top of the lower, water cooled rf electrode in order to study the etching process. The gases are fed through mass flow controllers and introduced homogeneously through a slit around the rf electrode. The plasma is sustained by an ENI rf generator combined with an automatic matching network to optimize the power dissipation in the discharge. Typical conditions in this work are: 200 mTorr pressure, 100 W power input and 30 sccm gas flow.

The microwave resonance method, used to measure the electron density, is described elsewhere [1, 2]. The electron density in halocarbon discharges increases with the rf power and it reaches typically 10^{15} m^{-3} at 100 W. It is independent of the gas flow rate and has a weak pressure dependence.

Infrared absorption spectra have been obtained using a Bruker IFS-66 Fourier transform infrared spectrometer and a Laser Photonics tunable diode laser system. A detailed description of the setup is given in [1, 3].

Results and discussion

Typical absorption spectra for CCl_2F_2 are given in Fig. 1. It can be seen that the fraction of CCl_2F_2 remaining in the plasma is low. Fluorine rich molecules like CClF_3 , $\text{C}_2\text{Cl}_2\text{F}_4$ and CF_4 appear in significant amounts. Furthermore, in presence of a Si wafer on the rf electrode SiF_4 absorption is detected. Fig. 2 shows the fraction of CCl_2F_2 in the plasma as a function of the gas flow. In order to determine the dissociation rate (k_{dis}) of a feed gas molecule we consider the following production/destruction balance:

$$k_{dis}n_en_p + \nu_{\mathcal{F}}n_p = \nu_{\mathcal{F}}n_{total} + \nu_{ass}(n_{total} - n_p), \quad (1)$$

where n_p is the parent molecule density, n_e the electron density and $\nu_{\mathcal{F}}$ the reciprocal of the residence time of particles in the plasma volume (in our case $\nu_{\mathcal{F}} = 21 \times \mathcal{F}/p$, where the flow rate \mathcal{F} is given in sccm and the pressure p in mTorr). Here n_{total} denotes the total gas density, obtained from pressure, and ν_{ass} the association frequency. Eq. 1 can be rewritten as:

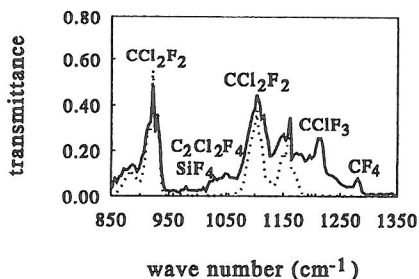


Figure 1: Typical absorption spectra of CCl_2F_2 at 200 mTorr, obtained with the Fourier transform infrared spectrometer: dotted curve - without plasma, solid curve - with a 100 W plasma (5 times enlarged). Note the presence of absorption bands of CF_4 at 1280 cm^{-1} , CClF_3 at 1110 and 1215 cm^{-1} and SiF_4 at 1030 cm^{-1} .

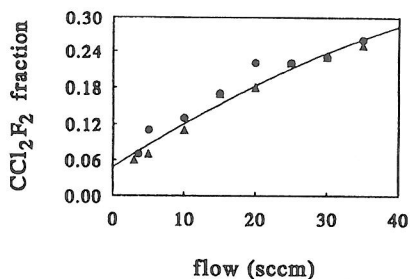


Figure 2: Fraction of the parent gas in a CCl_2F_2 plasma as a function of the gas flow rate. The pressure is 200 mTorr and the input power is 100 W. The dots denote measurements with and the triangles without a silicon wafer on the rf electrode. The solid curve denotes the fit to the data points, obtained using Eq. 2.

$$\frac{n_p}{n_{\text{total}}} = \frac{\nu_F + \nu_{\text{ass}}}{k_{\text{dis}} \cdot n_e + \nu_F + \nu_{\text{ass}}}. \quad (2)$$

Eq. 2 has been used to fit the experimental data. Extrapolation of the flow dependence (Fig. 2) to zero flow yields a relation between the dissociation and association frequencies: $\nu_{\text{ass}} \approx 0.05 \times k_{\text{dis}} n_e$. Substituting this relation into Eq. 2 and assuming that ν_{ass} is flow independent, we obtain $k_{\text{dis}} n_e = 12\text{ Hz}$, which in combination with the experimental electron density in these conditions $n_e = 1.5 \times 10^{15}\text{ m}^{-3}$ gives $k_{\text{dis}} = 8 \times 10^{-15}\text{ m}^3\text{s}^{-1}$. As the dissociative attachment and ionization rates for CCl_2F_2 are only about $10^{-15}\text{ m}^3\text{s}^{-1}$, this result suggests that electron impact dissociation is the major dissociation process for CCl_2F_2 in an rf discharge.

From Fig. 2 it can be seen that the presence of a Si wafer on the electrode has no significant influence on the dissociation degree of CCl_2F_2 . This conclusion, however, is not valid for the products of CCl_2F_2 conversion. In Fig. 3 the densities of various molecules are plotted as a function of the gas flow in presence and absence of a silicon wafer. The densities of halocarbon species are a factor of

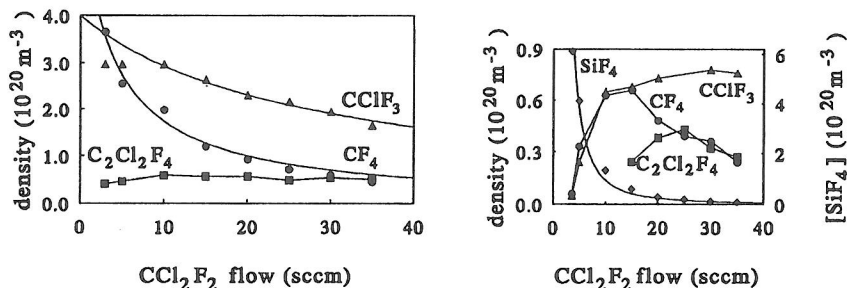


Figure 3: Densities of reaction products in the plasma as a function of CCl₂F₂ flow rate, at 200 mTorr and 100 W; left - without and right - with a silicon wafer.

two lower in presence of a silicon wafer on the electrode. Also the intensities of emission lines of Cl ($\lambda = 725.7$ nm) and F ($\lambda = 685.6$ and 703.7 nm) in presence of Si are reduced by the same factor. This suggests that Si is a sink for halogen radicals. In a pure CCl₂F₂ discharge, without Si, the molecules are formed by gas phase or surface radical association (e.g. CF₃ + F) and lost by flow and gas phase dissociation. Their densities can therefore be described by:

$$n = \frac{P}{\nu_F + k_{dis}n_e} \quad (3)$$

As the radical densities are fairly constant with flow [3], the production terms P are flow independent. The above equation is used to fit the experimental flow dependencies from Fig. 3. The best fit is obtained for $P = 1.2 \times 10^{21} \text{ m}^{-3}\text{s}^{-1}$, $k_{dis} = 2 \times 10^{-15} \text{ m}^3\text{s}^{-1}$ for CClF₃ and $P = 2.6 \times 10^{20} \text{ m}^{-3}\text{s}^{-1}$, $k_{dis} = 2 \times 10^{-16} \text{ m}^3\text{s}^{-1}$ for CF₄. Finally, the density of the dimer (1,2-C₂Cl₂F₄) does not depend on flow, which suggests that its gas phase loss frequency is higher than 7.5 Hz ($k_{dis} > 5 \times 10^{-15} \text{ m}^3\text{s}^{-1}$). The presence of a silicon wafer not only affects the absolute molecular densities, but also their dependencies on gas flow. At low flow rates even the densities of stable halocarbons (CF₄) are depleted. The drastic reduction of halocarbon species densities at low flow rates correlates with the decrease of the halogen and halocarbon radical densities, observed in these conditions. The density of SiF₄ increases quadratically with decreasing flow, which indicates that SiF₄ is not the primary etch product [3].

Mixtures of halocarbons with argon attract much attention due to their enhanced etching capacity. The behavior of various molecule densities in an Ar/CCl₂F₂ plasma is shown in Fig. 4. The density of the etch product SiF₄ reaches a maxi-

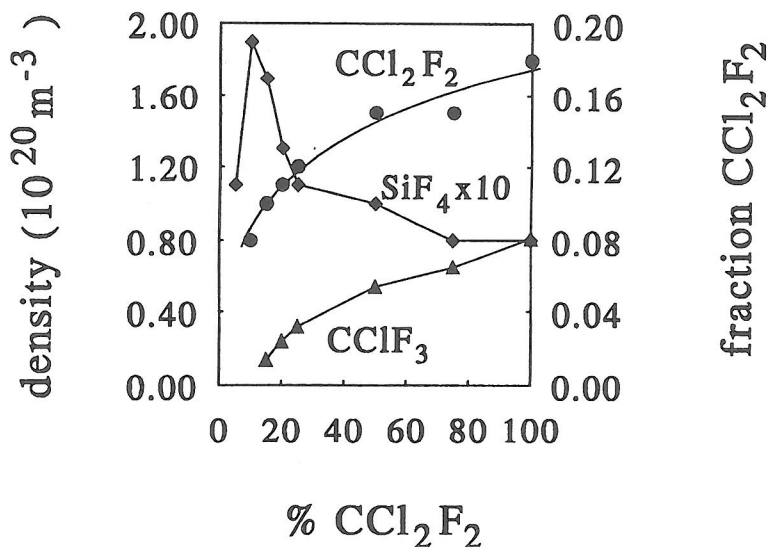


Figure 4: Fraction of CCl_2F_2 remaining in the plasma and densities of reaction products in an $\text{Ar}/\text{CCl}_2\text{F}_2$ discharge as a function of CCl_2F_2 partial pressure, at 200 mTorr, 100 W and 30 sccm total flow. A silicon wafer is placed on the rf electrode.

mum at about 10% of CCl_2F_2 in argon. Like in Fig. 3, the densities of halocarbon molecules decrease strongly as SiF_4 emerges.

The CF_2 radical is relatively stable and therefore it is expected to be one of the most abundant halocarbon radicals in our discharge. Its density has been measured for various discharge conditions by absorption spectroscopy using a tunable diode laser. The axial profiles of the CF_2 density in CCl_2F_2 and CHF_3 are shown in Figure 5. The peculiar increase of the CF_2 density towards the wall indicates that CF_2 is formed mainly at the electrodes. This effect is stronger at the powered electrode and at high rf power levels. This suggests that CF_2 is produced in an ion-induced reaction. A more detailed treatment of this effect is given by Haverlag *et al.* [4].

Also the CH radical in a CHF_3 plasma is formed at the electrodes. The $A^2\Delta - X^2\Pi$ emission at 430 nm is localized near the powered electrode. Optical emission spectroscopy reveals that CH^* , formed at the electrode, is vibrationally and ro-

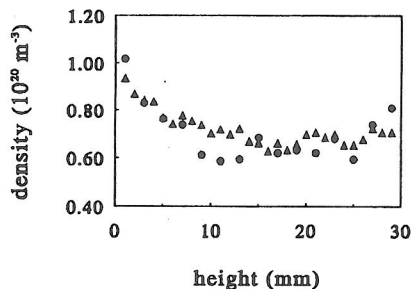


Figure 5: Axial profile of the CF_2 radical density in a CCl_2F_2 (dots) and CHF_3 (triangles) discharge at 200 mTorr, 100 W and 30 sccm. The rf electrode is at 0 mm and the grounded electrode at 30 mm.

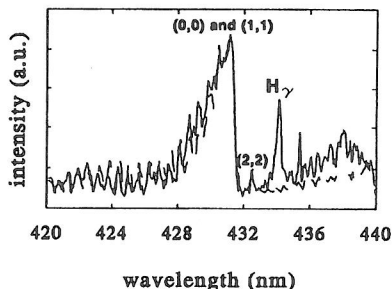


Figure 6: A typical CH emission spectrum at 50 mTorr, 100 W, 50 sccm, 1 mm above the rf electrode (solid curve) and a simulated spectrum (dashed curve) with 6000 K rotational and 4000 K vibrational temperature.

tationally excited. By fitting the spectrum (see Fig. 6) a rotational temperature of 6000 K and a vibrational temperature of 4000 K have been found [5]. These temperatures are much higher than the gas temperature (350 K, [1]).

References

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