Vacuum 85 (2010) 482–485

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Measurement of CH_4-concentration in HMDSO-containing process plasmas by quantum cascade laser absorption spectroscopy

Matthias Wolter*, Morten Hundt, Holger Kersten

Christian-Albrechts-University Kiel, Institute for Experimental and Applied Physics, Plasma Technology Group, Leibnizstr. 11–19, D-24118 Kiel, Germany

Keywords:
Plasma diagnostics
Plasma processing
Laser absorption spectroscopy
HMDSO

A B S T R A C T

For thin film deposition or plasma etching often organic precursors are used in the process plasma and related transient species are formed. In general it is not possible to measure the converted quantity of these precursors directly. In the present work we have used a special laser absorption spectroscopy to investigate characteristic molecular lines in the plasma to determine the concentration of stable organic molecules. Quantum cascade laser absorption spectroscopy (QCLAS) is a rather new technique for the precise measurement of absolute molecule concentrations. QCL's can be operated at room temperature. They emit light within the mid infrared and have similar spectroscopic characteristics to Tunable Diode Lasers (TDL). The commercially available system Q-MACS (Quantum Cascade Laser Measurement and Control System) offers a solid platform for the measurement of absolute molecule concentrations in plasmas and gas mixtures. The used Q-MACS is due to its laser characteristics particularly well suitable for determination of the concentrations of acetylene and methane. Molecular concentrations of methane were measured in hexamethyldisiloxane (HMDSO) containing plasmas, too. The methane concentration was found to depend on rf power and HMDSO flow.

1. Introduction

For Plasma Enhanced Chemical Vapor Deposition (PECVD) processes plasmas containing organosilicon precursors, e.g. hexamethyldisiloxane (HMDSO), are used to deposit thin films with superior electrical, optical or mechanical properties. The key to an improved understanding of plasma kinetics and chemistry in reactive plasmas containing HMDSO is the analysis of the fragmentation of the precursor. Measurement of ground state concentrations of stable or transient molecules will give way to estimate the quantity of the dissociated HMDSO [1,2].

In the past, many attempts of analysing plasma products emerging from chemical reactions in the gas phase have been made. Especially mass spectrometry was used to identify high weight reaction products, charged and neutral species [3–5]. On the other hand, optical methods such as optical emission spectroscopy (OES) were used to determine relative intensities of the various species in reactive plasmas [6]. In addition often ex-situ measurements like Fourier transform infrared spectroscopy (FTIR) or X-ray photoelectron spectroscopy (XPS) are used to characterise the deposited films and to get some insight to their chemical composition.

Since the mid nineties absorption spectroscopy is used to investigate molecular plasmas. FTIR spectroscopy was already used in-situ to study the fragmentation of HMDSO [7–9]. The application of tunable diode laser absorption spectroscopy (TDLAS) in the mid infrared opened the possibility of measuring absolute molecule concentrations of infrared active species [2]. The major disadvantage of TDLAS based on lead salt lasers is the necessity of cryogenic cooling because they work at temperatures below 100 K. With the development of quantum cascade lasers (QCL) a new optical source for laser absorption spectroscopy at room temperature is available [10]. This allowed the development of a new compact device for the measurement of molecule concentrations at room temperature called Q-MACS [2]. QCL's are characterised by narrow line width combined with single-frequency operation and considerably higher power up to tens of mW [11]. The emitted radiation of narrow bandwidth (0.01 cm^{-1}) leading to a high spectral resolution over a typical tuning range of several wavenumbers. In absorption spectroscopy the Beer–Lambert law can be used to determine the absolute molecular concentration, assuming homogeneity along the absorption path. The ratio of the incident (I_0) and transmitted (I) intensity is given by:

* Corresponding author.
E-mail address: wolter@physik.uni-kiel.de (M. Wolter).

0042-207X/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2010.01.016

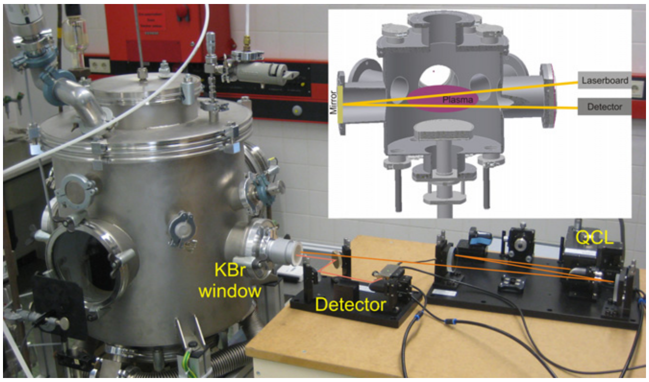

Fig. 1. Photograph and scheme of the used experimental set-up. Through the KBr window the laser light comes into the vacuum chamber, crosses the plasma, is reflected on a mirror and goes to the detector.

$$\ln[I_o(\upsilon)/I(\upsilon)] = nL\sigma(\upsilon,T,p),$$

where $\sigma(\upsilon,T,p)$ is the absorption cross section which depends on temperature and pressure, L is the absorption length and n the total number of molecules.

As far as it is known quantum cascade laser absorption spectroscopy has not been used in HMDSO containing plasmas, yet.

This work describes recent experiments using QCLAS to determine molecular concentrations of CH_4 in HMDSO containing plasmas. The experiments were performed in an asymmetric capacitively coupled radio frequency discharge with a frequency of 13.56 MHz.

2. Experimental

A photograph and a scheme of the used experimental set-up are shown in Fig. 1. The QCL beam goes into the plasma chamber through a KBr window. Here the beam interacts with the plasma and is reflected by a gold coated mirror back to the detector.

The radio frequency discharge is ignited in a cylindrical steel reactor with a volume of 80 L. The rf power of up to 120 W was coupled capacitively to the powered electrode by an automatically tuned matching network. The diameter of the powered electrode at the bottom of the reactor is 12 cm and the grounded reactor wall is the counter electrode. In the experiments argon and HMDSO mixtures were used. The argon gas flow was controlled with an MKS mass flow controller while the HMDSO flow was controlled with a needle valve. The gas inlet is above the powered electrode through a shower head. During the variation of the HMDSO/Ar mixture the total pressure inside the vacuum chamber was kept constant at 10 Pa. The HMDSO/Ar ratio is the partial pressure ratio which was measured with a gas independent Baratron gauge.

The Q-MACS determines the methane concentration using an absorption line at 1342.65 cm^{-1}. The line position was found using a well documented reference gas spectrum and a Ge-etalon with known fringe spacing [12]. The QCL is driven by short pulses (10 ns) and its tuning is temperature dependent [11]. By adding an additional current ramp to the driving pulses the laser heats up and tunes over about 0.25 cm^{-1}. This is done to tune over a single absorption line. Full range tuning to find line positions is achieved by heating the laser with a Peltier element between −30 and 30 °C. An overview scan of the HMDSO plasma from 4 to 25 °C laser temperature can be seen in Fig. 2 and Fig. 3 shows the methane absorption line that was used to determine the concentrations. By using this procedure with real-time line shape fitting routines a time resolution of up to 1 μs can be provided, allowing the study of kinetic processes in the plasma or relatively low concentration of the interested molecules. To increase the signal to noise ratio the measurement can be averaged over several seconds. Methane is produced in HMDSO plasma because methyl groups are split off from the HMDSO and then react with free hydrogen to form methane.

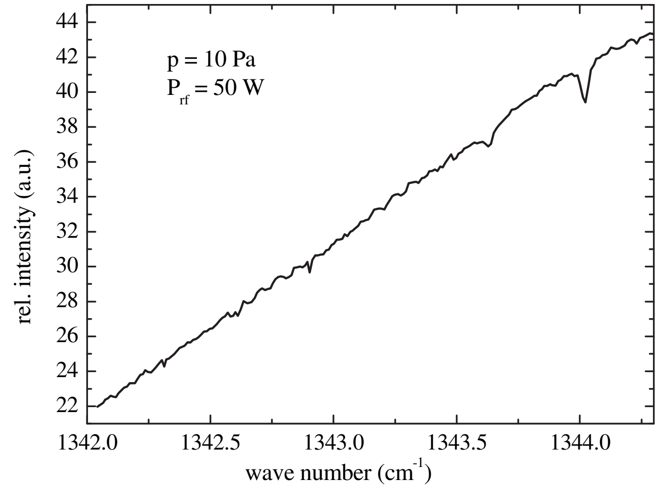

Fig. 2. Overview spectrum of the laser tuning range. Several absorption lines can be seen.

The stable methane molecules were assumed to diffuse in the whole vacuum chamber so the absorption length is the length of the optical path, i.e. 113 cm. The infrared laser is coupled into the chamber through a KBr window, reflected at an aluminium mirror and leaves the chamber through the same window. Because HMDSO was vaporised in a special bubbler the neutral gas temperature was assumed to be about 330 K and not at room temperature.

3. Results and discussion

First an overview spectrum of the laser was taken (Fig. 2). The spectrum shows a large number of absorption lines that have to be identified to determine concentrations of other stable or transient species. For the wavelength calibration of the overview spectrum it was necessary to take an overview spectrum of the Ge-etalon with

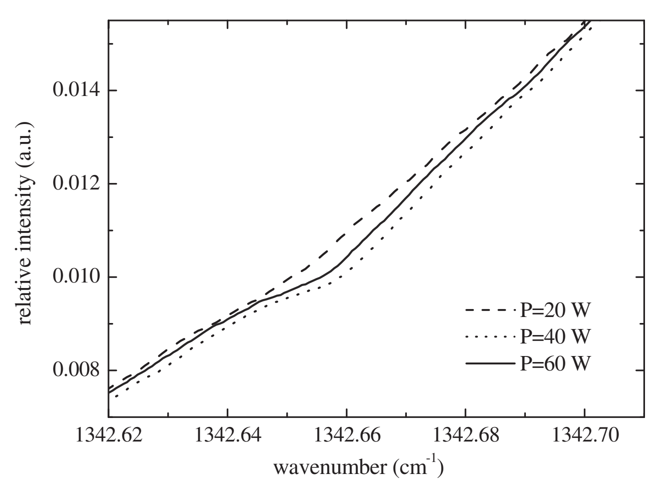

Fig. 3. Part of absorption spectrum in an HMDSO containing rf discharge. Stable CH_4 molecules are detected.