Application of quantum cascade lasers and infrared-fibres for the monitoring and control of industrial plasma processes

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Abstract. Quantum cascade lasers (QCL) offer attractive options for the application of mid-infrared absorption spectroscopy for industrial process monitoring and control. In particular the in-situ measurement of reactive plasma compounds can give new insight into the reaction kinetics of industrial plasma processes. For these purposes the compact quantum cascade laser measurement and control system (Q-MACS) has been combined with an infrared-fibre to allow a flexible and completely dust-sealed incoupling of the infrared radiation into the reactor chamber of an industrial plasma surface modification system. The system has been completed with a fast and compact detector and a data acquisition system to monitor concentrations of species of interest in the plasma process online. First tests proofed the potential of this approach.

1. Introduction

Molecular plasmas are valuable tools in plasma enhanced chemical vapour deposition and in etching systems to deposit or remove thin films with advantageous mechanical, electrical or optical properties. By varying the plasma parameters coatings with a wide range of chemical and physical properties can be produced. Therefore and for reasons of enhanced efficiency, increased stability and product quality the direct control of such plasma applications is a goal and challenging subject for plasma technology. The key to an improved understanding and control of plasma chemistry and kinetics in such chemical active discharges is the analysis of the fragmentation of the precursor gas and the monitoring of transient or stable plasma reaction products, in particular the measurement of their ground state concentrations. Information on absolute concentrations of plasma species can be used e.g. for improvements of productivity, reliability and reproducibility.

In plasmas the measurement of absolute molecular species number densities can be done using absorption spectroscopic methods in the mid infrared spectral region. Tuneable infrared diode laser absorption spectroscopy (TDLAS) in the spectral region between 3 and 20 µm is a well known non-invasive technique for the detection and the measurement of concentrations of stable and transient molecular species not only in the gas phase but in gas discharges as well [1,2]. It can also be used to determine neutral gas temperatures and to investigate dissociation processes in a wide range of molecular discharge plasmas. The TDLAS method also allows time resolved measurements.
The main disadvantage of TDLAS systems is the necessary cryogenic cooling of the lead salt diode lasers and of the detectors, since TDLs operate at cryogenic temperatures below 100 Kelvin. Systems using lead salt diode lasers are typically large in size and require closed cycle refrigerators and/or consumables like liquid nitrogen.

Quantum cascade lasers (QCL) are a new type of mid infrared laser sources, operating at room temperature and having similar spectroscopic properties as TDLs. The output power is sufficient to combine them with thermoelectrically cooled infrared detectors, which permits a decrease of the instrument size and gives the opportunity to design compact liquid nitrogen-free mid-IR spectroscopic systems. “Turn-Key” operation and unattended remote monitoring and control at an improved safety level and at a low level of maintenance could be ensured. These positive features of QCLAS systems can open up new fields of application in research and industry, including studies of gases in atmospheric, environmental and plasma chemistry but also to study and monitor industrial plasma processes.

The applicability of QCLAS has been proven using the quantum cascade laser measurement and control system “Q-MACS” for on-line process monitoring in research and industry. Results of such measurements and features of Q-MACS are given in [3,4,5]. In this paper we present a family of QCLAS measurement systems, which were developed taking especially the requirements of measurements in industrial plasma reactors for boriding of metal parts into account.

2. The Q-MACS Process
The Q-MACS Process is a robust compact and transportable measurement system which was developed and build with the focus on measuring and monitoring borone containing species in industrial plasma process reactors. Figure 1 shows the Q-MACS Process in a test at an industrial plasma reactor; figure 2 illustrates the optical arrangement of the system.

Figure 1. Photo of the Q-MACS Process with industrial plasma reactor in the background

Figure 2. Opto-mechanical scheme and beam propagation simulation of the optical arrangement of the Q-MACS Process
The optical design consists of three independent beam paths to achieve long term stability and low signal-to-noise ratios of the measurement. The infrared laser beam emitted by a QCL, which is mounted in a Q-MACS laser head, is divided by two ZnSe beam splitter plates for this purpose. In addition to the measurement path a pulse normalization path is added to neglect fluctuations of the pulse height of the QCL pulses and a reference locking path is used to assure the stability of the laser frequency by line locking employing a reference gas cell. While the reference locking is good for long term stability of the system, pulse normalization may result in an increase of the device sensitivity of up to an order of magnitude. Beam shaping transfer optics are included in the measurement path to decrease the laser beam diameter to a size which fits to the diameter of the windows of the plasma reactor and which allows to set up a dual-path arrangement through the reactor. In this case a retro reflective mirror is placed on the other side of the plasma reactor.

To achieve a compact size of the optical arrangement a dual platform setup was designed. This is a good compromise between compact dimensions, robust and compact installation, accessibility and easy alignment possibilities.

The measurement signals from the three thermoelectrically cooled infrared detectors are digitized by data acquisition cards. The rack contains the optics, the controlling computer, a thermo chiller and the supplies for all devices. The Q-MACS Process needs an external power source and a retro mirror (in the case of dual path measurements) for operability, only.

Recently, the Q-MACS Process was completed by a long path cell module, holding a 76 m astigmatic Herriot cell, to extend the measurement opportunities of the system to high sensitive trace gas analysis. With this additional board sensitiveness in the ppb range can be achieved.

3. The Q-MACS Process 2

Tests of the Q-MACS Process at the plasma reactor of the industrial partner showed some drawbacks of this system and its approach for the special purpose of measuring species with dense spectra in plasma reactors for industrial boriding of steel parts. Even though the optics were boxed dust contamination of the mirrors of the optical arrangement due to the industrial environment was observed. While the Q-MACS Process rack has a stable and fixed stand besides the plasma reactor the vessel itself moves with its flanges and windows due to the thermal expansion caused by the heating of the wall chambers. The laser beam passes a beam splitter and four times through dirty windows which results after some time of operation in weak measurement signals and insufficient signal to noise ratios due to depositions on the reactor windows. Besides, there is no free choice of the positioning of the Q-MACS Process since the infrared laser beam is leaving the system at a fixed position and angle and has to come back in a defined way (in the case of dual path measurements). This limits the flexibility of positioning the system significantly and blocks the access to the chamber in case of maintenance or part exchange.

Therefore, it was appropriate to design a Q-MACS Process 2, following an adapted approach.

The Q-MACS Process 2 is also designed for monitoring and control of plasma aided industrial surface treatment processes. It combines Q-MACS as the infrared source with an infrared-fibre to allow a flexible and enclosed laser beam handling and remote positioning of the laser source and control unit. The optics are simplified to the greatest possible extent to simplify the alignment and enhance the robustness of the system. Therefore no normalization or reference locking path is used. The QCL emission is directly coupled into the infrared-fibre by a compact and sealed set of optics. The incoupling of the laser beam into the plasma reactor and the detection of the signal is done by compact and light weight modules which are directly mounted to the reactor flanges. Since these enclosed modules are dust-sealed as well, the complete optical arrangement does not have any open optical paths outside the reactor. This is in combination with the flexible positioning of the system rack an important advantage and improvement of the Q-MACS Process 2, using infrared-fibres. Figure 3 shows the scheme of the experimental arrangement and figure 4 a photo of the device at an industrial plasma reactor.
The housing of the Q-MACS laser head with its fibre coupling module (figure 5) is integrated in an industrial standard 19-inch-rack (figure 6). The rack contains the Q-MACS supply, the laser head and a computer system with fast data acquisition boards. The rack is connected to the reactor-fibre-coupling module by a commercial infrared-fibre. This coupling module is a dust-sealed set of optics to parallelize the infrared beam and to guide it through the plasma chamber. On the other side of the reactor the detector module is located. It consists of dust-sealed optics which focuses the laser beam on the detector. Since this detector allows temporal resolutions in the nanosecond-range it is possible to measure in intrapulse mode as well as in the interpulse mode. Temporal resolutions of the measured concentration development down to the microsecond-range can be achieved. The detector signal is digitized by fast data acquisition boards in the computer system.
4. Examples of applications

4.1. Concentration monitoring of gases in industrial plasma processes

QCLs emit radiation of narrow bandwidth (0.01 cm\(^{-1}\)) leading to a high spectral resolution over a typical tuning range of several wavenumbers. Therefore with QCLs single vibration-rotational absorption lines can be measured. In this case Beer-Lambert’s law can be used to determine the molecular concentrations, assuming homogeneity over the absorption path and neglecting absorption saturation effects:

\[ I(v) = I_0(v) \exp[-\sigma(T, p, v)nl] \]

\(I(v)\) is the transmitted intensity, \(I_0(v)\) is the irradiated intensity, \(\sigma(T,p,v)\) is the temperature-and pressure dependent absorption coefficient of a specific absorption line of the frequency \(v\) with a typical dimension of a cross section per molecule [cm\(^2\) molecule\(^{-1}\)], \(n\) is the total number of molecules and \(l\) is the absorption length. The absorption coefficient can be written as the product of a line strength \(S\) of a specific line and of the normalized line profile function \(f\):

\[ \sigma(v) = S \int f(v-v_0) dv = 1. \]

While the influence of the line profile \(f\) can be calculated, the value of the line strength \(S\) has to be taken from literature [6] or to be determined.

Several molecular gases, which are used in industrial processes, show absorption spectra which cannot be spectrally resolved at room temperature caused by a variety of overlapping absorption lines, e.g. in case of different isotomers of high abundance. For example BCl\(_3\) combines \(^{11}\)B (80.1 %) and \(^{10}\)B (19.9 %) with \(^{35}\)Cl (75.8 %) and \(^{37}\)Cl (24.2 %). The molecules formed by the different combinations of these isotopes have marginally differing spectra overlapping each other in the spectral range between 920 cm\(^{-1}\) and 1010 cm\(^{-1}\) (figure 7). Despite the high spectral resolution the resulting spectrum cannot be resolved; it is a dense, multi-peak spectrum without any zero-absorption parts in between (figure 8).

![Figure 7](image1.png)  
**Figure 7.** FTIR spectra of BCl\(_3\) in the spectral range 900 cm\(^{-1}\) to 1040 cm\(^{-1}\) with measurement position (grey)

![Figure 8](image2.png)  
**Figure 8.** QCLAS spectrum (black, blue) of BCl\(_3\) at 963.5 cm\(^{-1}\) with multi peak fit (red) position (grey)

For such complex spectra normally no line strength data are available in literature. Therefore, special routines have to be used to determine the line strength data experimentally for quantitative measurements of these species. For this purpose in the present case the spectrum of BCl\(_3\) was recorded and analysed by means of FTIR spectroscopy first (figure 7 shows the part with the main absorption band of BCl\(_3\)). In the most intense part of the band HITRAN-format files containing line
positions and strengths [6] were estimated from highly resolved spectra, recorded between 963 cm \(^{-1}\) and 965 cm \(^{-1}\) using a tunable diode laser (TDL) absorption spectrometer [7]. Particular attention was given to the calibration of the wavenumber scale and the correct gas mixture and pressure. More details on handling complex spectra can be found in [8,9]. Tests of the deduced HITRAN-format files showed a good agreement of measured and fitted spectra regarding the position and absorption strength of mean spectral features of BCl\(_3\) in this range. Figure 8 shows results of tests of a part of this file using 292 line entries to fit the measured data taken with a Q-MACS Process spectrometer.

Stancu et al [5] used another approach for non-resolvable spectra in the mid-infrared region. Instead of determining line strengths they use the absorption coefficient \(\sigma(T,p,v)\) for a spectral position at the temperature and pressure of interest for the measurement. The absorption coefficient has to be determined before experimentally. Since industrial plasma processes usually run at given pressures and temperatures this approach is possible even although it limits the flexibility for changes of process parameters. Assuming constant values of the absorption coefficient \(\sigma\), of the absorption length \(l\) and of the intensity \(I_0\) irradiated from the laser it is sufficient to measure the transmitted intensity \(I\) only for getting absolute concentration values.

4.2. Results with Q-MACS Process

The data acquisition unit of Q-MACS Process was designed for the requirements of the TDLWintel software package [10,11]. This program can be used to control QCLs, e.g. using the Q-MAC system, to analyze the recorded spectra in real time and to display results of measured concentrations. By using this rapid scan software with real-time line shape fitting routines a time resolution of up to 1 \(\mu\)s can be provided, allowing the study of kinetic processes of infrared active compounds in plasmas or gases. To increase the signal to noise ratio the measurement can be averaged for several seconds, being a sufficient temporal resolution for most of the industrial plasma process monitoring applications. With TDLWintel, using the prerecorded HITRAN-file it was possible to monitor the development of the concentration of the precursor gas BCl\(_3\) in an industrial pulsed dc plasma reactor while driving process plasmas to deposit boron-based hard coatings. The measurement results of the BCl\(_3\) percentage in the chamber are not only displayed but can be transferred via hardware (serial) or software (network TCP/IP) interfaces to other systems, e.g. for the use in automated process monitoring and controlling. This was tested using the Q-MACS Process.

**Figure 9.** Measurement of the BCl\(_3\) concentration in the gas inlet with Q-MACS Process

**Figure 10.** Comparison of the BCl\(_3\) concentration for plasma on and off phase in a microwave discharge reactor
First test measurements of well known BCl₃ concentration in the gas inlet were performed with the Q-MACS Process without starting a plasma. Figure 9 shows the measured concentration steps of decreasing BCl₃ content in a mixture with hydrogen and argon. Using TDLWintel it was possible to reproduce the admixed ratios within sufficient error limits allowing to monitor the concentration change of BCl₃ permanently and over a wide range of concentrations while driving plasma processes.

In figure 10 the temporal development of the BCl₃ concentration during a test in a microwave discharge chamber is shown. In such mixtures with Argon the ignition of the plasma resulted in an increase of the degree of dissociation of more than 50%. The BCl₃ concentration signal could be followed after switching off the plasma, the gas inlet and the starting to pump for about 2 minutes.

Using a QCL the scan through an infrared spectrum may be commonly achieved in two different methods. In the interpulse mode, used by TDLWintel, a bias DC ramp is applied to a series of short laser pulses of a few tens of nanoseconds. Another option is the intra pulse mode, i.e. the scanning in single, longer pulses acquiring an entire spectrum in this pulse. Since this scan is performed in tens up to a few hundred nanoseconds with duty cycles of the QCL of several percent time resolutions in the microsecond range have become possible for quantitative in-situ measurements of molecular concentrations in plasmas with QCLs as well.

4.3. Results with Q-MACS Process 2

The Q-MACS Process 2 system has been designed for improved adaptation to industrial applications. The system allows the same measurements as described in chapter 4.2. Concentration values of various molecular species can be measured with temporal resolutions from μs to s in the intrapulse mode as well as in the interpulse mode. Figure 11 shows the change of the BCl₃ concentration in the gas flow during such test measurements. In comparison to the calculated BCl₃ concentration determined by fitting the complex spectra using TDLWintel (red) the change of the recorded signal (blue) is displayed as well. The similarity of both results is a good proof for the approach to measure the transmitted signal only for monitoring species concentration values.

Figure 12 shows an example of a plasma process monitoring with various contents of BCl₃ in the gas mixture and for various plasma duty cycles. Even though fluctuations caused by long-term changes of the irradiated laser intensity were observed, these results proofed that it is possible to monitor industrial plasma processes using the Q-MACS Process 2. For further improvements of the signal stability, of the signal to noise ratio and of the measurement sensitivity it is planned to implement a simplified signal normalization path into the optical arrangement.

![Figure 11. Comparison of the BCl₃ concentration (red) in the gas inlet with the signal (blue)](image)

![Figure 12. Change of the BCl₃ signal in an industrial plasma process](image)
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References
[1] Röpcke J, Mechold L, Käning M, Fan W Y and Davies P B 1999 Plasma Chem. Plasma Process. 19 395
[2] Hempel F, Davies P B, Loffhagen D, Mechold L and Röpcke J 2003 Plasma Sources Sci. Technol. 12 598
[3] Hempel F, Glitsch S, Röpcke J, Saß S and Zimmermann H 2005 Plasma Polymers and Related Materials ed M Mutlu 142
[4] Röpcke J, Glitsch S, Hempel F, Lang N, Macherius U, Saß S, Stancu G D, Weichbrodt F, Weltmann K-D and Welzel S 2006 VDI-Berichte Nr 1959 279
[5] Stancu G D, Lang N, Röpcke J, Reinicke M, Steinbach A and Wege S 2007 Chem. Vap. Deposition 13 351
[6] Rothman L S, Jacquemart D, Barbe A, Benner D C, Birk M, Brown L R, Carleer M R, Chackerian C, Chance K, Coudert L H, Dana V, Devi V M, Flaud J M, Gamache R R, Goldman A, Hartmann J M, Jucks K W, Maki A G, Massie S T, Orphal J, Perrin A, Rinsland C P, Smith M A H, Tennyson J, Tolchenov R N, Toth R A, Vander Auwera J, Varanasi P, Wagner G 2005 Journal of Quantitative Spectroscopy & Radiative Transfer 96 (2): 139
[7] Röpcke J, Mechold L, Käning M, Anders J, Wienhold F G, Nelson D D and Zahniser M 2000 Rev. Sci. Instrum. 71 3706
[8] Harward C N, Baren R E and Parrish M E 2004 Spectrochem. Acta Part A 60 3421
[9] Harward C N, Thweatt W D, Baren R E and Parrish M E 2006 Spectrochem. Acta Part A 63 970
[10] Zahniser M S, Nelson D D and Kolb C E 2002 in Applied Combustion Diagnostics, Kohse-Hoinghaus K and Jeffries J (eds), Tallor and Francis, New York 648
[11] Nelson D D, Shorter J H, McManus J B and Zahniser M S 2002 Appl. Phys. B 75 343