Correlation between CF2-and C2F4-concentrations in pulsed capacitively coupled CF4/H2 rf plasma

Correlation between CF_2- and C_2F_4-concentrations in pulsed capacitively coupled CF_4 / H_2 rf plasma

S. Stepanov, O. Gabriel[1] and J. Meichsner

Institute of Physics, University of Greifswald, Felix-Hausdorff-Str. 6, D-17487 Greifswald, Germany
[1] present address: Department of Applied Physics, TU Eindhoven, The Netherlands

The CF_2 and C_2F_4 absolute concentrations were measured in pulsed low pressure CF_4/H_2 rf plasmas (13.56 MHz, CCP) by means of Infra-Red Tuneable Diode Laser Absorption Spectroscopy. For measurement of CF_2 radicals the $P_2(21)$ line at *1096.3433* cm^{-1} was chosen with its calculated line strength of $4.09 \cdot 10^{-20}$ *cm/molecule*. In case of C_2F_4 there is no detailed spectroscopic data available. Therefore, the C_2F_4 gas was produced by thermal decomposition of polytetrafluoroethylene for spectroscopic analysis. An absorption structure of several overlapping C_2F_4 lines was found around *1337.11* cm^{-1} and manually fitted. In pulsed plasma the time dependencies of the CF_2 and C_2F_4 concentration correlated with each other. In plasma off-phase, the recombination of two CF_2 radicals forming C_2F_4 was found to be dominant in CF_2 kinetics, but of minor importance in C_2F_4 production.

1. Introduction

Fluorocarbon low pressure rf plasmas containing C_2F_6, C_4F_8 or CF_4 (possibly with H_2-admixture) as feed gases have already found wide applications in plasma surface treatment. The material surfaces, e.g. polymers, modified with these plasmas have low surface energy and show hydrophobic and oleophobic properties. On the other hand, thin deposited fluorocarbon films are characterized by low dielectric coefficient (low-k films) or higher elasticity. They also get an increasing interest in applications for biomaterials. Although these plasmas have been studied for decades, there are many chemical processes, particularly, the kinetics of transient species (atoms, molecular radicals) or stable intermediate products in the gas phase and at the reactor walls that are not yet understood in detail. In order to gain more insight into these processes, the knowledge about the absolute species concentrations and their kinetics is necessary.

Both, the CF_2 radical and C_2F_4 as an intermediate stable reaction product play an important role in the kinetics of CF_4/H_2 plasmas. They also show a strong correlation with each other. Therefore, the purpose of the present paper is to measure their absolute concentrations and temporal behaviour in pulsed low pressure capacitively coupled CF_4/H_2 rf plasmas as well as to analyze the correlations between them.

2. Experimental Setup and Methods

Low pressure (10-100 Pa) asymmetrical capacitively coupled CF_4/H_2 rf-plasma (CCP, 13.56 MHz) with powers up to 200 W was produced in a stainless steel vacuum chamber with volume of about 20 litres. The measurements were carried out under fixed total flow of feed gases (10 sccm, various CF_4/H_2-ratio) in a pulsed mode of the rf-power (pulse frequency less than 1 Hz). The *Figure 1* shows a scheme of the experimental setup which is described in detail in [1].

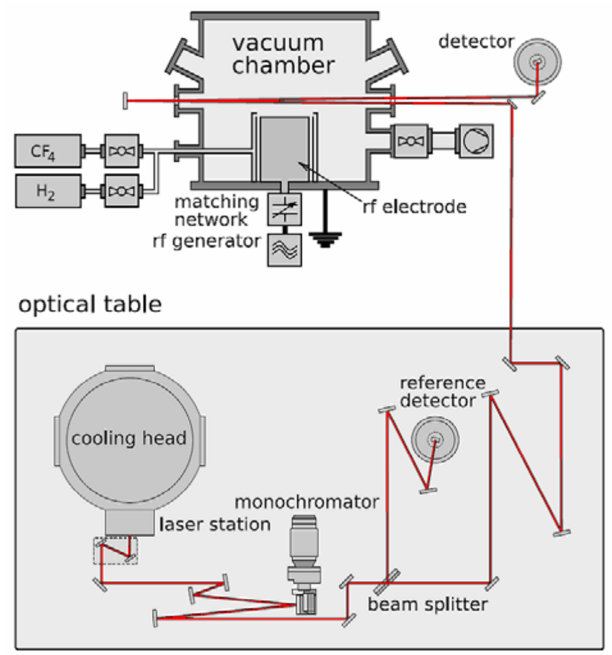

Figure 1. Scheme of experimental setup.

Infra-Red Tuneable Diode Laser Absorption Spectroscopy (IR-TDLAS) using special laser control and data acquisition software TDLWintel (Aerodyne Research Inc., Billerica, USA) was applied to measure the absolute concentrations of CF_2 and C_2F_4 during the pulsed rf-plasma in real time. Thereby the wavenumber and the strength of measured absorption lines should be known as input parameters of this procedure [1]. In case of relatively simple CF_2-radical they were calculated theoretically for ν_3-band and were found to be in a good agreement with ones measured by *Burkholder et al.* [2]. The $P_2(21)$ line at $\nu=1096.3433\ cm^{-1}$ with the line strength of $S=4.09\cdot10^{-20}$ *cm/molecule* was chosen for further measurements of CF_2 concentration.

In contrast to CF_2, there is no detailed spectroscopic data for C_2F_4 available in literature. Its FTIR spectrum reveals only strong absorption at *1187* cm^{-1} (ν_{11} band, symmetric stretching) and at *1337* cm^{-1} (ν_9 band, asymmetric stretching) (*Figure 2*). The IR-TDLAS in pulsed plasma around *1180* cm^{-1} provided only relative C_2F_4 concentrations. The specification of accurate wavenumbers for measured absorption lines failed because it was no reference gas available in this spectral range (*Figure 3*). Following, these concentrations were calibrated using the absolute CF_2 concentrations under assumption that the only channel of C_2F_4 production in plasma-off phase is the recombination of two CF_2-radicals:

$$CF_2 + CF_2\ \ (+M) \rightarrow C_2F_4\ \ (+M) \qquad (1)$$

On the other hand, C_2F_4 gas was separately produced by thermal decomposition of polytetrafluoroethylene for spectroscopic analysis. An absorption structure consisting of few overlapping C_2F_4 absorption lines was found at *1337.11* cm^{-1}. Using N_2O as a reference gas, this structure was manually fitted with absolute wavenumbers and effective line strengths for further direct determination of absolute C_2F_4 concentration in pulsed plasma (*Figure 4*).

3. Results and Discussion

3.1. CF_2-concentrations

Absolute CF_2 concentration profiles measured for various H_2-admixtures are shown in *Figure 5*. Taking into account processes of first (k_1) and second (k_2) order, their temporal behaviour in plasma-off phase can be roughly described by the following kinetic equation:

$$\frac{dn}{dt} = -k_1 n - 2k_2 n^2 \qquad (2)$$

If second order processes are dominant, solution of (2) can be written as:

$$\frac{n_0}{n(t)} = 2k_2 n_0 t + 1 \qquad (3)$$

where n_0 is CF_2-concentration at the end of plasma-on phase. There is a linear dependence of the ratio $n_0/n(t)$ on time.

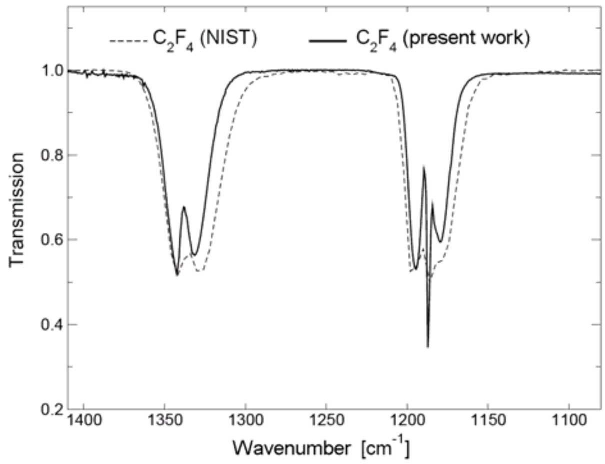

Figure 2. FTIR spectrum of C_2F_4.

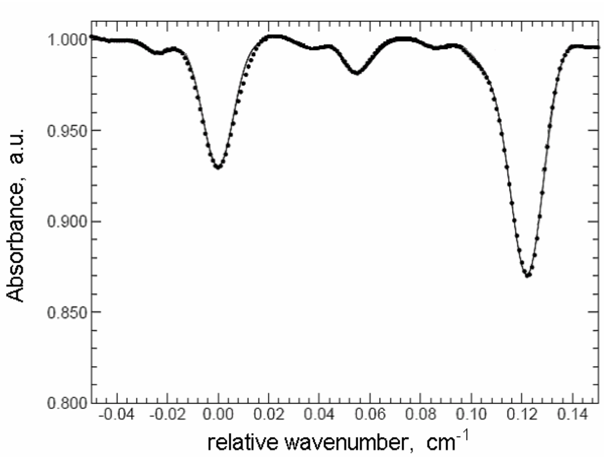

Figure 3. C_2F_4 absorption lines about 1180 cm^{-1}.

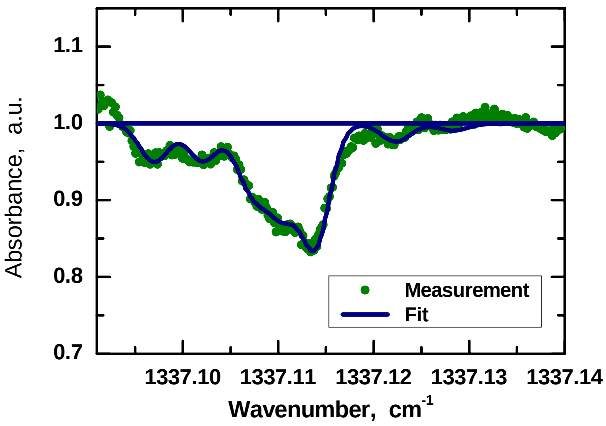

Figure 4. C_2F_4 absorption structure at 1337.11 cm^{-1}.

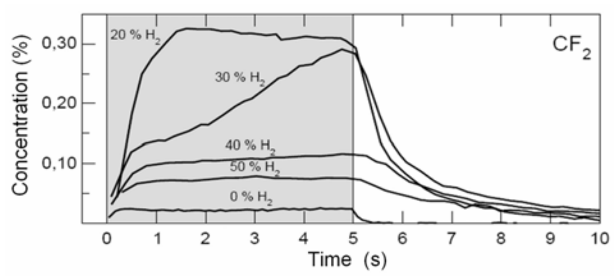

Figure 5. CF_2 density profiles (50 Pa, 50 W, 5 sec on, 5 sec off, total gas flow 10 sccm).

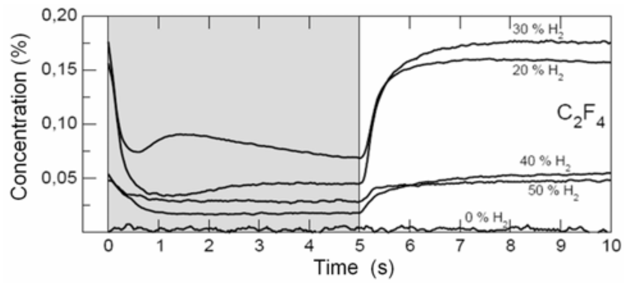

Figure 7. Calibrated C_2F_4 density profiles measured at 1180 cm^{-1} (50 Pa, 50 W, 5 sec on, 5 sec off, total gas flow 10 sccm).

Thus, the CF_2 curves from *Figure 5* rearranged according to (3) demonstrated that the CF_2 behaviour in plasma-off phase at higher H_2 admixture can be described only by second order processes (*Figure 6*). Moreover, an effective rate coefficient k_2 of the recombination (1) could be easily found from (3) to be about $3{\cdot}10^{-14}$ cm^3s^{-1}. This value stays in a good agreement with that measured by *Sharpe et al.* directly by means of UV-Absorption [3].

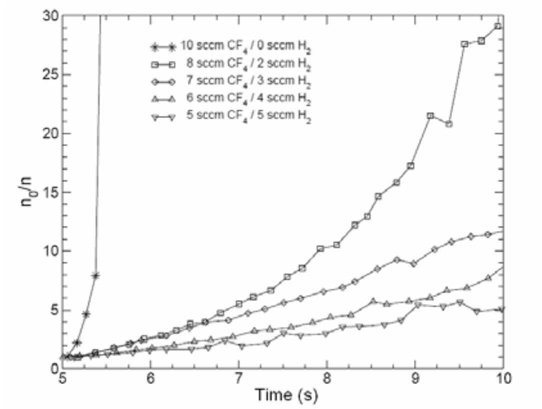

Figure 6. Rearranged CF_2-profiles from Figure 5.

3.2. C_2F_4-calibration (indirect method)

The relative C_2F_4 measurements at *1180 cm^{-1}* showed a strong correlation with absolute CF_2 concentrations gained for the same plasma conditions (*Figures 5 and 7*). Under assumption that the reaction (1) is a dominant channel of C_2F_4 production in plasma-off phase it could be written as:

$$\frac{d[C_2F_4]}{dt} = -\frac{1}{2}\frac{d[CF_2]}{dt} \qquad (4)$$

Hence, the measured C_2F_4 relative concentrations were calibrated according to (4). As a result, the absolute C_2F_4-concentrations in plasma-off phase were found to be less than 0.2% (*Figure 7*).

3.3. C_2F_4-calibration (direct method)

Figure 8 shows an example of C_2F_4 kinetics measured in pulsed plasma with fitted absorption structure at *1337.11 cm^{-1}*. The absolute C_2F_4 concentrations in plasma-off phase gained in this way seemed to be an order of magnitude higher than that from the indirect method discussed above. This fact indicates that the assumption (4) is not valid. In other words, there is not only simple CF_2 recombination (1). Some other significant processes for C_2F_4 production should be also taken into consideration in plasma-off phase.

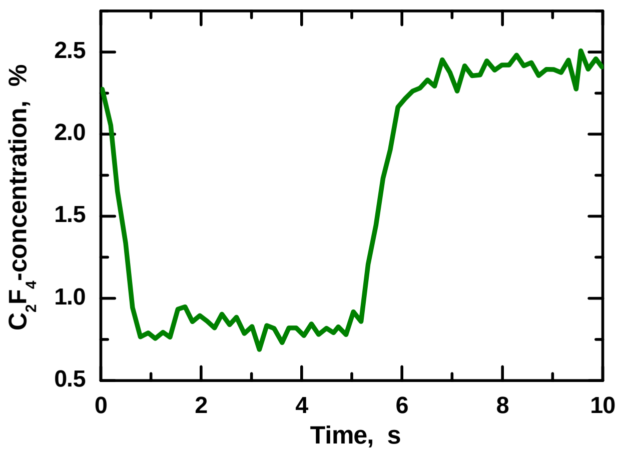

Figure 8. C_2F_4 density profile measured at 1337.11 cm^{-1} (50 Pa, 100 W, 5 sec on, 5 sec off, 7 sccm CF_4, 3 sccm H_2).

Under low pressure conditions this channel of the C_2F_4 production in plasma-off phase might be conceived as a result of fast reactions of currently unknown species *[X]* with thin fluorocarbon layer at the reactor wall:

$$X_{gas} + M_{layer} \xrightarrow{k} C_2F_{4\,gas} + M_{layer} + \ldots \qquad (5)$$

where k is the effective rate coefficient of the reaction (5) and the concentration of species *[X]* is only determined by first order reaction kinetics in the gas phase:

$$[X](t) = [X_0] exp(-(t - t_0)/\tau) \quad (6)$$

Here, $[X_0]$ is the X-concentration at the end of plasma-on phase $t=t_0$, τ is the effective time constant for the loss of $[X]$ in gas phase.

Taking reaction (5) into account, the equation (4) for the C_2F_4 production in plasma-off phase can be extended as follows:

$$\frac{d[C_2F_4]}{dt} = -\frac{1}{2}\frac{d[CF_2]}{dt} + k\cdot[X_0]\cdot\exp(-(t-t_0)/\tau) \quad (7)$$

The solution of (7) can be written than as:

$$[C_2F_4]_t = [C_2F_4]_{t_0} - \frac{1}{2}\left([CF_2]_t - [CF_2]_{t_0}\right) + k\cdot[X_0]\cdot\tau\cdot\left(1 - exp\left(-\left(t - t_0\right)/\tau\right)\right) \quad (8)$$

Using (8), the C_2F_4 concentrations measured at *1337.11 cm*$^{-1}$ could be very good fitted and the contribution of its both terms, the processes (1) and (5) respectively, could be separated (*Figure 9*).

Taking into account the experimental data for the total pressure of 50 Pa the effective time constant τ for the loss of $[X]$ in gas phase and initial production rate of C_2F_4 at the surface were estimated to be:

$$\tau = 0.51 s$$
$$d[C_2F_4]/dt\big|_{t_0} = k\cdot[X_0] = 3.31\cdot10^{14}\, cm^{-3}s^{-1} \quad (9)$$

4. Conclusions and Outlook

CF_2 and C_2F_4 absolute concentrations were measured in pulsed CF_4/H_2 rf plasmas. The kinetics of them showed a strong correlation.

The recombination reaction (1) of two CF_2-radicals was found to be the dominant loss process in the kinetics of CF_2 in plasma-off phase at higher H_2-admixtures. In contrast to that, surfaces processes like (5) at the reactor walls seemed to play a significant role in the off-phase kinetics of C_2F_4 production. That will be studied in more detail on further experiments.

5. Acknowledgements

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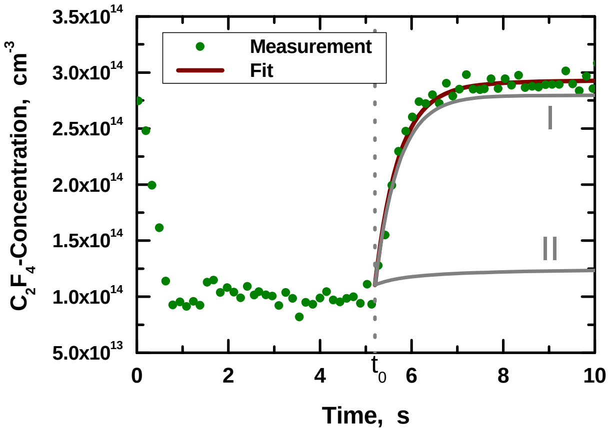

Figure 9. Fit of the C_2F_4-profile from Figure 8. Here: I – contribution of the surface processes like (5); II - contribution of the recombination of two CF_2-radicals.

6. References

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