LASER DETECTION

Dr Lars Hildebrandt, nanoplus, Germany, provides an overview of gas sensing using semiconductor laser spectroscopy.

The use of laser spectroscopy in research and industry has grown continuously in recent decades. It is the workhorse for fields such as process control, gas concentration monitoring or environmental tracing, where tunable diode laser absorption spectroscopy (TDLAS) is applied.[1]

TDLAS exploits the rotational vibrational optical absorption features of gases for single-mode semiconductor laser-based trace gas detection. It is used for highly selective and sensitive measurements, enabling detection of parts per million to parts per billion, and even parts per trillion level concentrations for in-situ measurements. Both portable devices and contactless techniques are available.

Compared to other highly-selective techniques, such as gas chromatography or mass spectrometry, long-lifetime TDLAS instruments combine low cost of ownership with fail-safe and easy handling. As illustrated in Figure 1, a standard TDLAS setup consists of a wavelength tuning distributed feedback (DFB) semiconductor laser emitting monochromatic light at the absorption line of the trace gas, an optical lens to collimate the light, a gas cell or space containing the gas to be measured (CH_4 in this case) and a photodetector (PD) on which the light is focused.

Major improvements in sensing speed, noise reduction and sensor miniaturisation are achieved using the strongest absorption bands of the measured gases. For a large number of industrially and environmentally significant gases, these bands are in the mid-infrared (MIR) wavelength range of approximately 3 – 6 µm. As an example, Figure 2 shows the absorption strength for methane.

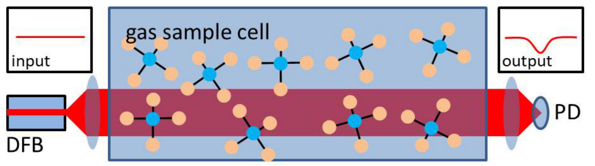

Figure 1. A standard TDLAS setup.

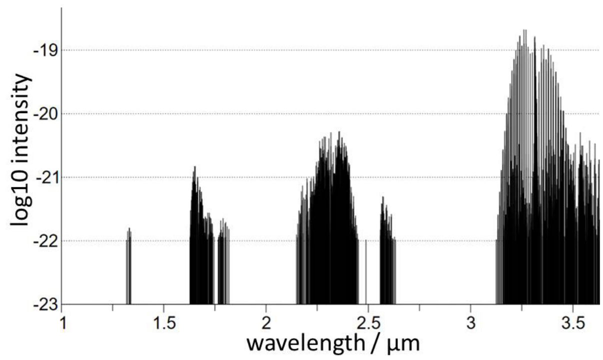

Figure 2. Absorption lines for methane between 1 µm and 3.5 µm. The line strength at 3270 nm is two orders of magnitude larger than the widely-used feature at 1654 nm.

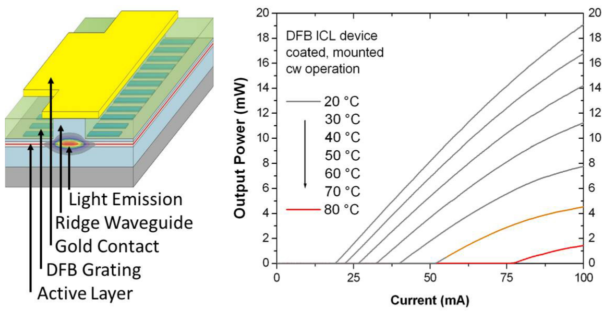

Figure 3. A complex coupled DFB laser design with a typical PI curve at different temperatures.

A complex coupled DFB design is used by nanoplus. This concept is based on an overgrowth-free etching process. The complex coupling is obtained by combining a ridge waveguide structure with metal gratings on top of the waveguide layer on both sides of the ridge, as shown in Figure 3. This image also illustrates a typical power current (PI) curve of such a device at different temperatures. Continuous wave (CW) output power of a few mW with tuning ranges of a few nanometres is sufficient for most TDLAS applications.

There are three types of semiconductor DFB lasers commercially available. In bipolar laser diodes, electrons and holes have an optical interband recombination at the p-n-junction. This transition has a high-energy gap, which allows shorter wavelengths to be reached with these devices. In interband cascade lasers (ICLs), electrons and holes have an optical interband recombination at a W-shaped quantum well of the semiconductor material.[2] The energy of this transition is lower than those of bipolar diodes, which is why ICLs cover higher wavelengths. Finally, for quantum cascade lasers (QCLs) the valence band is irrelevant for the optical transition. Electrons and holes have an optical intraband recombination within the conductive band of the semiconductor material. The energy is lower than ICLs, so the achievable wavelengths are higher.

To obtain a low power consumption system that is easy to design, a low threshold power density is required. In the MIR, an ICL with a DFB structure can be utilised. These ICLs are GaSb based.

The performances of the three different semiconductor laser designs in this spectral region are compared in Figure 4. GaSb-based type-I transition bipolar single-mode DFB laser diodes operating in CW mode at room temperature (RT) show a rise in threshold power density towards wavelengths of above 3 µm. Longer wavelengths are hardly realisable. Approaching from above, the situation is similar for DFB QCLs based on InP. The only sources for this MIR region are ICLs featuring CW operation at or near RT with low energy consumption.

Applications

For TDLAS, single-mode semiconductor laser sources emitting CW in the 3 – 6 µm MIR range have been commercially available for a few years from a small number of vendors. Their low power consumption makes them preferable to QCLs. Most applications now feature ICLs or, at least, developments are ongoing to replace QCLs because many gases (CO_2, CO, HCl, NO, N_2O, H_2O and H_2S) and most hydrocarbons (CH_4, CH_2O, HCN and C_2H_6) have their strongest absorption feature in the MIR. Other gases such as SO_2, C_2H_2, NO_2, NH_3 or O_3 show at least strong and attractive absorption features here.

Applications for hydrocarbon gas detection systems using ICLs include the following:

Combustion control in high temperature processes by quantifying CO_2 and CH_4

Continuous monitoring of CO_2 or CH_4 concentrations is essential for the efficiency of high-temperature processes in incinerators, furnaces or petrochemical refineries. Managing the CO_2 content in combustion processes simultaneously reduces greenhouse gas (GHG) emissions.

Quality and safety control in natural gas pipelines by monitoring CO_2 and CH_4

CO_2 is a natural diluent in oil and gas deposits. When it reacts with H_2S and H_2O, steel pipelines corrode. Real time monitoring of CO_2 at natural gas custody transfer points is necessary to prevent contaminated gas from flowing downstream. Immediate measures can be taken to purify the natural gas. CH_4 leaks can cause dangerous situations and are hard to locate precisely. Hence, maintenance of underground pipelines incurs high costs. These leaks are also an important source for GHGs.

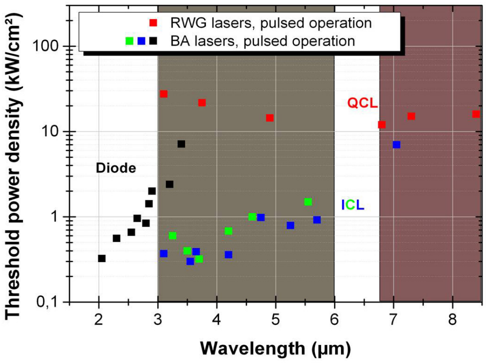

Figure 4. Comparison of power threshold densities for type-I transition (black), QCL (red) and ICL (green and blue) DFB lasers at different wavelengths.

With TDLAS, a strong tool is available for the manufacture of portable leak detectors.

Emission control of GHGs

GHGs and climate change have triggered global emission monitoring of pollutants such as methane and ethane. The global warming potential of methane is approximately 30 times higher than that of CO_2. Studies are executed on behalf of the US Environmental Protection Agency (EPA) to quantify the methane emissions caused by the increased natural gas exploration and production in the US. Ethane equally has a critical impact on climate change. Emissions are related to fossil fuel and biofuel consumption, biomass combustion and natural gas losses. Trace gas detection of ethane is an important tool for monitoring GHGs.

Emission control by methane source identification

Ethane is a byproduct of methane emissions. Ethane ratio varies between methane emissions from thermogenic and biogenic sources, which allows for differentiating oil and gas reserves from those of livestock, landfills, wetlands or stagnant water.

Combustion control in integrated gasification fuel cell cycles

The methane content of syngas is controlled to improve the combustion efficiency of integrated gasification fuel cell cycles.

Quality control of ethylene production in the petrochemical industry

Acetylene is a byproduct in the cracking process of ethylene production. The petrochemical industry minimises the compound via hydrogenation. This process enhances the purity and quality of the ethylene that is manufactured.

Explosion prevention by monitoring acetylene

Acetylene is used for gas welding because the flame is easily adjustable. At the same time, it is highly explosive when mixed with oxygen or when there is a sudden change in pressure or temperature. For workers' safety, the acetylene concentration has to be continuously monitored.

Monitoring of workplace exposure to formaldehyde

Formaldehyde has been used in consumer and industrial products since the beginning of the 19th Century. Current annual formaldehyde production accounts for 21 million t, of which approximately 50% are processed as adhesives in pressed wood panels. In 2004, formaldehyde was classified carcinogenic by the International Agency for Research on Cancer. Since then, formaldehyde concentrations have been strictly controlled in the production process as well as in the finished product. Laser-based measurement systems are required to detect the maximum levels of 0.01 ppb (USA) and 2 ppb (EU). A similar instrument detects formaldehyde in the air on the International Space Station (ISS).

Studies and projects

Collaboration and knowledge exchange with industry and research partners is vital to develop products and technologies for laser-based gas sensing. nanoplus regularly participates in projects and studies supported by the European Union (EU) and the German Federal Ministry of Education and Research. For example, SensHy and WideLase were collaborative efforts, where scientists and engineers from across Europe teamed up to develop a new generation of laser-based gas sensing systems for both hydrocarbon detection and other applications. The MirPhab project is concentrating on a pilot line for fabricating chemical sensors. Targets are the quality control of hydrocarbons in chemical processes and early warning systems for leaks in gas distribution networks. iCspec focuses on the in-line process control of many technical relevant gases, such as hydrocarbons. The main purpose of this project is to develop gas analysers beyond the state-of-the-art for fast in-line multi-component monitoring of gas composition in a process steam and to replace currently employed analysers.

Conclusion

The technology, applications and studies outlined in this article highlight the importance of TDLAS gas detection systems, particularly for hydrocarbons in the MIR spectral region. Many new instruments for both novel and common applications are entering the market with improved specifications, such as lower detection limits and enhanced usability. These cost-effective solutions can benefit users by leading to greater return on investment.

References

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