Quantum Cascade Laser Absorption Spectroscopy – a New Method to Study Molecular Plasma Components

J Röpcke1, S Glitsch1, P Davies2, F Hempel1, N Lang1, A Rousseau3, S Wege4 and S Welzel1a
1INP Greifswald, F.-Hausdorff-Str. 2, 17489 Greifswald, Germany
2University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom
3LPP, Ecole Polytechnique, CNRS, 91128 Palaiseau Cedex, France
4Plasway, Hauptstr. 7a, 01328 Dresden, Germany

E-mail: roepcke@inp-greifswald.de

Abstract The recent development of quantum cascade lasers (QCLs) offers an attractive new option for the monitoring and control of industrial plasma processes and for trace-gas analysis as well as for highly time-resolved studies on the kinetics of plasma processes. The contribution reviews selected examples of the application of QCLs for infrared absorption studies in basic research and for plasma monitoring and control in industry.

1. Introduction

Plasmas with molecular feed gases are used in many applications such as thin film deposition, semiconductor processing, surface activation and cleaning, and materials and waste treatment. Within the last decade this has stimulated the adaptation of infrared spectroscopic techniques because most of the used compounds and their decomposition products are infrared active. The availability of quantum cascade lasers (QCL) opens up new attractive possibilities for the application of Infrared Laser Absorption Spectroscopy (IRLAS) for in situ plasma process monitoring and control. QCLs emit in the mid infra red spectral range (MIR) at room temperature, i.e. without the need for cryogenic cooling. Because of this it is possible to design very compact MIR sources which are characterized by single mode operation and high radiance power (mW). Sensitivities in the range of ppb with time resolutions of better than ms are feasible. The aim of the present contribution is to review recent achievements using QCLs for plasma diagnostics and monitoring in research and industry. This review will include (i) time resolved studies on pulsed DC discharges using QCL, (ii) application of QCLs and PIR-fibres for monitoring and control of industrial surface treatment and (iii) in situ monitoring of plasma etch processes with a QCL arrangement in semiconductor industrial environment.

2. Chirp-based spectroscopic studies of NO containing discharges

2.1. Highly time resolved QCLAS in pulsed plasmas

The broad range of applications where the chemistry is exploited in N2-O2 containing discharges, such as pollution abatement or atmospheric pressure plasmas used for thin film deposition or
biomedical applications, has stimulated extensive studies of these plasmas. Different diagnostic
techniques (e.g., laser induced fluorescence, mass spectrometry, IRLAS) have been applied [1 - 3].
The important role of surface reactions on the molecule formation has also been recognised [4].
Additionally, the filamentary structure of discharges at atmospheric pressure usually complicates
the experimental approach. Thus, low pressure plasmas, being typically more homogeneous in nature, are
preferably used for fundamental studies. Consequently, the time resolved in situ detection of ground
state NO densities in pulsed plasmas may provide an improved understanding of the main chemical
processes and a discrimination of gas phase and surface reactions.

Since pulsed QCLs exhibit an inherent frequency sweep (also known as frequency down chirp) of
typically 0.005 cm\(^{-1}\)/ns (150 MHz/ns) an entire absorption spectrum may be acquired within a few tens
of nanoseconds and thus enable highly time resolved plasma diagnostics. Recently, this approach has
been used to study the time decay of NO in situ in single discharge pulses [5]. Considering the
increase of the gas temperature in the DC discharge the NO concentration was found to remain almost
unchanged during a 1 ms plasma pulse. However, the application of successive pulses suggested a
conversion of NO. Selecting an adequate absorption line provides a sensitive, non-invasive
temperature probe if the experiments can be carried out under static and flowing gas conditions.

These initial experiments have been extended to long plasma pulses of 100 ms to study the
suggested chemical removal of NO after several short plasma pulses, which would correspond to the
millisecond time scale. The experimental setup is almost essentially the same as employed in ref. [5]
and thus only the few changes are described here. A replaced power supply enabled the long plasma
pulse experiments to be performed. In order to facilitate a chemical modelling in the future the gas
mixture consisted of 1 % NO in pure N\(_2\) (instead of an Ar/N\(_2\) mixture). The sensitivity of the
measurement system could be increased by means of an optical double pass configuration yielding
about 100 cm absorption path length through the cylindrical discharge tube. A new thermoelectrically
cooled detector (neoplas control GmbH) was also employed. The detector element (VIGO) was
slightly more sensitive than before at the expense of an increased rise time. Finally, this led to less
pronounced rapid passage structures in the recorded spectra (figure 1). Since the absolute NO number
densities were retrieved from calibrated line strength values of unresolved R 5.5 transitions at
1897.35 cm\(^{-1}\) the change of the detector performance is automatically included (see ref. [5] for details
of the calibration procedure). The shift of QCL emission to the present spectral position was
accompanied by a higher laser output power to achieve a reasonable signal-to-noise ratio in the double
pass configuration.

2.2. Results

NO absorption signals have been recorded under flowing and static gas conditions at constant
pressure (266 Pa) during the entire plasma pulse and the off-phase (figures 2 and 3). The time
resolution, which could be in principle 90 ns (i.e. the QCL pulse length), was adapted to the detected
variations of the absorption signal. Examples are shown in figure 1. The experiments have been
carried out at two discharge currents, i.e. 19 mA and 35 mA (figure 2). The lower current case
corresponds to the minimum input power required to obtain a stable discharge.

The integrated NO absorption coefficient (product of number density and line strength) as a
function of time (figures 2 and 3) can clearly be divided into 3 parts during the plasma on-phase. The
eyarly stage plasma pulse (t ≤ 1 ms) is characterised by a gradually decreasing absorption coefficient.
The drop of typically not more than 15 % is comparable to the mainly temperature induced decrease of
the NO line strength which was also observed for short plasma pulses. After ~ 1 ms the decrease of the
NO signal is more pronounced until the integrated absorption coefficient levels off after 25 ms at
~ 20 % of its initial value (figure 2, 35 mA). This plateau is caused by the detection limit of the
configuration (3 × 10\(^{13}\) cm\(^{-3}\)). During the off-phase an increase of the NO signal can be observed. After
about 5 s the initial value is reached which agrees with the residence time of the system under flowing
conditions. It is also clear from figure 2 that the onset of the rapid decrease (5 ms) and the detection
limit (80 ms) are observed later if the discharge current is reduced to 19 mA. Applying a 35 mA
discharge pulse yields a difference between the temporal evolution of the NO absorption signal under
static and flowing gas conditions (figure 3) while almost no difference is detected for 19 mA. Since
the additional depletion of NO under flowing conditions is caused by an increase of the gas
temperature at constant pressure the observed difference between the two gas regimes can be used to estimate the (relative) temperature increase during the discharge pulse [5].

Figure 1. Sample transmission spectra of NO at 1897.35 cm\(^{-1}\) under flowing (grey) and static (black) gas conditions. The absorption features were recorded 0.1 ms (dotted), 1 ms (dashed) and 10 ms (solid) after the ignition of the discharge using 35 mA. (The comparison between the two gas conditions has been shifted for clarity.)

Figure 2. Time dependence of the integrated NO absorption coefficient during 100 ms plasma pulses under flowing gas conditions at 19 mA (triangle up) and 35 mA (triangle down). The plateau at \(\sim 0.2\) corresponds the detection limit of the system.

Figure 3. Comparison of the time dependent integrated NO absorption coefficient under static (full black) and flowing (open grey) gas conditions observed for a 35 mA plasma pulse.

Figure 4. Estimated temporal evolution of the absolute gas temperature for a 35 mA plasma pulse inferred from the difference of the integrated NO absorption coefficients. Data close to the detection limit (\(t > 20\) ms) were considered.

A calculation using a simplified model based on the measured injected power density [5] yields a much more pronounced temperature increase which appears unrealistic. A straightforward downscaling of the injected power density leads to the conclusion that less than 50% of the input power are used for neutral gas heating in the present case of pure \(\text{N}_2\) as background gas. The increase after 10 ms may be explained by vibrational-translational exchange. The identification of the main reactions requires a chemical modelling work which is now in progress.
3. Time resolved studies on industrial pulsed DC discharges containing Boron

3.1 General considerations

Non-equilibrium low-pressure molecular plasmas containing boron are valuable tools in plasma enhanced chemical vapor deposition (PECVD) processes as well as in etching systems to deposit or remove thin films and to treat surfaces for improved properties. Various precursor molecules like BCl$_3$, BF$_3$ or B$_2$H$_6$ are used to provide active boron-containing species in the plasmas. In particular Boron Trichloride (BCl$_3$) is a source gas of considerable interest in plasma research and industry since it is used for the surface modification of steel components in mechanical engineering and automotive industries as well as for plasma etching of semiconductor devices. In contrast to the widespread application of gas discharges containing BCl$_3$ in industry, not much is known about the internal discharge parameters and phenomena, including processes of precursor fragmentation, plasma heating and chemical conversion processes. Even though IRLAS is well suited for this purpose, it is rarely applied for investigations in gas discharges containing BCl$_3$. Due to the high intensity and its good match with CO$_2$ laser modes, in particular the $v_3$ vibrational band of BCl$_3$ around 958 cm$^{-1}$ was used for investigations in BCl$_3$ [6,7] with and without rf discharge in the lab and for plasma process monitoring [8].

3.2 Experimental

For the present work QCL absorption spectroscopy (QCLAS) was applied for the investigation of the discharge chemistry in a industrial pulsed-dc-discharge-reactor (Type CVD4, ELTRO GmbH, Germany). The plasma reactor was a bell furnace style ($\varnothing$ 80 cm, h: 150 cm) with walls heatable to temperatures up to 900 °C. The substrate holder acts together with the electro conductive steel substrates as the cathode of the discharge while the bottom is grounded together with all other metal parts and forms the anode. The plasma is ignited as a thin layer around the substrates, as typically for pulsed dc-discharges. The process gases (BCl$_3$ + H$_2$ + Ar) were pumped through a port at the other side of the plate. The furnace and the plasma processing were controlled by an industrial computer system. First measurements have been performed using the Q-MACS Process 2 (QCL Measurement and Control System). The optical design consists of a pulsed QCL 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. Figure 5 shows the scheme of the experimental arrangement.

3.3 Results

The data acquisition unit of Q-MACS Process was designed for the requirements of the TDLWinTel software package [9,10]. This program can be used to control QCLs and 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 ms 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.

The lack of absorption line data for several molecular source gases used in industrial plasmas is a major problem for the application of infrared absorption spectroscopic techniques for process analysis and control. Knowledge of exact wave number positions and line strength data of absorption features is an important precondition for quantitative measurements by absorption spectroscopy. Therefore this spectral information has to be acquired before measurements at industrial reactors can be performed. For the determination of the line data from the recorded spectra first the theoretical absorption line width was calculated from the pressure-, Doppler- and instrumental broadening. Then an initial guess of the unknown line positions and strengths was created and varied until the residuals of a least square fit, using this data, in comparison to the recorded spectra were below a given value. Following this, a final calculation of the line strength from resulting shapes was performed. Then a data file containing the line parameter was produced, which is compatible to the HITRAN database format [11]. The data set consists of 289 lines. This is a much smaller number than the 1600 lines per cm$^{-1}$ expected from literature [6] but sufficient to reproduce the actual spectra. The BCl$_3$ data file was used for
measurements with QCLs (Figure 6). If pulsed QCLs are tuned by a small DC current ramp provided by TDLWintel, they show typically a smaller scanning range and bigger instrumental broadening, compared to TDLs. Nevertheless, it was possible to fit absorptions of BCl$_3$ to verify test gas concentrations using QCLs. Therefore, spectral fits of BCl$_3$ spectra using the present data can be used for on-line process control. The data set gives sufficient flexibility for the monitoring of industrial plasma processes with changes of the total pressure or the gas temperature.

**Figure 5.** Experimental arrangement of the Q-MACS Process 2 with IR-fibre coupling to access the industrial plasma reactor.

**Figure 6.** Test-fit of a BCl$_3$ spectrum measured with QCLAS.

Figure 7 shows an example of a plasma process monitoring with various contents of BCl$_3$ 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 prove that it is possible to monitor industrial plasma processes using the Q-MACS Process 2. Particularly, it is possible to monitor the development of the concentration of the precursor gas BCl$_3$ in the pulsed DC plasma reactor while driving process plasmas to deposit Boron based hard coatings.

**Figure 7.** Change of the BCl$_3$ signal in the plasma process

**Figure 8.** Schematic of the optical board of the QCLAS arrangement with two QCLs, measurement detector (Det 1), reference detector (Det 2), reference gas cell (RGC), beamsplitter (BS) and the IR fiber. The IR radiation is coupled back to the IR fiber with an external mirror in the reactor [15].
4. In situ monitoring and control of plasma etch processes in semiconductor industry

4.1. QCLAS for MFC control

In plasma etch processes the gas composition in the plasma bulk is a key parameter determining process stability and process results. It depends on various factors like (i) feed gas flows and pump speed, (ii) gas adsorption and desorption at the reactor walls, (iii) chemical reactions in the plasma and at the surfaces and also (iv) on total gas pressure and temperature. Up to now, typically optical emission spectroscopy, self excited electron resonance spectroscopy and mass spectrometry have been applied for online monitoring of plasma etch processes. The drawback of all these methods is the lack of direct and quantitative access to etch relevant properties, like the concentration of precursors or of molecular etch products in the bulk plasma.

With the compact and modular measurement device Q-MACS [12,13], it is possible to use the potential of the QCL for plasma process control. First applications of an especially designed Q-MACS for in situ process monitoring of the industrial production of DRAMs have been published recently [14]. It was shown, that important etch products, like the SiF$_4$ molecule, can be monitored in situ during etch processes for deep trench structures in silicon in real-time and under conditions of high volume production. With this, such concentrations can be used for process control purposes, like feeding them back to the process hardware in a control loop. This has successfully been shown for the control of mass flow controllers (MFC) [15]. The feed gas flow can be adjusted at the MFC on the basis of the measured concentration in the plasma reactor via QCLAS in order to keep the target concentration constant, whatever the process is.

Additionally, it could be demonstrated, that process control with the help of QCLAS is not only applicable for one species but also for two molecular species simultaneously. For this purposes the optical board of the Q-MACS was redesigned having integrated a second QCL as depicted schematically in figure 8. The IR radiation of both QCLs is combined by a beam splitter and transmitted via an optical fiber to the reactor. Using a mirror inside the plasma chamber the IR radiation is reflected back to the detector (Det 1) on the optical board. The radiation of both lasers is measured with the same detector, because they are multiplexed. In addition, in a reference path the spectral emission stability of the QCLs is monitored using a gas cell filled with C$_2$H$_4$ and controlled via line locking. For this proof of principle a planar microwave (MW) plasma reactor has been used as plasma source. Details of the plasma reactor can be found elsewhere [16].

The QCLs were selected for the detection of the SiF$_4$ and C$_4$F$_6$ molecule, which are important precursors in semiconductor industry. The QCLAS measurements of the precursor C$_4$F$_6$ have been based on FTIR studies of the absorption behaviour of the molecule [15]. For the measurement of C$_4$F$_6$ one QCL was selected to emit at 973 cm$^{-1}$, whereas the other QCL detects SiF$_4$ at 1028 cm$^{-1}$.

![Figure 9](image-url)
4.2. Results

To demonstrate the potential of QCLAS for process control, the in situ measured molecular concentrations were fed back via a proportional-integral-derivative (PID) control loop to the MFCs. The aim was to control the gas feed into the MW plasma reactor via concentration measurements in the chamber. Therewith, the gas concentration is the control variable, the gas flow is the actuating variable respectively. If the actual concentration deviates from a given target concentration, a special developed control loop changes the flow at the MFC, until the difference vanishes. The results for the measurements in the gas phase are shown in the left graph of figure 9. In a first step a gas composition of SiF$_4$, C$_4$F$_6$ and N$_2$ was monitored keeping the total pressure constant at 30Pa. With the help of the PID control loop the concentrations of SiF$_4$ and C$_4$F$_6$ were kept constant independently but simultaneously even in case of changing the admixture of N$_2$. Based on these gas phase experiments the control of species concentrations was also applied for a SiF$_4$/N$_2$ MW plasma. The right side of figure 9 shows (i) how effective the plasma leads to a fragmentation of the SiF$_4$ precursor and (ii) how the concentration of the SiF$_4$ is kept constant by controlling its flow. In this example the PID control loop enforced more than a doubling of the SiF$_4$ flow when the plasma is switched on in order to keep the SiF$_4$ concentration constant in the reactor. In the plasma off-phase the target concentration of the SiF$_4$ precursor of $5 \times 10^{14}$ cm$^{-3}$ is again automatically achieved after approximate 1min. This system response is directly connected to the time needed for measurable changes in the concentrations in the reactor since the flow was changed at the MFC. Therefore it strongly depends on properties like reactor geometry, flowing conditions, pump speed and the MFC itself. Compared to typical process times for etching deep trench structures in silicon for DRAM production of more than 10min [14], the MFC control via QCLAS in the present configuration would be adaptable.

Acknowledgments

K.-D. Weltmann is gratefully acknowledged for his continuous encouragement and general support. The authors are especially thankful to D. Dahl, H. Zimmermann, F. Weichbrodt and U. Macherius for their permanent support. The stimulating climate in working with O. Guaitella and C. Lazzaroni is especially acknowledged. The authors give sincere thanks to S. Strämke and C. Harward for valuable long term cooperation.

References

[1] De Benedictis S, Dilecce G, Simek M 1997 J. Phys. D: Appl. Phys. 30 2887
[2] Castillo M, Herrero V J, Mendez I, Tanarro I 2004 Plasma Sources Sci. Technol. 13 343
[3] Rousseau A, Dantier A, Gatilova L V, Ionikh Y, Röpcke J, Tolmachev J A 2005 Plasma Sources Sci. Technol. 14 70
[4] Zijlmans R A B 2008 Ph.D. Thesis Eindhoven University of Technology
[5] Welzel S, Gatilova L, Röpcke J and Rousseau A 2007 Plasma Sources Sci. Technol. 16 822
[6] Richton R E and Farrow L A 1982 J. Chem. Phys. 76 (11) 5256
[7] Farrow L A 1985 J. Chem. Phys. 82 (8) 3625
[8] Hempel F, Artysyenko V, Weichbrodt F and Röpcke J 2009 J. Phys.: Conf. Series 175 012003
[9] Zahniser M S, Nelson D D and Kolb C E 2002 in Applied Combustion Diagnostics, Kuhse-Hoinghaus K and Jeffries J (eds), Taylor and Francis, New York 648
[10] Nelson D D, Shorter J H, McManus J B and Zahniser M S 2002 Appl. Phys. B 75 343
[11] Rothman L S, Jacqueurt D, Barbe A, Benner D C, Birk M, Brown L R, Carlear 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, Mandin J Y, Massie S T, Orphal J, Perrin A, Rinsland C P, Smith M A H, Tennyson J, Tolchonov R N, Toth R A, Vander Auwera J, Varanasi P, Wagner G 2005 J. Quant. Spectrosc. Radiat. Transfer 96 (2): 139
[12] Röpcke J, Welzel S, Lang N, Hempel F, Gatilova L, Guaitella O, Rousseau A and Davies P B 2008 Appl. Phys. B 92 335
[13] Stancu G D, Lang N, Röpcke J, Reinicke M, Steinbach A and Wege S 2007 Chem. Vap. Deposition 13 351
[14] Lang N, Röpcke J, Steinbach A and Wege S 2009 IEEE Trans. Plasma Sci. in print.
[15] Lang N, Röpcke J, Wege S and Steinbach A 2009 Eur. Phys. J. Appl. Phys. in print.
[16] Ohl A 1998 J. Phys. IV France 8 7