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Project title: Terahertz Detection of Atoms in Plasma Processes

Project number: K54/2017

Executive Summary

The most important result and success is the development of a high-resolution absorption spectroscopy (HRAS) setup based on a single-mode 4.745-terahertz quantum-cascade laser (THz QCL). This novel diagnostic technique based on THz HRAS allows for absolute measurements of ground state densities of atomic species in plasma processes. The performance of the HRAS setup was demonstrated by the detection of absolute densities of oxygen atoms in a capacitively coupled radio frequency oxygen plasma at low pressure. To our knowledge, this is the first demonstration of detecting atoms using THz HRAS.

The development of single-mode QCLs based on the GaAs/AlAs materials system for 3.36, 3.92, and 4.75 THz has been completed. Optimized lasers based on the hybrid design allow for unrivalled wall plug efficiencies of lasers based on straightforward Fabry-Pérot resonators with single-plasmon waveguides. The development of GaAs/(Al,Ga)As QCLs operating at 2.31 THz [milestone (MS) 3] has not been completed insofar as the required frequency tuning and output power has not been sufficient for application in a HRAS setup. MS 4, the demonstration of the detection of N^+ ions and Si atoms with a HRAS setup, was not completed during the duration of the project. Since the HRAS setup for 4.75 THz has been completed and suitable QCLs are available at 3.36 and 3.92 THz, the realization of HRAS setups for Al and N^+ atoms/ions is immediately possible. However, a HRAS setup for the detection of Si has to be postponed to a follow-up project.

Single-mode operation of THz QCLs is usually achieved by using two-section cavities or distributed feedback. Here, single-mode GaAs/AlAs QCLs with high wall plug efficiencies and output powers were realized using straightforward Fabry-Pérot resonators with cavity lengths between 0.5 and 1.0 mm. Due to their large mode spacing, a single mode remains in many cases within the gain spectrum. For the fabrication of lasers for a certain target frequency, the correlation between the maximum of the gain spectrum and the position on the wafer was analysed, and a convenient method for the selection of an appropriate wafer piece was developed. To achieve the target frequency with a precision of about 1 GHz, a method for static fine tuning of the laser frequency based on polishing the front facet was demonstrated.

MSs 5 and 6, which contain the development of QCL-based THz frequency combs, could not be completed during the duration of the project. Due to unexpected instabilities during the fast sweep over a relatively large current range necessary for the operation of the HRAS setup, we had to shift our focus to provide QCLs with sufficiently stable light output-current characteristics. Nevertheless, preliminary results on the frequency combs have been achieved, which include the determination of the effective refractive index of THz QCL waveguides and the discussion of its correlation with several parameters of the laser structures. Furthermore, first laser structures with an inhomogeneous cascade for a broad gain spectrum between 3.3 and 4.0 THz have been developed, and continuous-wave operation of a 10-mm-long QCL with narrow mode spacing has been shown.

The Covid-19 pandemic resulted in a significant delay of the project work. In addition, an increasing instability, in particular of the Si flux, of the molecular beam epitaxy (MBE) system, which is more than 20 years old, resulted in an unsatisfactory reproducibility of the growth, which in some cases disrupted the systematic and empirical investigations of the QCLs.

An industrial application of the HRAS setup for plasma science and technology will be in reach after a certain optimization of both, the QCLs and the HRAS setup. The main challenges are to further increase the practical operating temperature, i.e., the maximum operating temperature with an output power of at least 1 mW, beyond 75 K, and to further increase the wall plug efficiency of THz QCLs, which would allow for their use in even smaller cooling devices, since THz QCLs cannot be operated at room temperature.

1. Achievement of objectives and milestones

Single-mode GaAs/AlAs QCLs operating at 3.36 THz (MS 1) with sufficient output power-were achieved. While the detection of O atoms and the determination of their density in a plasma chamber with the HRAS setup was demonstrated, the detection of Al atoms has not been achieved yet (MS 2). The development of GaAs/(Al,Ga)As QCLs operating at 2.31 THz (MS 3) has not been completed insofar as the required frequency tuning and output power have not been sufficient for application in the HRAS setup. The demonstration of the HRAS setup for N^+ ions and Si atoms (MS 4) as well as the development and application of frequency combs (FCs) for 3.3–4.0 THz (MSs 5 and 6) could not be completed during the duration of the project. Due to unexpected instabilities during the fast sweep over a relatively large current range necessary for the operation in the HRAS setup, we had to shift our focus to provide QCLs with sufficiently stable light output-current characteristics for the detection of Al, N^+, and O at 3.36, 3.92, and 4.75 THz, respectively. Nevertheless, preliminary results on the FCs have been obtained. The funding was mainly spent according to the original financial plan. From March 2020 on, all project meetings between PDI and INP were conducted online.

2. Activities and obstacles

The project partner PDI provided first single-mode QCLs at 4.75 THz based on the GaAs/AlAs materials system for the demonstration of an HRAS setup for the oxygen line at 4.75 THz. In order to obtain lasers emitting precisely at the target frequency and in a single mode, the resonator length was optimized. A larger number of lasers with different ridge lengths were fabricated and investigated. The project partner PDI developed a post-processing method for a fine-tuning of the laser length to achieve the exact frequency based on polishing the front facet.

The initial HRAS setup at INP was based on a pyroelectric detector. A tuning range of 7 GHz was achieved, which was sufficient to obtain the first spectra of NH_3 in a reference gas cell using QCLs with emission frequencies around 4.75 THz. This result demonstrated the feasibility of the THz QCL-based spectrometer to detect atomic or molecular species. However, the pyroelectric detector turned out not to be sufficiently sensitive for the detection of Al and O atoms in a plasma reactor. A more sensitive detector, a THz bolometer, was required. During a measurement campaign of one week of INP at PDI, the THz bolometer at PDI was tested successfully as a promising detector for the HRAS detector at the INP. Therefore, a THz bolometer was purchased using financial resources of the INP. Its installation took a rather long time and was further delayed by the Covid-19 pandemic until May 2020. The operation of the new HRAS setup revealed that an upgrade of the bolometer was required, which was finally installed in July 2021. In the meantime, the procedure for recording spectra by continuously tuning THz QCLs was developed at the INP. The performance of the final HRAS setup was evaluated by measuring NH_3 in a reference gas cell with known concentrations, and important parameters such as the tuning characteristics of the laser, the instrumental linewidth, and high accuracy of the concentrations were obtained. Finally, we were able to demonstrate the detection of O atoms in a low pressure capacitively coupled radio frequency (CCRF) oxygen plasma and the measurement of their temperatures and concentrations. At the same time, single-mode GaAs/AlAs QCLs for 3.92 and 3.36 THz were developed, and their performance was tested in the HRAS setup. Single-mode operation was achieved using Fabry-Pérot resonators with sufficiently short laser bars. For the detection of Si atoms, we have developed first lasers emitting at 2.31 THz. This work has not yet been completed. For all lasers, the specific operating conditions at the HRAS setup, namely a fast ramping over a rather large current range, has revealed instabilities of the output power-current characteristics for some of the lasers. The origin of these instabilities has not yet been fully understood.

The development for THz FCs based on QCLs started with the design, fabrication, and investigation of lasers with an inhomogeneous cascade containing 11 sets with 7 different periods in each set with calculated gain maxima at 3.2, 3.35, 3.5, 3.65, 3.8, 3.95, and 4.1 THz. Since the effective refractive index of the waveguides is a crucial parameter for comb operation, the PDI systematically investigated the dispersion of the refractive index for 121 QCLs.

All activities which have not been completed so far require systematic empirical studies by growing a larger number of wafers and the investigation of the related lasers. These studies suffer from an increasing irreproducibility of the operation of the more than 20-year-old MBE system, in particular from an instability of the Si flux. The related non-reproducible doping concentration of the lasers makes systematic investigation very difficult, since the operating properties of THz QCLs depend critically on the correct doping concentration. PDI has acquired a new MBE system, which is expected to be in operation at the end of 2022.

3. Results and successes

The most important result and success is the development of the HRAS setup for plasma diagnostics at INP based on a single-mode, 4.745-THz QCL developed at PDI. This novel diagnostic technique based on THz HRAS allows for absolute measurements of ground state densities of atomic species in a low-pressure plasma. One major breakthrough in the process was the development of QCLs with sufficient frequency tunability to perform spectroscopy. The performance of the HRAS setup was demonstrated by the detection of absolute densities of O atoms in a low pressure CCRF oxygen plasma. To our knowledge, this is the first demonstration of detecting atoms using THz absorption spectroscopy and a manuscript for submission to the high-impact journal Optica is in preparation [1].

The newly developed method for the detection of the absolute density of oxygen atoms could potentially improve the accuracy of the calibration procedure required for two-photon absorption laser-induced fluorescence (TALIF) measurements, the standard method for detecting oxygen atoms up to now. Furthermore, compared to TALIF, the developed HRAS setup is much more compact, robust and easier to implement, even in an industrial environment.

A very important result and success is the development of QCLs based on the GaAs/AlAs materials system for 3.36 and 3.92 and the optimization for 4.75 THz [2]. These optimized QCLs are based on the hybrid design and allow for unrivaled wall plug efficiencies of QCLs based on straightforward Fabry-Pérot resonators with single-plasmon waveguides [3]. The operating parameters of these lasers are very competitive and state of the art.

First results have been achieved with respect to the development of FCs. We investigated the effective group dispersion of THz QCLs [4] as an important parameter for FCs. Furthermore, we demonstrated multimode operation of a THz QCL with a mode spacing as small as 3.6 GHz, which may pave the way for high-resolution frequency comb spectroscopy. For the development of THz QCLs with a given target frequency, PDI reported an approach for in-situ control of MBE growth [5], a method for the selection of the most appropriate location on the wafer [6], and on their long-term stability [7]. In order to achieve emission of the QCLs precisely at the target frequency, the project partner PDI has developed a post-processing approach for a static fine-tuning of the emission frequency by a controlled reduction of the resonator length in sub-µm steps based on polishing the front facet as reported in Ref. [8].

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4. Equal opportunities, career development and internationalisation

The PDI offers positions for scientific projects in international announcements, in which the application of female scientists is encouraged. The PDI possesses a certified strategy for measures in order to enhance a good work-life balance. Unfortunately, postdoctoral applicants with sufficient experience, in particular in the field of THz QCLs, are difficult to find. Therefore, the PDI was not able to hire a female postdoctoral scientist. At PDI, the project work was embedded in the Core Research Area *Intersubband Emitters: GaAs-based Quantum-Cascade Lasers*, which included two international postdoctoral scientists.

At the INP, a scientist from the Netherlands, who was already working there, took up the scientific position financed by the project. He was the most suitable candidate as he is a world-wide known expert in QCL absorption spectroscopy. He was supported by two German technicians funded out of the core support of the INP. In the second half of the project, the scientist from the Netherlands became the new Head of the Department Plasma Diagnostics at the INP, and the scientific position was taken over by a scientist from the United Kingdom, supported by a German scientist. In the final year of the project, a female PhD student from the Netherlands, financed by INP's core funding, also worked on the project. She will continue working on the HRAS setup during the remainder of her PhD.

5. Structures and collaboration

The cooperation within the TERAPLAS project was carried out between the INP and the PDI as originally planned. It has been very constructive and fruitful during the whole duration of the project. There have been a number of one-day project meetings, when necessary, taking place on a regular basis (about every four months) alternating between the PDI and INP as the host institution. From March 2020 on, project meetings were only conducted online due to the Covid-19 pandemic. Furthermore, in the first quarter of the second project year, a measurement campaign of the INP took place at the PDI to test the HRAS setup built at the INP with the THz bolometer available at the PDI to determine the necessary operating parameters for the QCLs. Two members of the INP came to the PDI for about one week. During the whole duration of the project, the PDI delivered QCLs operating at 3.36, 3.92, and 4.75 THz to the INP, which have been tested at the INP and used in the HRAS setup.

For many years, the PDI has been cooperating with the DLR in the framework of both, formal and informal, projects in the field of THz spectroscopy and THz imaging. The TERAPLAS project benefited from the broad experience of the partners at the DLR in this field. In particular, the activities of the DLR in the field of heterodyne receivers at THz frequencies for astronomy motivated the development of THz QCLs with competitively large wall plug efficiency for operation in miniaturized mechanical coolers, which will allow for the future development of improved HRAS setups. The high operating temperatures for continuous-wave operation together with the achieved output powers of several mW of the THz QCLs developed at PDI led to a new project between the DLR and PDI funded by the European Space Agency.

6. Quality assurance

PDI and INP are bound to adhere to the guidelines for safeguarding good research praxis as defined by the code of conduct by the Deutsche Forschungsgemeinschaft (DFG). The application of the rules is monitored by the project leaders as well as the department heads at PDI and INP. The primary data of the research results are kept on trusted storage at the respective institutions. The scientific results have been or will be published as open access in international journals and presented at relevant conferences. Furthermore, selected research data with special value for the plasma science community, including in particular data shown and discussed in journal articles, will be published together with their metadata as citable data sets. The INPTDAT data platform (https://www.inptdat.de) is available at INP for this purpose. This enables an additional exchange between researchers interested in the data worldwide.

7. Additional resources

At PDI, additional resources were used to grow wafers for THz QCLs and to process as well as contact them. In addition, the infrared spectrometer with standard resolution, the Bruker IFS-66v, was replaced by a new model, the Bruker Vertex 80v, a few months before the start of the project. The infrared spectrometer with high resolution, the Bruker IFS 120HR, was upgraded in terms of electronic hardware and complete software to the Bruker IFS 125HR in early 2019. However, it does not make really sense to quote any partial amount for the project.

At the INP, a budget for personnel of € 79,500 was added form institute resources. The scientist working on the project is supported by two technicians, which are paid by the institute. These two technicians have worked on the project during 24 months for 30% and 10% of a fulltime position. During the last six months of the project, a PhD student was funded by the INP (67% of a fulltime position). The INP also contributed € 97,888 to the direct project costs. 1) A THz bolometer for € 92,500, which was implemented in the current HRAS setup as the detector for the THz radiation. Radiation between 1 and 10 THz can be detected without the necessity of a liquid helium cryostat. 2) A DLATGS detector for € 4,820 has been bought for the measurements of the THz radiation as originally planned to be used in the HRAS setup, but which turned out to be not sensitive enough for measurements in a plasma reactor. 3) Silicon windows for € 568 have been acquired as special windows for reference gas cells transparent for THz radiation, which are necessary for the calibration of the spectrometer.

8. Outlook

The successful demonstration of the prototype of the HRAS setup at 4.75 THz is the starting point for its adaption for Al and N^+ at 3.36 and 3.92 THz, respectively. After successful implementation of the new MBE system at PDI, comprehensive empirical studies of various QCL structures will be possible. This will allow for a number of activities, such as the completion of the development of QCLs for 2.3 THz and a systematic investigation of the stability of the lasers under the specific operating conditions due to the fast ramping of the current.

A possible follow-up project between PDI and INP may focus on both, the optimization of the HRAS setup and the development of spectrometers for additional species, such as fluorine atoms in the spectral range between 10 and 14 THz. The optimization of the operating parameters of the THz QCLs will lead to wider tuning ranges, improved operating stability, and higher wall plug efficiencies. The development of QCLs for 10 to 14 THz is rather challenging since this spectral range is the transition region between far- and mid-infrared radiation, for which only very few QCLs have been reported in the literature. The detection of atoms, such as O and F atoms, is of high interest for the semiconductor industry. The INP has a strong link to companies in this field, and future collaborations and technology transfer based on the results of this project are expected as we have already stimulated the interest of industrial companies.

The preliminary results for our THz frequency combs may be continued in a possible PhD project aiming at the development of a comb for spectroscopy between 3.3 and 4.0 THz for the detection on Al and N^+, because the new MBE system is expected to reproducibly grow the respective laser structures with inhomogeneous cascades for broad gain spectra.

Beyond HRAS, the understanding of the time-resolved output characteristics with respect to frequency and power based on a fast ramping of the driving current for recording the required spectra is very important, in particular, when the ramping speed is further increased.

One main challenge for the further development of THz QCLs consists in an increase of the practical operating temperature, i.e., the maximum operating temperature with an output power at least 1 mW, beyond 75 K. Another challenge is the further increase of the wall plug efficiency of THz QCLs, which would allow for even smaller cooling devices, since THz QCLs cannot be operated at room temperature. Both challenges are particularly important for the exploration of new areas of applications of THz QCLs.