Infrared Laser Absorption Spectroscopy with Quantum Cascade Lasers in Industrial Application

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Spectroscopic methods for gas analysis and plasma diagnostics in the field of the mid-infrared (MIR) spectral range were lacking in sufficient time resolution up to now, they were cumbersome and not robust enough or simply too expensive. Through quantum cascade lasers as radiation sources the application of the mid-infrared absorption spectroscopy in the industry can be revolutionized. Although the industrial use in the plasma process is still in its infancy, its enormous potential is already evident, as demonstrated by measurements on plasma etching systems in the semiconductor industry, which is impressively documented.

1. Introduction

Quality and efficiency demands of industrial production processes are not only rising for economic reasons in numerous industries but also ecological and security standards are becoming tighter. Fundamentally, a competitive constraint exists on the market that continuously demands smaller and lighter components and devices accompanied by increasing requirements on surface properties that go alongside increasingly complex component geometries.

Perspectively, plasma surface technology can offer solutions that cover all industry branches. Highly developed plasma diagnostics are an important requirement for the achievement of the objectives. Especially the diagnostics of molecular, chemical active plasmas are one of the prerequisites to control and monitor processes of complex, industrial plasma-chemical etching and coating processes as in the semiconductor industry, for instance. The mid-infrared laser absorption spectroscopy helps to optimize processes wherever a high degree of reliability, safety and speed as well as measurement sensitivity is required and demanded.

2. Infrared-Laser absorption spectroscopy

The absorbed radiation for rotational and vibrational transitions in molecules is in the infrared spectral range and typical for a certain species. The usage of infrared laser absorption spectrometer made it possible to clearly identify gases and plasma components as well as to determine their absolute concentration. Devices fulfilling current industrial standards in terms of costs, compactness and robustness exclusively function within the near infrared range (NIR; 0.7 - 3 μm). The absorption of most molecules is relatively low in this range so that the required highly sensitive measurements cannot be performed most of the time. The highest absorption of many molecular gases and plasma components is in the mid-infrared range (3 - 20 μm) where, in contrast, very high sensitivities in the ppb-range can be realized. Some gases, like SiF\textsubscript{4} and NF\textsubscript{3} that are important for plasma-technological processes, can only be detected in the mid-infrared range. However, tunable diode lasers (TDL) were the only option for laser absorption spectroscopy in the mid-infrared range for quite some time. Those required extensive cooling with liquid nitrogen or even helium. Furthermore, in order to attain an applicable signal-to-noise ratio, the detector had to be cooled due to the tunable diode lasers’ low integral power. Consequently, corresponding spectrometers are too cumbersome, not robust enough or too expensive for industrial applications.

3. Quantum Cascade Laser measurement systems

In recent years, quantum cascade lasers (QCL) have substantially improved the practical applicability of laser absorption spectroscopy in the mid-infrared range. Quantum cascade lasers have become increasingly more important in spectroscopic research, especially in industrial applications, since its first successful manufacture in 1994. These devices denote a class of highly efficient and powerful lasers with a wavelength between 3.5 μm and 14.1 μm in the mid- to far infrared range. They can be manufactured in a very compact form factor and can be used at room temperature without extensive cooling. Quantum cascade lasers, available on the market, often only have the size of a match head. They have high radiation intensities and can be spectrally tuned, what favors its application in optical measurement, especially in absorption spectroscopy. These lasers deliver the desired radiation without elaborate cooling.

In addition, the detector only requires a simple cooling (Peltier cooling) due to the high level of laser radiation. New attractive possibilities have been opened up for wide industrial use of highly sensitive mid-infrared spectroscopy. Besides, devices for mobile usage are easy to realize as of now. In the meantime, first measurement systems are available on the market that use quantum cascade lasers as radiation sources.
for different industrial and research-related applications, as offered by neoplas control GmbH in Greifswald, Germany, for example (Fig. 1). Quantum cascade laser measurement systems are characterized by a high time resolution at an extremely high selectivity and sensitivity that reaches detection limits in the low ppb-range for some gases. Under certain process conditions, even measurements in the ppt-range (parts per trillion) can be done. The systems are compact, robust and easy to handle and calibrate. Absolute concentrations of gases and plasma components can be determined virtually in real-time through high time resolutions down to nanoseconds. Examples include C₂H₆, CO, CO₂, COCl₂, NH₃, NO, NO₂, N₂O, NF₆, B₂H₆, BCl₃, SiF₄. A high level of flexibility and extensibility is guaranteed by the system’s modular design.

Neoplas control’s “Q-MACS Process fibre” is a quantum cascade laser measurement and control system that was exclusively developed for online measurements in plasma reactors. The system is equipped with an optical fiber coupling and a two-channel structure with a measuring and reference channel that allow highly sensitive online measurements within a plasma reactor. The optical fiber creates a direct connection between measurement system and the reactor chamber. For this to work, the laser beam is guided to the reactor through a window. Within the plasma, the laser beam’s intensity is reduced by absorption and finally reflected by a mirror and conducted back into the measurement system (Fig. 2). Thereby interferences affecting the measurement, which are caused by a temperature-induced extension of the reactor walls, can be compensated. The two-channel structure serves to compensate the laser beam’s small fluctuations in its wavelength.

A completely new QCL driver system, which integrates up to 8 independently running quantum cascade lasers, is on the market now. Figure 3 shows the 8 channel Q-MACS Basic MC control unit together with a laser head, which allows driving of TO3 housed pulsed and continuous wave lasers. Hence it is possible to simultaneously detect up to 8 molecular gases or plasma components in situ at different wavelengths for the first time with the help of a compact quantum cascade laser measuring system. Besides its industrial applications the system is expected to trigger new developments in fundamental research on molecular plasmas. Of particular interest is the so far insufficiently investigated role of unstable radicals, which determine the reaction kinetics in the gas phase as well as the interaction between plasmas and surfaces.

4. Applications of QCL measurement systems

There are various fields of application for quantum cascade laser measurement systems in plasma technology but also in other areas such as environmental, medical or security technology. Thanks to the capabilities of the quantum cascade laser measurement system to determine process gases’ or reaction products’ absolute concentrations in situ and close to real-time, the systems are well suited for industrial process control and monitoring. An improved control of gas and plasma pro-

Fig. 1 Measurement and control system Q-MACS Process fibre of the neoplas control GmbH.

Fig. 2 Layout of a QCL-Measuring system for controlling plasma reactors.

cesses can not only lead to improvements in quality, but also to efficiency enhancements in a wide range of industrial sectors. The semiconductor industry is one of the important client industries (see section 5) alongside the photovoltaic industry, display technology as well as engineering and vehicle construction. Areas of application in the general process technology can be found in chemical, petrochemical and pharmaceutical industries. Potential fields of application besides the process technology include, among others, the following: environmental monitoring of exhaust gases (road traffic, engines, power stations and waste incineration), medical technology (breath gas analysis for non-invasive diagnostics and therapy monitoring) and security technology (monitoring of production systems and gas tanks, detection of explosives and warfare agents).

5. Online measurement in plasma etching systems

The control of plasma systems in the semiconductor industry is a particularly important application for quantum cascade laser measurement systems. An increasing competitive pressure and a growing complexity of production demand quicker and more precise measuring techniques for controlling a variety of different plasma-based coating and etching processes, which are essential for the manufacture of microchips. In addition, environmental and safety demands are constantly increasing. The real-time measurement of concentrations, such as etching gases or molecular etching products, in a plasma reactor has a tremendous potential for a better understanding of plasma processes. Moreover the influence of control parameters, what was observable only to a limited extent up to this point, could now be determined with highest sensitivity and utilized to optimize process conditions. Applications of quantum cascade laser measurement systems for process control enable substantial improvements in quality by stable and reproducible coating and etching processes. As a result, waste and defective goods can be reduced while resources will be saved and used in a more efficient manner. This applies to both substrate materials like silicon as well as process gases that are environmentally problematic in some cases, such as fluorinated hydrocarbons.

The quantum cascade laser system Q-MACS Etch, a tailored configuration in the Q-MACS Process fibre product range, consists of a pulsed infrared QCL source with the laser wavelength tunable in the range of 1027 cm\(^{-1}\) to 1032 cm\(^{-1}\), optical components, detectors and data acquisition cards controlled by a computer. The laser driver used is a Q-MACS Basic, which provides a laser pulse width from 10 ns to 255 ns and a repetition frequency up to 1 MHz. The system operates in the inter pulse mode, where the QCL is driven with a pulse width of 12 ns and a repetition rate of 500 kHz. Thereby the average optical power for the lasers emission of about 1 mW and the narrower laser line width of less than 0.008 cm\(^{-1}\) assure highest sensitive detection of single absorption features. The central frequency of the QCL at 1027 ± 0.3 cm\(^{-1}\) is chosen by changing the working temperature between −30 °C and 30 °C and the pulse current through the laser in the range from 0.5 A to 15 A. In order to scan the wavelength over a certain spectral range, an additional DC voltage ramp was applied to the laser at a frequency of 1 kHz. Therewith each millisecond a complete spectral region is scanned, what allows a response time sufficient for various industrial in situ monitoring applications. Applied to an industrial plasma system used in the manufacturing process of DRAM memory chips by etching silicon, a reliable monitoring of the etching process for single wafers could be successfully demonstrated by the Q-MACS Process fiber (precursor gases were NF\(_3\), HBr and O\(_2\)). Therefore, the concentration of one of the molecular main etch products (SiF\(_4\)) was determined during the process. The results show a connection between the amount of SiF\(_4\) produced during the etching process, and the etched trenches’ dimensions (depth, bottom void). Absorption measurements of etch relevant species like SiF\(_4\), the particular MIR-light conductor for coupling the laser beam into the plasma will be installed on the reactor’s side access; the reflection of the beam is transmitted through a mirror in the reactor interior. If the light conductor will be installed on the reactor’s top access, the silicon-wafer will function as a reflective surface. This arrangement demonstrated that the partial permeability of silicon and SiO\(_2\) in the mid-infrared range could be used to determine the etching rate of SiO\(_2\) and silicon-wafers through interferometry during the process.

Beyond that the potential of quantum cascade laser absorption spectroscopy (QCLAS) for online process control was successfully demonstrated by feeding back the in situ measured molecular concentrations via a proportional-integral-derivative (PID) control loop to the relevant mass flow controllers (MFC). The aim was to control the balance of the gas composition in the microwave plasma reactor via concentration measurements in the chamber. Therewith, the gas concentrations is used as the control variable and the gas flow is the actuating variable respectively.

The results for the measurements in the gas phase are shown in Fig. 4. In a first step a gas composition of SiF\(_4\), C\(_2\)F\(_6\) and N\(_2\) was monitored keeping the total pressure constant at 30 Pa. With the help of the PID control loop the concentrations of SiF\(_4\), C\(_2\)F\(_6\) and C\(_2\)F\(_7\) 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\(_2\) microwave plasma. Figure 5 shows the efficiency of the fragmentation of the SiF\(_4\) precursor in the plasma as well as how the concentration of the SiF\(_4\) is kept constant by controlling its flow.

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 mass flow controller. Therefore, it strongly depends on properties like reactor geometry, flowing conditions, pump speed and the mass flow controller itself. Compared to typical process times of more than 10 min for etching deep trench structures in silicon for DRAM production, the mass flow control for precursor gases via QCLAS in the present configuration is adaptable.
These results demonstrate the ability of in situ QCLAS for process control of plasma processes by controlling the concentration of process relevant molecules via dynamically adjusted precursor flows, what has been exemplarily shown for important gases in semiconductor production $\text{C}_2\text{H}_4$ and $\text{SiF}_3$.  

6. Conclusion and summary

The invention of quantum cascade lasers emitting in the mid infrared spectral range, where some chemical compounds absorb exclusively and generally much stronger compared to other spectral ranges, opens up new opportunities for industrial measurement tasks. QCLAS measurement systems provide highest sensitivity and long term stability, while assuring a high degree of compactness and robustness. This makes these devices well suited for high performance industrial concentration monitoring applications. As an example the outstanding characteristics of laser absorption spectroscopic devices based on quantum cascade lasers are illustrated by the measurement of precursors and etching products in industrial etching plasmas used for semiconductor processing.

This challenging application shows the enormous potential of that technology, which is on its way to capture other markets in the automotive industry as well as in medical diagnostics.

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