Measurement of the gas temperature in fluorocarbon radio frequency discharges using infrared absorption spectroscopy

Citation for published version (APA):

Haverlag, M., Stoffels, E., Stoffels, W. W., Kroesen, G. M. W., & Hoog, de, F. J. (1996). Measurement of the gas temperature in fluorocarbon radio frequency discharges using infrared absorption spectroscopy. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films*, 14(2), 380-383.
<https://doi.org/10.1116/1.580093>

DOI:

[10.1116/1.580093](https://doi.org/10.1116/1.580093)

Document status and date:

Published: 01/01/1996

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Measurement of the gas temperature in fluorocarbon radio frequency discharges using infrared absorption spectroscopy

M. Haverlag,^{a)} E. Stoffels, W. W. Stoffels, G. M. W. Kroesen, and F. J. de Hoog
Department of Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

(Received 14 August 1995; accepted 2 December 1995)

The translational gas temperature was measured in 13.56 MHz radio-frequency (rf) discharges in CF₄ and CHF₃. Infrared absorption spectra of CF₄ and CF₂ were recorded using a tunable diode laser and the gas temperature was deduced from the linewidths of the absorption lines of these molecules. It is shown that linewidth measurements yield a simple and direct method to determine the gas temperature, with an accuracy up to ~10 K. The results obtained in CF₄ and CHF₃ plasmas indicate that the translational temperatures of all particles investigated in these plasmas are, at most, 50 K above the room temperature. The temperature increases with increasing gas pressure and rf power, but it is independent of the flow rate. This is attributed to an increased heating rate of the gas. Moreover, it was found that the temperature rise is significantly smaller in CHF₃ than in CF₄, under the same plasma conditions. This can be attributed to a higher power dissipation by chemical conversion of the parent gas in a CHF₃ discharge, as compared with a CF₄ plasma. © 1996 American Vacuum Society.

I. INTRODUCTION

Radio-frequency (rf) discharges are widely used in the industry for dry etching to produce small structures in semiconductor substrates. To improve the performance of these processes a good understanding of the chemical processes that take place in these plasmas is needed. Since many chemical reaction rates are strong functions of the temperature of the species involved,¹ it is essential to know the accurate temperature in the plasma. Moreover, in order to be able to interpret spatially resolved density measurements,²⁻⁴ it is necessary to know the spatial distribution of the temperature in the reactor.

Several methods to measure gas temperatures in plasmas have been applied in the past. Emission spectroscopy of electronic transitions has been widely used. For instance, the rotational temperature (which is close to the translational gas temperature) of N₂ impurities in an inductively coupled CF₄ plasma was measured by van Veldhuizen *et al.*⁵ However, a drawback of this method is that the rotational distribution of the upper electronic level is measured, which, in low pressure discharges, is not necessarily a good representation of the population of the different rotational levels in the ground electronic state. Alternatively, it is possible to derive the average temperature in the plasma from the pressure change directly after ignition of the discharge.⁶ However, this technique does not offer any spatial information and can only be used if the gas does not dissociate significantly. Therefore its application is limited to noble gases and a few molecular gases like CF₄. Finally, Boltzmann plots of individual rotational infrared absorption were used to infer the rotational temperature of species.^{6,7} This technique is accurate, but to extract the temperature from the data, a large

number of individual lines must be measured, which requires a good spectral resolution *and* a wide spectral range. Furthermore, each line must be assigned and the relevant molecular constants must be known. The temperature determination becomes much easier if the Doppler width of a single absorption line is used. In this article we make use of the latter method. In this way the rotational temperature is not measured, but the translational temperature is obtained directly.

II. THEORY

In general, the width of an infrared absorption line is determined by a superposition of three broadening mechanisms. First of all, the transition has a natural width which is given by the radiative lifetime of the upper level of the transition. This contribution can, however, be neglected with respect to the other two due to the long radiative lifetime of vibrational-rotational transitions. The second contribution comes from collisions of the absorbing species with surrounding gas molecules that induce phase changes in the molecular wave function and therefore broaden the absorption profile.^{8,9} The collisional line profile is given by a Lorentz function:⁸

$$f(\sigma) = \frac{\Delta\sigma_p^2}{(\sigma - \sigma_0)^2 + \Delta\sigma_p^2}, \quad \text{with the width at half-height:} \quad (1)$$
$$\Delta\sigma_p = \frac{4d^2p}{c} \sqrt{\frac{\pi}{kTm}},$$

where σ_0 is the central wave number of the line, d is the distance of closest approach during the collision, p is the gas pressure, k is Boltzmann's constant, m is the molecular mass, c is the speed of light, and T is the absolute temperature. The third contribution is caused by Doppler broadening due to the velocity distribution of the absorbing molecular species. This results in a Gaussian line profile:⁸

^{a)}Present address: Philips Lighting B. V., Central Development Laboratories, Lamps I, EEA-526, P.O. Box 80020, 5600 JM Eindhoven, The Netherlands.

FIG. 1. Measurement of a small part of the second derivative absorption spectrum of CF_2 . The measurement was performed in a 300 mTorr CHF_3 plasma at 100 W rf power. The width of the lines can be obtained by fitting the lines with the second derivative of the line profile function.

$$f(\sigma) = \exp\left(-\frac{(\sigma - \sigma_0)^2 \ln 2}{\Delta\sigma_d^2}\right), \quad (2)$$

with the width at half-height:

$$\Delta\sigma_d = \frac{\sigma_0}{c} \sqrt{8 \ln 2 \frac{kT}{m}}.$$

If both collisional broadening and Doppler broadening are important, the total line profile is described by a Voigt⁸ function which consists of a convolution of the collisional and Doppler profiles. However, in the pressure region where our measurements are taken, Doppler broadening is the dominant broadening mechanism. A typical second-derivative absorption spectrum of a small region of the CF_2 ν_3 band is given in Fig. 1. The width of the lines can be obtained by fitting the spectrum with the second derivative of the line profile function. In order to verify that pressure broadening is only a very small factor, a measurement was performed of the width of a CF_4 absorption line as a function of the gas pressure, in the absence of a plasma. To obtain a measure of the linewidth, the line was fit using the second derivative of a Gaussian function. To keep the absorption of CF_4 in the linear regime, spectra were collected at 15 mTorr of CF_4 and varying pressures of CHF_3 . The results are depicted in Fig. 2. Up to pressures of 0.3 Torr the contribution of collisional broadening is less than 1% of the total linewidth. Therefore we can safely assume that the profile is only determined by Doppler broadening in the pressure region of interest in this study (≤ 300 mTorr).

III. EXPERIMENT

The experimental setup and the measurement procedure were explained extensively in an earlier article,⁴ so only a brief description will be given here. The experiments were performed in a 13.56 MHz capacitively coupled rf plasma reactor with a 12.4-cm-diam planar parallel-plate configuration and an electrode separation of 3 cm. The lower, powered electrode is water cooled. The infrared beam of a Laser Photonics tunable diode laser system (TDLS) enters and exits the

FIG. 2. Variation of the full width at half-maximum of a CF_4 absorption line with pressure. The measurement was performed using 15 mTorr of CF_4 and the total pressure was varied by admixing CHF_3 . It can be seen that the contribution of collisional broadening is less than 1% for pressures up to 300 mTorr.

reactor through two BaF_2 windows. The beam diameter is aligned parallel to the electrodes and focused into the center of the reactor to obtain a spatial resolution of 1 mm along the line of sight. After passing through the reactor the light is focused on a photovoltaic mercury cadmium telluride (MCT) detector. The wavelength of the laser is modulated by modulating the temperature and/or the current through the laser diode. Absorption spectra are obtained by varying the dc current through the laser diode at a constant external diode temperature and using phase-sensitive detection. For an accurate measurement of a linewidth of $\sim 10^{-3} \text{ cm}^{-1}$ it is necessary that the external temperature of the laser is stable within 10^{-4} K . Since in our system this can only be reached for a short period of time, the laser is scanned relatively fast ($\sim 0.5 \text{ s}$) through the line profile and several scans (typically 20) are recorded. Each scan is subsequently fitted (using a least-squares procedure) with the second derivative of a Doppler profile:

$$\frac{\partial^2 f}{\partial \sigma^2} = \left(-\frac{2 \ln 2}{\Delta\sigma_d^2} + \frac{4(\sigma - \sigma_0)^2 (\ln 2)^2}{\Delta\sigma_d^4} \right) \times \exp\left(-\frac{(\sigma - \sigma_0)^2 \ln 2}{\Delta\sigma_d^2}\right) \quad (3)$$

and then the obtained values of $\Delta\sigma_d$ are averaged. Since the value of the width at half-height that comes out of the experiment is given in terms of the laser current, this value must be converted into wave numbers. This is done by measuring the second derivative transmission spectrum of an etalon with a known fringe spacing and calculating the distance in mA between successive maxima in this spectrum. To check whether this procedure yields the correct value for the gas temperature, a measurement was performed in which the reactor was filled with 15 mTorr of CF_4 . This yields a value of $\Delta\sigma_d$ which is only 2% lower than the one which is calculated using Eq. (2) for a room temperature of 298 K. This 2% deviation is probably caused by an inaccuracy in the calibration of the etalon. The last result was used to correct the etalon spacing.

FIG. 3. Measurement of the temperature of CF₄ in a CHF₃ plasma at 250 mTorr pressure and 100 W rf power as a function of the axial position in the plasma. The temperature appears to have a uniform profile and is only slightly higher than room temperature.

Rotational lines, belonging to the *P* branches of the ν_3 transitions of CF₂ and CF₄ ($\sigma \sim 1100$ and 1280 cm^{-1} , respectively), were used to determine the gas temperature. In a CF₄ plasma a line with a high *J* value (where *J* is the quantum number for the total angular momentum) in the *P* band of CF₄ was used in order to keep the absorption in the linear regime and enable measurements of the line profile up to pressures of 250 mTorr.

IV. RESULTS AND DISCUSSION

In Fig. 3 the gas temperature, determined from the CF₄ linewidth in a CHF₃ plasma at 250 mTorr pressure and 100 W rf power, is shown as a function of axial position. Apart from some scatter in the measurement, the axial temperature profile is flat, indicating that the temperature is uniform over the whole plasma volume. Moreover, the temperature is only slightly above the room temperature, which means that very little rf power is coupled into heating of the neutral particles. Measurements of the temperature of the CF₂ radical from its line profile yield about the same value. Moreover, from Fourier transform infrared absorption measurements, presented in an earlier article,⁴ it was established that HF molecules produced in a CHF₃ plasma have a rotational temperature close to the room temperature. This confirms that all long-living neutral particles in the plasma are in thermal equilibrium with each other, which can be expected due to the long residence times ($\sim 100 \text{ ms}$) of species in the plasma volume and the long lifetime¹⁰ of CF₂ in a CHF₃ plasma.

In Figs. 4 and 5 the pressure and rf power dependencies of the temperature of CF₄ are shown for a CF₄ plasma. The magnitude of the temperature effect and its pressure dependence are consistent with earlier results obtained using different techniques.^{6,11} The behavior of the gas temperature with pressure and rf power can be interpreted in terms of heating of the neutral particles in elastic and inelastic collisions with charged particles (electrons in the plasma glow and high energetic ions in the sheath). The heating rate is proportional to the density of the charged particles and to the neutral density. In the previous work the electron and ion

FIG. 4. Measurement of the temperature of CF₄ in a CF₄ plasma as a function of the gas pressure. The temperature rise in CF₄ is two to three times higher compared to a CHF₃ plasma at the same conditions.

densities in CF₄ were measured under similar conditions. The charge density increases as a function of rf power and slightly decreases as a function of pressure (for pressures higher than 50 mTorr). Therefore the heating rate increases with increasing pressure and power input. As the energy loss rate for the neutral species does not increase with increasing pressure or power (e.g., in case of convection, thermal diffusion, or conduction losses to the walls of the reactor), the increase of the gas temperature with pressure and rf power can be understood. To investigate what kind of cooling processes in the plasma eventually give rise to stabilization of the gas temperature, a measurement was performed as a function of the gas flow in the reactor. The results are displayed in Fig. 6. It is clear that convection by the gas flow is not an important cooling process. Therefore it is concluded that heat conduction and diffusion are responsible for the cooling of the gas.

It is interesting to note that the temperature rise after plasma ignition is about two to three times higher in a CF₄ plasma than in a CHF₃ plasma under the same conditions. Since the cooling rates for neutral particles in these plasmas are comparable, it is clear that a larger fraction of the rf power is used to heat the neutral species in a CF₄ plasma. First of all, the electron density in a CF₄ discharge is about a

FIG. 5. The dependence of gas temperature on the rf power coupled into the CF₄ plasma at 200 mTorr gas pressure.

FIG. 6. Measurement of gas temperature in a CF_4 plasma as a function of the flow rate at 200 mTorr gas pressure and 100 W rf power. It is clear that flow is not an important cooling process.

factor of 2 higher than in CHF_3 . However, direct collisional heating by electrons cannot account for the observed effects because the vibrational temperature of CF_4 is low¹¹ and vibrational relaxation is a slow effect.¹² A possible gas heating mechanism in CF_4 is the electron or ion-induced dissociation of the source gas. In a previous study¹¹ a low dissociation degree of the parent gas in a CF_4 plasma was found, despite a relatively high electron-impact dissociation rate. This effect was attributed to an efficient recombination of CF_x and F radicals, again yielding CF_4 . In the three-particle recombination reaction the binding energy is transferred into kinetic energy of the reaction products and the source gas. In case of surface recombination also the products can retain a significant part of the reaction energy. In contrast to CF_4 , a high degree of conversion of the parent gas in a CHF_3 plasma was found.¹¹ Recombination of the dissociation products of CHF_3 mostly leads to the formation of other species than the source gas.⁴ In these reactions less energy is transferred into kinetic energy of the products. Consequently, in a CHF_3 discharge the rf power is dissipated in the chemical conversion of the parent gas rather than in heating of the neutrals, which can explain the observed low gas temperature in this plasma.

V. CONCLUSIONS

High-resolution infrared absorption spectroscopy using a tunable diode laser provides an accurate method to determine

the gas temperature in a rf plasma by a measurement of the linewidth of a single absorption line. The accuracy that can be achieved is ~ 10 K. The gas temperature in low pressure fluorocarbon rf discharges differs from the room temperature by at most 50 K. The gas temperature increases as a function of pressure and rf power and appears to be independent of the gas flow rate. These results can be explained if dissociation of the source gas and recombination of radicals are the major heating mechanisms for the neutral species in these plasmas. Cooling of the gas takes place mainly by diffusion and conduction. Measurements in CF_4 and CHF_3 discharges indicate that the rise of the gas temperature after plasma ignition is two to three times higher in CF_4 than in CHF_3 under the same conditions. This can be attributed to a higher power dissipation in the chemical conversion of the parent gas in a CHF_3 plasma compared to CF_4 .

ACKNOWLEDGMENTS

This work was supported in part by The Netherlands Technology Foundation (STW). The research of Dr. Haverlag was made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences.

- ¹K. R. Ryan and I. C. Plumb, *Plasma Chem. Plasma Proc.* **6**, 231 (1986).
- ²J. P. Booth, G. Hancock, N. D. Perry, and M. J. Toogood, *J. Appl. Phys.* **66**, 5251 (1989).
- ³S. G. Hansen, G. Luckman, G. C. Nieman, and S. D. Colson, *J. Appl. Phys.* **68**, 2013 (1990).
- ⁴M. Haverlag, E. Stoffels, W. W. Stoffels, G. M. W. Kroesen, and F. J. de Hoog, *J. Vac. Sci. Technol. A* **12**, 3102 (1994).
- ⁵E. M. van Veldhuizen, T. H. J. Bisschops, E. J. W. van Vliembergen, and H. M. C. van Wolput, *J. Vac. Sci. Technol. A* **3**, 2205 (1985).
- ⁶E. Stoffels and W. W. Stoffels, Ph.D. thesis, Eindhoven University of Technology, The Netherlands, 1994.
- ⁷N. Itabashi, Ph.D. thesis, Nagoya University, Japan, 1991.
- ⁸R. Loudon, *The Quantum Theory of Light*, 2nd ed. (Clarendon, Oxford, United Kingdom, 1983).
- ⁹J. H. van Vleck and D. L. Huber, *Rev. Mod. Phys.* **49**, 939 (1977).
- ¹⁰M. Haverlag, W. W. Stoffels, E. Stoffels, G. M. W. Kroesen, and F. J. de Hoog, *J. Vac. Sci. Technol. A* **14**, 384 (1996).
- ¹¹M. Haverlag, Ph.D. thesis, Eindhoven University of Technology, The Netherlands, 1991.
- ¹²J. A. G. Baggerman, Ph.D. thesis, Delft University of Technology, The Netherlands, 1993.