NEWSLETTER

IN THIS ISSUE

EDITION 11— 6/2021

- Research Progress - new publications
- Visions for the next funding period of the CRC 1316
- Promotion of Early Career Researchers
- Research Seminar Reports

SFB-TR 87

SFB 1316 **Transient Atmospheric Plasmas**
from plasmas to liquids to solids

FOREWORD.

A continuous dissemination of research progress is the aim of the research centres, SFB-TR 87 and CRC 1316. With this edition, we introduce future research ideas, which are planned to be realised within the next funding phase of the CRC 1316. Preparations for the continuation of this CRC are in full swing. For many, this was also a chance to reflect on the recent years, to look back on this eventful time and to set new goals for the next years.

Next to proposal writing, several workshops have also been offered online in recent months, and several further training measures and equal opportunity offers are also coming up in the coming period.

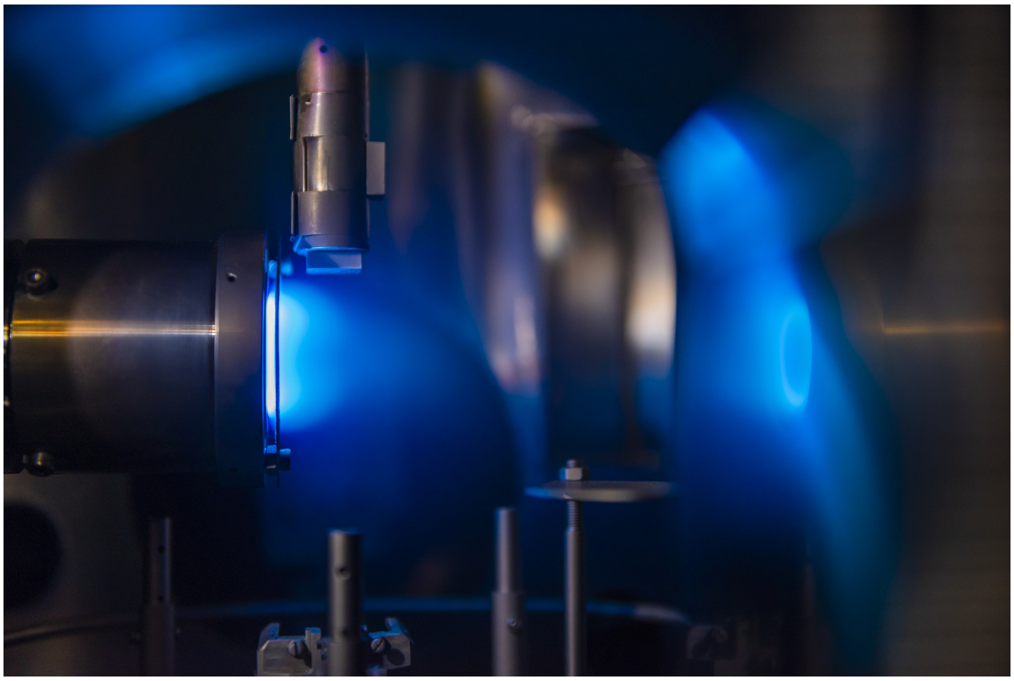
Furthermore, an online tour about the CRC 1316 is currently being developed to introduce the projects to a broader audience and to present the people behind the projects. This should be available to the public in late summer and offers a deeper insight into the projects and work within the CRC.

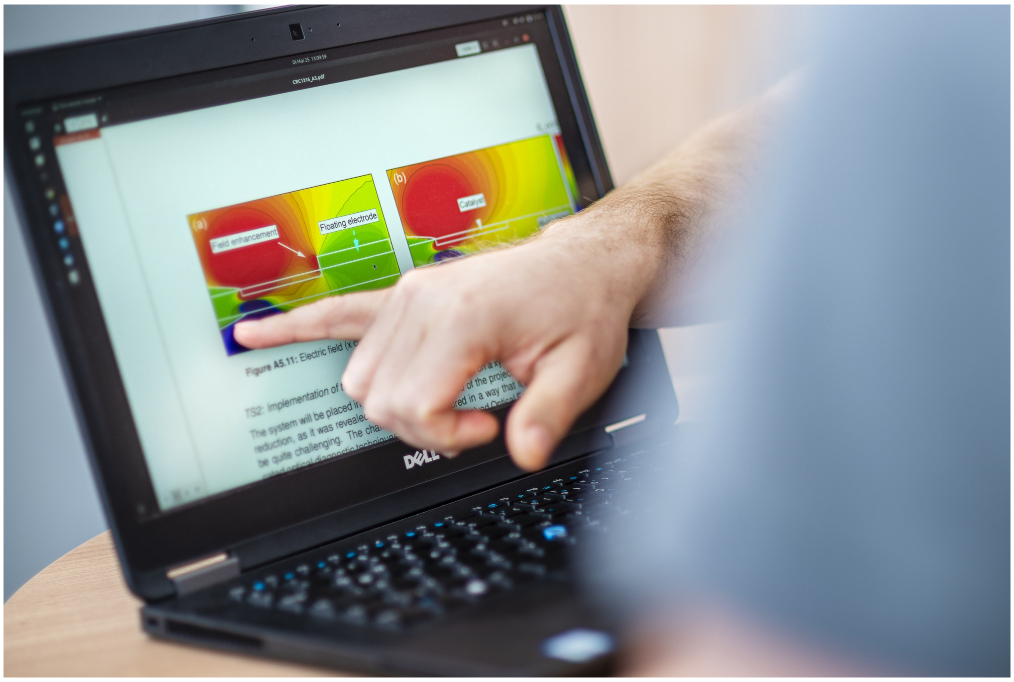
We wish everyone a good start into the summer, further successful research and an enjoyable second half of 2021.

Maike Kai, public relations
for the SFB-TR 87 and CRC1316

Content

IMPRESSIONS FROM THE PROJECTS





fotos by Damian Gorczany

DAVID STEUER studied physics at the Ruhr University in Bochum. As part of his bachelor's and master's thesis, he already worked on project B2 of the CRC 1316. His research focus was the investigation of the densities of reactive oxygen atoms within the COST micro-plasma jet.

He joined the project A6 as a research assistant in December 2020. This project studies the interaction of plasmas and catalytic surfaces in micro-structured array devices.

In the course of his work, the array device will be used for plasma catalysis. In this context, the focus is on the investigation of the species generated inside the plasma, as well as on the further characterization of the discharge.

NEW STAFF

DR. KATHARINA GROSSE has successfully completed her PhD studies in project B7 of the CRC 1316. Her thesis *Discharge ignition, dynamics and chemistry of nanosecond pulsed plasmas in water* covers the in-depth study of discharges in liquids ranging from their ignition to the final chemical products. Two main research questions are discussed in the work: “Which physical processes cause ignition of a high voltage, nanosecond pulsed discharge in a liquid environment?” and “How is the discharge propagating inside the liquid medium and how is this correlating with the chemical species created by the plasma?”.

She is now continuing her work at the Chair for Experimental Physics II in the CRC 1316. Next to her research work, she is engaging in gender equality as a member of the Gender Board as well as social media activities within the upcoming project within the CRC 1316.

PROMOTION OF EARLY CAREER RESEARCHERS - VIRTUAL MGK COLLOQUIUM

The scientific exchange among the CRC 1316 members and the group of Early Career Researcher occurred continuously during the three yearly project meetings and in the workshops organized by the CRC 1316 since 01/2018. However, it is very important that the ECR have also a platform to interact in a conference setting without the impact of their adviser to stimulate the discussions among the ECR. The CRC 1316 initiated such a conference as a so-called MGK Colloquium for the ECR from the CRC 1316 and from the SFB-TR 87. This meeting was organized by the ECRs Jan Kuhfeld and Patrick Preissing in a virtual format on April 21st 2021.

Prominent invited speakers at this event were Prof. A. Bogaerts (university Antwerp), Dr. S. Iseni (GREMI, Orléans) and Dr. T.L. Chng (LPP Paris). Beside presentations within a zoom meeting, virtual poster sessions were performed, enhancing the interaction between the ECR.

Marina Prenzel, public relations
for the SFB-TR 87 and CRC 1316

UPCOMING EVENTS OF THE CRC 1316 & SFB-TR 87

SCHEDULED	**8.-9. JUN**	SFB-TR 87	**Workshop:** Project areas B and A+C
	12.-13. JUL	CRC 1316	**Project Meeting:** Virtual Project Meeting
	10. NOV	SFB-TR 87	**Board Meeting**
	11.-12. NOV		**Workshop:** Project areas A+C and B
COMING UP	**Autumn 2021**		**Conference:** 1st Frontiers in Plasmas in Industry and PT20
	2022	CRC 1316	**Workshop:** Plasma Surface Interaction Kiel-Bochum Workshop
			Workshop: How do different gender codes influence our communication? What can we learn from the other sex?

Please check the CRC 1316 and SFB-TR 87 websites for up-to-date information on the events.

NUMERICAL INVESTIGATIONS OF MICRO ATMOSPHERIC PRESSURE PLASMA JETS IN HE/O2 MIXTURES BASED ON A HYBRID MODEL

Yue Liu, Ihor Korolov, Jan Trieschmann, David Steuer, Volker Schulz-von der Gathen, Marc Böke, Lena Bischoff, Gerrit Hübner, Julian Schulze, and Thomas Mussenbrock

Radio frequency (RF) micro-atmospheric pressure plasma jets (μAPPJs) have been widely used in various fields. For each application, control of the production and delivery of selected species are desired via the use of external parameters. Numerical simulations are efficient for such investigations. Most of previous simulations were performed based on fluid models, including the treatment of charged species dynamics and neutral transport. However, the electron energy distribution function (EEDF) is calculated in 0-dimension with a certain time interval based on the 2-term approximation [Kushner et al. 2005], thus, incapable of describing the fast resolved electron heating dynamics in both time and space domain precisely. The Particle-in-cell/Monte Carlo Collision (PIC/MCC) algorithm can describe electron kinetic behaviors accurately [Korolov et al. 2019], but neutral transport and collisions between heavy particles can hardly be handled due to the vast computational cost and the lack of cross sections.

Considering the characteristics of each numerical model, we develop a numerical hybrid code. Electrons are treated fully kinetically by the PIC/MCC algorithm, while ions and neutral species are handled by a fluid model. Electrons and ions are simulated in 1-dimension perpendicular to the electrodes. Reactive neutral species, due to relative slow reaction rates and the effect of the gas flow, are simulated in 2-dimensions, i.e. the flux caused by diffusion between the electrodes, and a laminar flow in steady state parallel to the electrodes. The neutral densities are updated based on a sequential technique to resolve the distribution along the gas flow. An iterative scheme is designed to separately simulate charged particles and the neutral densities in order to reduce the time cost caused by the responses of various species on different time scales.

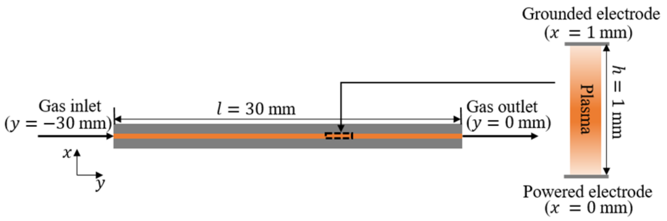


Figure 1. Schematic of the simulation geometry. The figure is taken from Liu et al. 2020; DOI:10.1088/1361-6595/abd0e0].

The schematic of the simulated model is shown in figure 1, including the geometry of the jet and the coordinate system. The working gas is helium with 0.1% oxygen admixtures. The gas flow is fixed at 1 slm. The species considered in simulations include electrons, He+, $O2^+$, O^+, O^-, O_2^-, O_3^-, He*(ensemble of triplet and singlet states), O, O(1D), O_2(v=1-4, first four vibrational states), O_2(a1Δg), O_2(b1Σg+), O_3 and O_3(v) (Gudmundson et al. 2013). The voltage waveform tailoring (VWT) [Schulze et al. 2011] is applied to the powered electrode, with a fixed peak-to-peak voltage of 400 V, and a constant fundamental frequency of 13.56 MHz. The number of consecutive harmonics is varied from 1 to 4.

Figure 2 shows the spatially and temporally resolved electron impact helium excitation rate from the ground state to the state of He(33S) from simulations (the second row) and PROES measurements (the third row), and the corresponding applied voltage waveform for different numbers of harmonics (the first row). The excitation rates are normalized to the maximal value for each case. The simulations and experi-

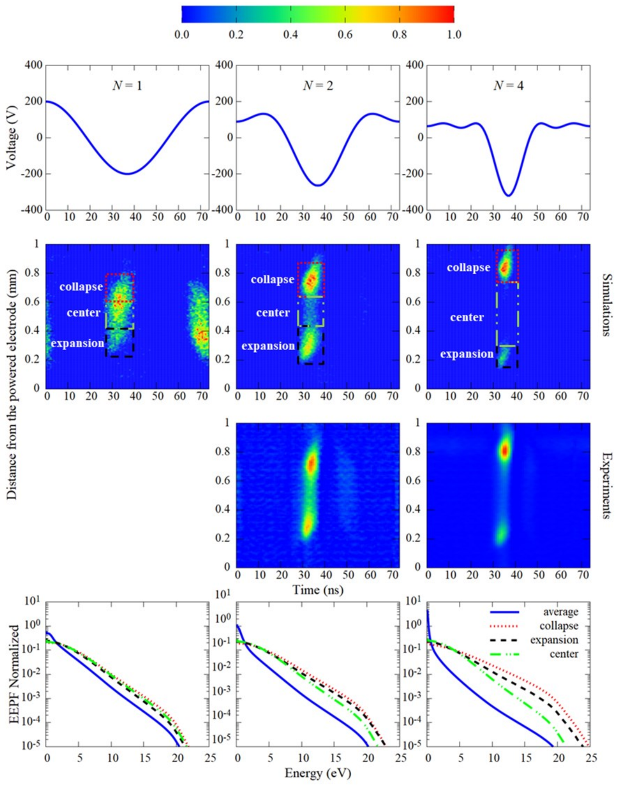


Figure 2. First row: applied voltage waveform in one fundamental RF cycle for different numbers of harmonics. Second and third rows: spatially and temporally resolved He (3^3S) excitation rates from the ground state by electron impact for different numbers of harmonics from simulations and experiments (PROES), respectively. The experimental results are taken at y=-15 mm. Fourth row: normalized electron energy probability function averaged over spatial-temporal regions of interest as marked in the second row and averaged over the whole region of the discharge gap in one RF period. The figure is taken from [Liu et al. 2020; DOI:10.1088/1361-6595/abd0e0].

mental results are in good agreement. For N=1, the diagnostic signal is quite weak, since only a few electrons can be accelerated to such high energy to cause the excitation. The excitation occurs in the bulk and is symmetrical in space and time domain within one RF period. As the number of harmonics is increased, the excitation rate becomes more asymmetrical and more localized in a small spatial and temporal region. The excitation dynamics occur during the time of grounded electrode sheath collapse. A high electron conduction current is generated to balance the positive ion flux to the grounded electrode during the short term of the local sheath collapse, leading to a strong drift electric field due to a low electron conductivity at atmospheric pressure. The tailoring of the electron energy probability function (EEPF) caused by VWT is shown in the fourth row of figure 2, including the EEPF averaged over the discharge gap in one RF period (blue solid line), and over the regions of interest highlighted in the second row of the figure. The EEPFs deviate from the Maxwellian distribution. By increasing the number of consecutive harmonics, the high energy tail is enhanced significantly for the expansion and collapse regions. It can be seen that the EEPF is strongly dependent on time and space, and can be controlled by the use of VWT.

Another comparison between simulations and experiments is made for the absolute density of atomic oxygen, which is measured by TALIF in collaboration with project B2. As can be seen in figure 3, quantitative agreement is reached between simulations and experimental results. Due to the change of the electron heating dynamics induced by the VWT, the atomic oxygen density becomes asymmetric as a function of the number of harmonics. The maximal density is increased more than 3 times from N=1 to N=4, indicating that the production of reactive species can be optimized and controlled by the use of VWT.

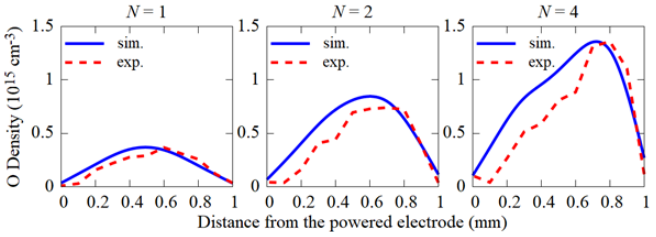


Figure 1. Simulated and measured (TALIF) time averaged atomic oxygen density profiles as a function of the number of harmonics. Both results are taken at y=-15 mm. The figure is taken from [Liu et al. 2020; DOI:10.1088/1361-6595/abd0e0].

To conclude, a numerical hybrid code was developed to investigate a capacitively coupled COST reference micro atmospheric pressure helium plasma jet with 0.1% oxygen admixture driven by a tailored voltage waveform. The simulation results achieve quantitative agreement with various experimental measurements. We demonstrate that VWT allows to control the electron heating dynamics, and thus, the electron energy probability function in the regions of interest. As a consequence, the desired reactive species, such as the atomic oxygen density can be remarkably enhanced by the use of VWT.

DATA DRIVEN ANALYSIS OF PLASMA CATALYSIS EVOLUTION

Dr. D. Reiser

Since my diploma thesis at the University Duisburg, the focus of my work has been in the field of numerical mathematics. In this work I have dealt with the electron structure of ferromagnetic layers. With the beginning of my PhD thesis at the Research Center Jülich (FZJ), I changed to the field of high temperature plasma physics and since then I have been working on different problems from fusion research. These included numerical modeling of impurity ions, fluid theoretical investigations of plasma edge transport, simulations of turbulent plasma flows, and analysis of morphological changes of wall materials under plasma exposure. In recent years, I have increasingly used modern statistical methods to model the processes involved in plasma-surface interactions and have also applied them to low-temperature plasmas and ion beam experiments. In my current work, I am now transferring these methods to the field of plasma-assisted CO_2 conversion. This topic immediately gave rise to a variety of opportunities for cooperation between the RUB and the FZJ, which have already maintained close contact and scientific collaboration for many years. I see my task here in the provision and application of numerical codes for the analysis of experiments on plasma catalysis at the RUB. In addition, the expertise of FZJ-IEK-4 in material characterization could also be brought into the collaboration. In the last year, we have already been able to develop approaches in the existing collaboration that allow us to derive reaction kinetic models for experimental data of subproject A3 of CRC 1316. These numerical tools are based on optimization methods for non-linear regression. In this context, a genetic algorithm has proven to be particularly successful and flexible and has opened up diverse application possibilities. For the second phase of CRC 1316, I hope to use and further develop these methods for further experiments. In particular, I would like to have the opportunities to study the plasma chemistry of CO_2 and the synergy of plasma impact and surface processes on oxide catalysts (TiO_2), as these topics are also being investigated at FZJ. From the point of view of numerical methods, however, the many other excellent experiments at RUB also offer many opportunities to test and further develop the theoretical models and algorithms. For example, my goal is to extend the aforementioned genetic algorithm and to use it in a combination with ABC (Approximate Bayesian Inference) methods for sensitivity and correlation analysis to obtain more detailed information about dominant processes in plasma chemistry and on catalyst surfaces. Specifically for catalysts, I would like to address the question of whether direct electron impact excitation causes catalytic reactions, or electron-hole pair generation. It is also possible that the experiments and data-driven model discovery will allow us to conclude whether primarily Eley-Rideal or Langmuir-Hinshelwood reactions dominate on the surface. In any case, I am looking forward to further collaboration and exchange with the many competent colleagues at the RUB, from which I will certainly benefit enormously.

Dirk Reiser, FZJ Jülich

PLASMA DERIVED NANOCATALYSTS FOR THE ELECTROCHEMICAL PRODUCTION OF GREEN HYDROGEN

Prof. K. Tschulik

“Plasma-derived nanocatalysts for electrochemical hydrogen evolution” – this is the research idea for the CRC 1316 in the field of electrochemistry.

The research is arranged around the subject of hydrogen production by the hydrogen evolution reaction (HER). Hydrogen already has a high priority in research and industry. Regarding the current technological development aiming to face the upcoming challenges caused by climate change, hydrogen is of utmost importance for energy conversion and storage. As a candidate as a green fuel, it should contribute to the reduction of the use of fossil fuels.

The research will focus on the development of plasma -derived, platinum-free HER catalysts, meaning that the nanocatalysists will be produced based on the plasma techniques developed in the collaborative research centre. These will be characterised according to their electrochemical activity, as well as with respect to their individual material properties. The catalytic and material properties will then be linked to identify property-activity relations and how to fabricate catalysts with favourable properties utilizing atmospheric plasmas.

The aim of the project is to fabricate novel and improved catalysts for the hydrogen evolution reaction, reaching to produce highly durable and active catalysts. Rather than a conventional approach, two precursors which are fixed in a matrix (micelles) will serve as the starting materials to produce bimetallic nanoparticles. The plasma is used to nucleate nanoparticles as catalysts based on these precursors. These which will then be employed for proton reduction to generate hydrogen.

A multitude of methods are utilised to reach the outlined goal. At first, different synthesis methods are used for the material for the micelles and precursors to ensure that the nanoparticles will contain different components. Also, different ways to nucleate these precursors are applied, using either ambient pressure plasmas of different gas compositions or plasmas in the liquid phase. Also, these types of nucleation will be compared to electrochemical means.

To characterise these materials by their electrochemical properties, methods including linear sweep voltammetry, rotating disc electrode experiments and chronoamperometry are utilized. Size, shape and configuration (e.g. core/shell) of the materials are also determined and linked to their electrocatalytic properties.

Based on the thus derived particle property-activity -relations, best suitable plasma conditions can then be selected to fabricate highly active catalysts.

Kristina Tschulik, RUB,
adapted by Maike Kai, public relations

RATIONAL TUNING OF PLASMA AND LIQUID CHEMISTRY FOR BIOCATALYSIS

Jun.-Prof. Dr. J. Golda

The conventional synthesis of many chemicals relies heavily on high energy consumption, harsh reaction conditions, and produces large quantities of solvent and heavy metal waste. Due to environmental concerns and the finite availability of fossil resources, green chemistry tries to provide alternative reaction pathways with more sustainable, resource-efficient and inherently safer designs. One important example reaction is the selective oxidation of carbon atoms that is traditionally based on metal catalysis. The biotechnological, green alternative pathway for this reaction is biocatalysis where enzymes catalyse the conversion. Some enzymes are highly selective, performing regio- or even stereo-selective reactions with specific precursor substances (substrates) and reactants. Compared to chemical synthesis, this reduces side reactions and thus simplifies downstream purification. However, biocatalysts are biological macromolecules requiring mild and stable operating conditions which often include the supply of substrates and reactants within a narrow concentration range.

In the first period of CRC 1316, project B8 provided proof that enantioselective biocatalysis can be performed with reactant generated by non-thermal plasma. A promising reaction scheme was established involving unspecific peroxygenase (UPO) in aqueous solution which consumes H_2O_2 delivered by a non-thermal plasma. It demonstrated that plasma-driven biocatalysis is competitive with regard to enzyme lifetime. However, the plasma-biocatalytic reaction scheme has limitations with respect to reactant supply and reaction scale. In the future, these shortcomings have to be addressed by developing a rational approach for tuning the plasma and liquid chemistry for biocatalysis and by providing a first evaluation of parallel plasma sources as scale-up strategy. To this end, three complementary fields of expertise, namely biotechnology, experimental and computational plasma science, will be combined to investigate reaction pathways that supply reactants for biocatalysis.

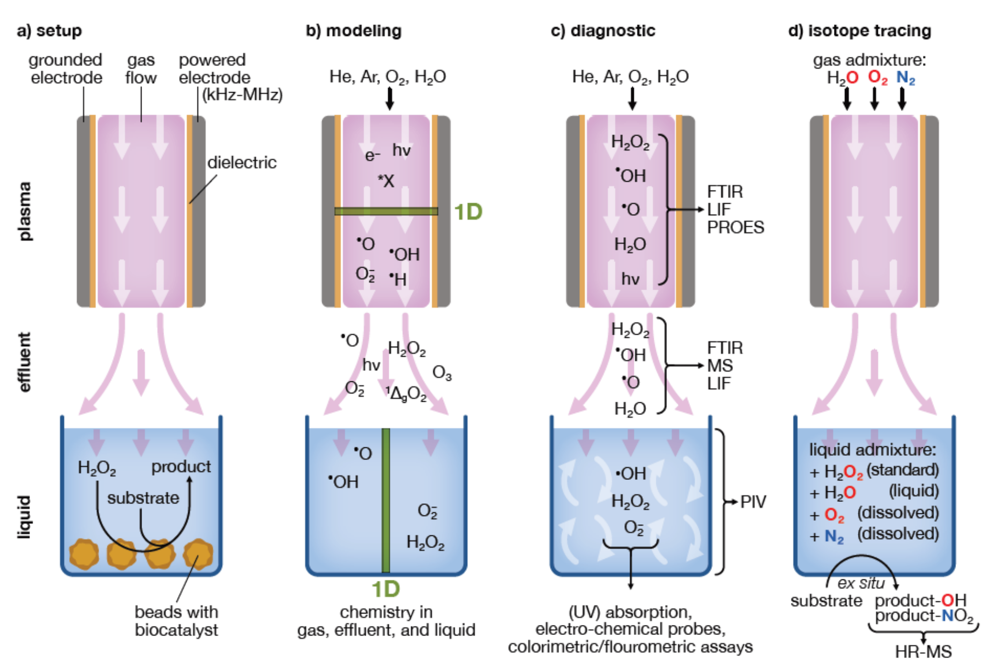


Figure: Schematic showing the major approaches used in B11(N) for (a) treatment of enzymes and substrate, (b) gas and liquid phase simulations, (c) diagnostics of reactive species concentrations and (d) experimental pathway analysis via isotope tracing.

One important goal will be the design of a capillary plasma source to accommodate a large range of operating parameters for the control of H_2O_2 production and the investigation of reaction pathways. To diagnose H_2O_2 and precursors thereof in the gas and liquid phase, one- and two-photon laser-induced fluorescence (e.g. O, OH, NO) and Fourier transform infrared spectroscopy (e.g. H_2O_2) will be employed. Power measurements will provide the basis for estimating the energy efficiency of plasma-based H_2O_2 generation.

Furthermore a heterologous production of the biocatalyst unspecific peroxygenease (UPO) in E. coli will be established and the plasma source performance under different plasma operating conditions based on biocatalysis rates and enzyme lifetime productivity will be evaluated. Isotope labeling experiments combined with high-resolution mass spectrometry of the reaction product will allow the origin of O atoms in reaction products to be determined (from O_2 or H_2O in feed gas, liquid H_2O or water-dissolved O_2). The experimental data will support the mapping of reaction pathways relevant to H_2O_2 formation. High-resolution protein mass spectrometry analysis will also be performed to investigate catalyst inactivation mechanisms. The tunability of the new source will be validated using enzymes derived from project B8 that tolerate different concentration ranges of plasma-produced species.

To gain deeper insights into the chemical kinetics involved in plasma-driven biocatalysis, the project will expand on existing models to develop a model of the plasma-induced liquid chemistry of the system. Simulation development will be carried out in close collaboration with the experiments in order to quantitatively validate reactive species concentrations predicted by the simulations in both the gas- and liquid -phase against experimental measurements. The validated simulations will provide concentrations of all relevant reactive species in the system, including those that cannot be measured experimentally.

The combination of these project goals will provide deeper insights into the reaction pathways to be targeted to enhance the efficiency of plasma-driven biocatalysis and to configure a plasma source for scale-up. The combination of capillary sources will be used for an initial evaluation of parallel plasma source operation as a scale-upstrategy.

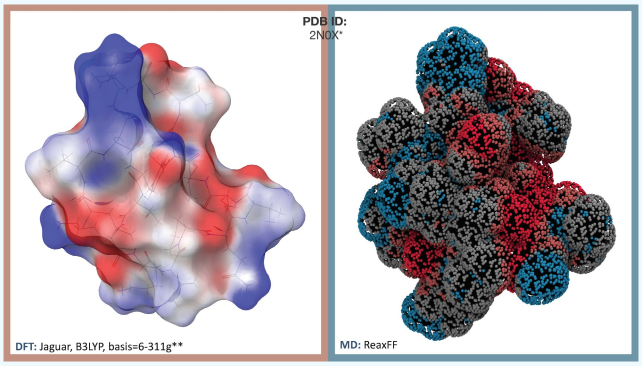
Sascha Chur, public relations for the CRC 1316

THEORETICAL CHEMISTRY

Dr. C. Jung (B8)

Theoretical chemistry, based on mathematical methods in combination with the fundamental laws of physics, makes it possible to study processes of chemical, physical or biological relevance, to explain experimentally obtained results or even to predict them. The processes of interest here take place at the atomic level: The interaction of plasma products, the turnover of these at enzymes, or else the de-reaction. By parameterizing experimentally or theoretically obtained system properties, force fields attempt to bridge the gap to larger time and length scales through an analytically formulated Hamiltonian operator. The applicability of a given force field to different problems is determined by the form of the energy expression, but in particular by the quality of the parameterization. Here, the reactive force-field (ReaxFF) interatomic potential is utilized as computational tool for exploring properties. ReaxFF as a reactive force field method offers a suitable working platform for the investigation of large systems with several thousand atoms. The accuracy, respectively the number of terms considered, is high compared to classical force fields, since both hybridisation and polarizability are taken into account.

Marina Prenzel, public relations for the CRC 1316



IMPACT OF PLASMA IN LIQUID ON ELECTRODE STRUCTURE AND SOLUTION PROPERTIES

Prof. Dr. T. Jacob and Dr. A. Engstfeld

Polarizing two electrodes with very different sizes at high voltages in an aqueous electrolyte can lead to plasma electrolysis, also known as contact glow discharge electrolysis (CGDE). Possible applications of this process are the functionalization of plasma electrodes, nanoparticle generation (from the plasma electrode or from ions in the solution) or the purification of wastewater with short lived high energetic species and H_2O_2 formed by the plasma.

With our project at the Institute of Electrochemistry at Ulm University we aim at a fundamental understanding of the impact of in liquid plasma (i) on the electrolyte, focusing on thermal effects, voltage drops and electrolyte composition as well as (ii) on the plasma electrode, focusing on its stability, the onset of structure formation processes and temporal structural changes of the plasma electrode surfaces on an atomic scale, and (iii) ultimately the synergistic effect between these temporal changes at the interface between electrode and electrolyte.

To study the respective properties we will employ metal single crystal electrodes, which were so far not considered as electrode material for in liquid plasma studies. Their well-defined structural properties on the atomic scale allow for a direct and reliable connection between experiment and theory. This approach has been shown to be very constructive in research related to (electro-) catalysis. With our combined surface science, electrochemistry and theory approach we expect to provide the desired fundamental insights in this fascinating research field.

Timo Jacob and Albert Engstfeld,
project B4 of the CRC 1316

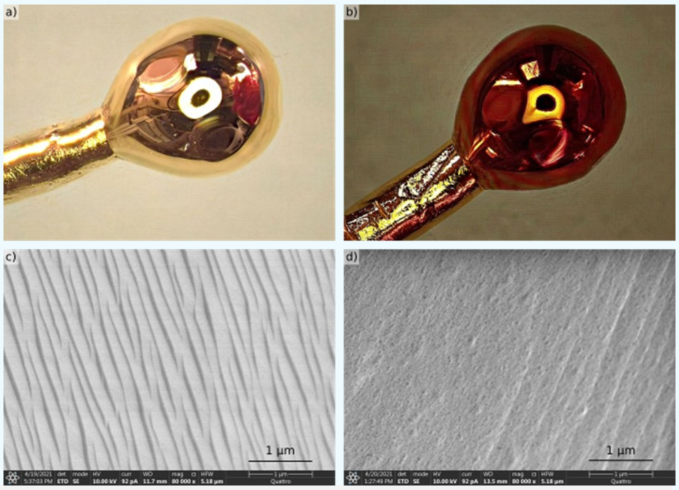


Figure: a) As-prepared Au poly-oriented single crystal electrode. b) The same Au POSC after polarization for 15 s at 540 V in 0.1 M KOH electrolyte. The electrode is red, indicating the formation of an Au-oxide on its surface. c) The scanning electron microscopy image shows a region on the as-prepared crystal with a distinct surface pattern. Image d) shows the same region after anodic polarization under the same conditions as in b). The fine structure of the original surface is lost and a new oxide structure is formed on top. [Figures by Evelyn Artmann und Tobias Schmider (both University Ulm)]

NEWEST DISHES FROM THE AUSTRIAN CUISINE: AN UPDATE ON THE LATEST PROGRESS IN DESIGNING AND UNDERSTANDING THE STABILITY AND MECHANICAL PROPERTIES OF TRANSITION-METAL NITRIDE-BASED COATINGS

Dr. David Holec from Montanuniversität Leoben gave a workshop entitled “Newest dishes from the Austrian cuisine: an update of the latest progress in designing and understanding the stability and mechanical properties of transition-metal nitride-based coatings" on 24 November 2020. Dr. Holec leads the “Computational Materials Science” group at the Chair of Physical Metallurgy and Metallic Materials and employs multiscale and multimethod modelling. In order to connect time and length scales from fs and Å to hours and meters, his group combines a variety of methods from ab initio molecular dynamics to continuum mechanics.

The workshop started with an introduction to the principles of modelling and was followed by latest findings on the phase stability, thermal stability as well as strength and toughness of binary nitride superlattices. Dr. Holec emphasized the importance of interface and surface energies for the epitaxial stabilization of metastable cubic AlN in an architecture of CrN/AlN multilayers. For off-stoichiometric $MoN_{0.5}$/TaN superlattices it was found that the fracture toughness was significantly enhanced upon formation of the zeta-TaN phase. As this system contains metal and non-metal vacancies, a similar strategy was adopted for the TiN/WN system in which the cubic phase is also stabilized by the formation of vacancies. Significantly enhanced fracture toughness of the TiN/WN superlattice compared to the monolithic TiN and WN systems was related to vastly disparate elastic moduli and chemical composition fluctuations. These insights were especially interesting for the mechanical model of SFB-TR 87.

Marcus Hans, project A3 of the SFB-TR 87

REVIEW OF INFRARED SPECTROSCOPY TECHNIQUES FOR THE DETERMINATION OF INTERNAL STRUCTURE IN THIN SIO$_2$ FILMS

Teresa de los Arcos, Hendrik Müller, Fuzeng Wang, Varun Raj Damerla, Christian Hoppe, Christian Weinberger, Michael Tiemann, Guido Grundmeier. https://doi.org/10.1016/j.vibspec.2021.103256

The projects within the B-block of the TR87 share a common goal for understanding and manipulating internal structure in thin films, in particular, Si-based films such as SiO$_2$. The idea behind is the development of strategies that eventually might allow control over molecular diffusion through these films. Within this context, subproject B3 has been strong in developing and adapting different experimental strategies for the characterization of internal structure, or porosity in thin films. One such technique is Fourier Transform Infrared Spectroscopy, which has been repeatedly used for the characterization of plasma-deposited SiO$_2$ films within (and without) this TR87. (See for example [1–3], among others.)

When confronted initially to the specific task of assessing porosity in thin SiO$_2$ films for different groups within the TR87, we evaluated IR spectra from coatings deposited by different techniques on different substrate types, and measured in different FTIR spectrometers. The evaluation of these spectra in terms of porosity lead to much frustration in the early stages, since spectra of apparently similar coatings showed stricking differences in the shape of the absorption bands that we did not fully understand. The very plentiful existing literature turned out to be sometimes confusing and therefore we took upon ourselves to write the reference paper that we would have like to have at our disposal when we started these investigations.

Due to the strong optical absorption and polar nature of SiO$_2$, the absorption bands show splitting into longitudinal (LO) and transversal (TO) modes. This is particularly true for the strong absorption band in the range between 900-1350 cm^{-1}, corresponding to the asymmetric stretching of the Si-O-Si groups, which is often investigated. In thin films, with thickness below the wavelength of the light used to sample them, TO modes oscillate within the film plane, while LO modes oscillate perpendicular to the film. This geometry determines whether TO or LO modes will be active in an IR measurement, depending on the

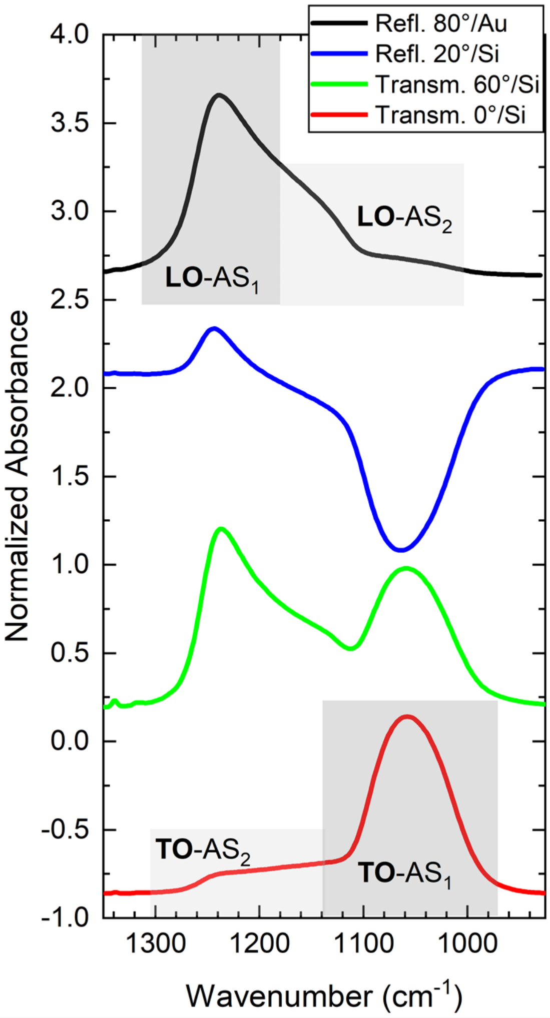


Figure 1: Normalized absorbance of four equivalent SiO$_2$ thin films between approximately 30-60 nm thickness deposited by magnetron sputtering at identical conditions. The spectral range shown corresponds to the intense asymmetric stretch band of the Si-O-Si vibration. The different shapes associated to this band are related to the activation of either LO or TO modes (or both) depending on the geometry of the IR measurement and on the selection rules imposed by the choice of substrate. The two upper spectra (black and blue) correspond to reflection measurements on either Si (blue) or Au-coated (black) Si substrates at different indicence angles (green: 60°; red: 0°); the lower spectra (green and red) are transmission spectra taken at different incidence angles. The shaded boxes mark the approximate range where pure TO or pure LO modes are localized.

angle of incidence of the light, and on whether the measurement is performed in transmission of reflection. In the latter case, detection of the TO or LO modes is further determined by the selection rules imposed by the substrate. In short, the final shape of the Si-O-Si band will depend strongly on a combination of the specific IR measurement and the substrate.

You can get a taste of the wealth of different possible band shapes when looking at the figure 1. It shows the Si-O-Si absorption band of four dense SiO_2 films of similar thickness, deposited by magnetron sputtering under practically identical experimental conditions. As you can see, the band shapes of these four equivalent samples vary wildly depending on the measurement technique used and the substrate. Measurements done by reflection (at any angle) onto metallic substrates activate only LO modes, so that the spectrum shown in the upper row in the figure corresponds to the pure LO modes of SiO_2. By contrast, measurements done in transmission at normal incidence activate only the TO modes, which is what you can see in the lower spectrum in the figure. Other measurement geometries, such as transmission at different angles, provide a combination of LO and TO modes. A simultaneous activation of both modes is also possible in reflection measurements when working with a semiconducting substrate, where modes that oscillate perpendicular to each other have absorption bands of different signs (as you can see in the blue spectrum shown in the figure). Thus, it is of central importance to understand the influence that the measurement has on the band shape, before attempting an analysis of the band in terms of porosity.

With this paper we wanted to clarify two main points. Firstly, we needed to understand the origin of the band shapes that result from the choice of measurement technique and substrate. For this, we compared the spectra of SiO_2 films using different types of IR measurements (transmission or reflection at different incidence angles, diffuse reflection) onto either metallic or semi-conducting substrates (Si and Au-coated Si wafers). Secondly, we performed an intense literature search and we identified markers for porosity based on the position and intensity of either TO- or LO-modes, and the magnitude of the LO-TO splitting. In the paper, we illustrated the effectiveness of these identifiers in combination with the different IR approaches, by using three well defined families of SiO_2 films: mesoporous (pore sizes around 8 nm), microporous (pore sizes around 2 nm) and dense. See Figure 2 for an illustration of porosity markers.

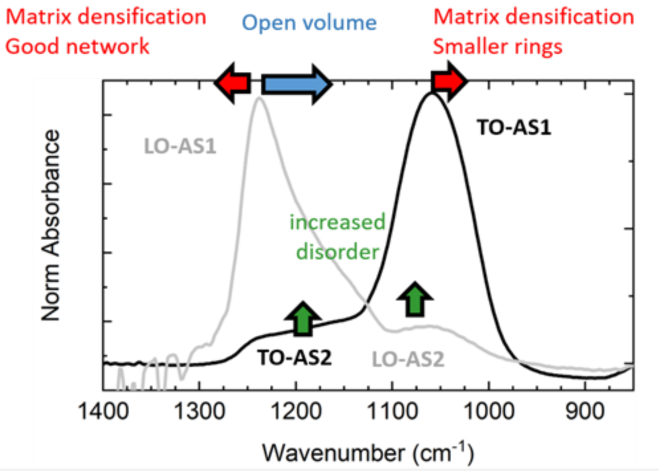


Figure 2: Identification of porosity/structure-related markers in the Si-O-Si assymetric stretching band of SiO_2.

Hopefully this illustrated review paper will provide a good starting point for all those who need to understand the peculiar characteristics of IR spectra of polar materials in general, and thin SiO_2 films in particular.

[1] C.-N. Liu et al., Combined in situ FTIR-spectroscopic and electrochemical analysis of nanopores in ultra-thin SiOx -like plasma polymer barrier films, J. Phys. D: Appl. Phys. 46 (2013) 84015. https://doi.org/10.1088/0022-3727/46/8/084015.

[2] C. Hoppe et al., Characterisation of micropores in plasma deposited SiO x films by means of positron annihilation lifetime spectroscopy, J. Phys. D: Appl. Phys. (2020). https://doi.org/10.1088/1361-6463/aba8ba.

[3] C. Hoppe et al., Influence of organic surface chemistry on the nucleation of plasma deposited SiOx films, J. Phys. D: Appl. Phys. 50 (2017) 204002. https://doi.org/10.1088/1361-6463/aa69e5.

X-RAY PHOTOELECTRON SPECTROSCOPY:

TOWARDS RELIABLE CHARACTERIZATION OF TRANSITION METAL NITRIDE THIN FILMS

Prof. Grzegorz Greczynski from Linköping University gave a Zoom-workshop on the topic of “X-ray photoelectron spectroscopy: towards reliable characterization of transition metal nitride films” on the 18th November 2020. In many fields, X-ray photoelectron spectroscopy (XPS) is a commonly used analysis tool to determine the surface chemistry, bonding structure as well chemical composition of surfaces and interfaces. Annually, more than 10,000 papers are published which deal with data obtained by XPS. However, it is estimated that 30 % of these publications are completely wrong and an additional 30 % contain serious flaws. Consequently, it is very important to handle data measured by XPS carefully, draw the right conclusions and being aware of its limitations.

During the workshop, Prof. Greczynski gave a general introduction about the technique of XPS. One interesting detail that can be obtained from XPS is, for instance, the chemical shift of elements depending on their chemical environment. For example, different chemical environments of a carbon atom may result in a shift of the detected binding energy. A carbon atom that is surrounded by three fluorine atoms shows a ~8 eV shift compared to a carbon atom which is surrounded by three hydrogen atoms. This can be explained by the fact, that it takes less energy to create a core hole on the carbon atom with higher negative valence charge density.

The binding energy of an obtained signal is often compared with existing literature to determine the chemical state of the element of interest. However, the accuracy of determining the chemical state relies on a trustworthy calibration of the binding energy scale. It is a well-established technique (> 95 % of all cases) to align the obtained spectra to the C 1s signal of adventitious carbon (AdC). However, Greczynski and Hultman (Progress in Materials Science 107, 2020) showed that the binding energy of the C 1s signal of AdC is not constant and varies by 2.66 eV depending on the sample that is measured. This range of binding energy is more than a typical chemical shift of elements and makes the C 1s signal of AdC an unreliable reference point. Instead, the Fermi edge should be used as a reference point for conducting samples, whereas for non -conducting samples, the focus should be on relative spectral changes within a sample series.

Besides these fundamental aspects of XPS analysis, Prof. Greczynski also introduced the audience to advanced approaches, e.g. the concept of Al-capping for TiN coatings to avoid surface oxidation during the transport to the XPS analysis chamber. All in all, the workshop gave an interesting overview of the XPS technique and was especially of relevance for the interaction model of SFB-TR 87.

Lena Patterer, project A3 of the SFB-TR 87

CATALYST MEETS MICRO CAVITY PLASMA ARRAY

Gas conversion and plasma catalysis play an important role in project A6. To receive an initial estimation about the potential conversion in a micro cavity plasma array (MCPA), this DBD device was investigated by using a quadrupole mass spectrometer (QMS) as a cooperation of projects A6 and A7. A further aspect of this investigation is that these QMS measurements serve as a first comparison to the SDBD as used in project A4, A5 and A7 since both devices differ significantly from each other with respect to the structure and operation parameters.

In this study the MCPA was operated with a triangular voltage waveform excitation having an amplitude up to 800 V in a frequency range between 5 and 25 kHz. In addition to the 2 slm helium flow, 25 sccm n-Butan were added. To avoid possible obstructions of the cavities by coking, cavities with a diameter of 200 µm were chosen. To investigate which influence a catalyst has on the conversion rates, this study was also performed with MnO2 covered previously with a load of 0.1 and 0.25 mg/cm2 on the dielectric in cooperation with A7.

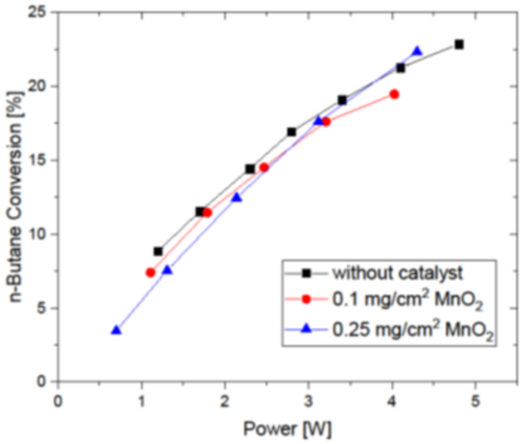


Figure 1: Conversion rate as a function of the power with and in absence of the catalyst.

Figure 1 shows the conversion as a function of the power with and without catalyst. For both cases the conversion increases up to 25 percent with a rising power up to 5 W. Despite a successful operation with a catalyst, a noticeable effect on the conversion cannot be detected even in the high-power range. This may be due to the fact that the catalyst has not reached its ideal operation temperature of about 180 ° C. As a result, the MCPA reactor will be modified relating to its temperature control comparable to the device of project A3. Afterwards, these measurements will be repeated in a higher temperature regime.

Christian Oberste-Beulmann, David Steuer, Sebastian Dzikowski, Niklas Peters, project A6 of the CRC 1316

ELECTRIC FIELD DISTRIBUTION AND DEVELOPMENT IN A NANOSECOND PULSED PLASMA

One of the most important parameters determining features of gas discharge plasmas is the value of the reduced electric field, E/N. The electric field heats the electrons and together with energy loss mechanisms, which are energy dependent, an EEDF is formed. Therefore, the measurement of E/N in the discharge is a subject of a prime interest.

In project A1, the electric field in a nanosecond Atmospheric Pressure Plasma Jet (ns-APPJ) is studied by picosecond Electric Field Induced Second Harmonic generation (EFISH). EFISH is a third-order nonlinear process involving an external applied electric field (in a discharge), and an electric field of a light wave (laser radiation). The process is non-resonant, i.e. it does not require the characteristic energy of the photon to match with any transitions in gaseous molecules/ atoms. Therefore, the same laser emission and optical scheme can be used for any gas.

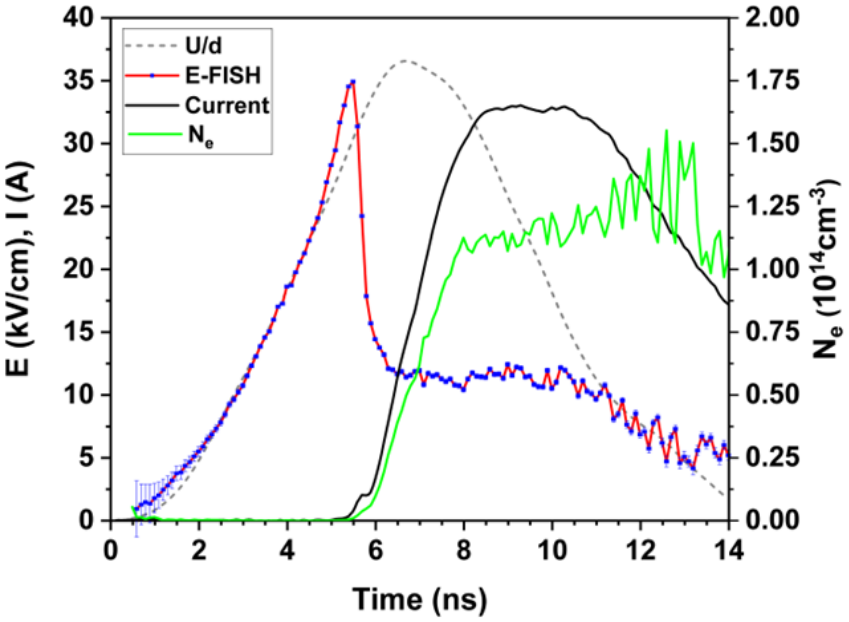


Figure 1. Electric field temporal profile obtained using the EFISH technique compared with the electric field temporal development calculated as a voltage over gap ratio; electron density and electric current temporal profiles. He:N_2=5:1 mixture at 900 mbar.

For example, discharges in He:N_2 mixture and pure N_2 have been studied recently. Two distinct phases of the discharge were identified: The fast breakdown at high electric fields is followed by a quasi-DC phase at a lower permanent electric field and high electron density, see Fig. 1.

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> *Plasma generation - which is almost entirely happening in the breakdown phase - and the subsequent quasi-DC phase are separated and can be controlled independently.*
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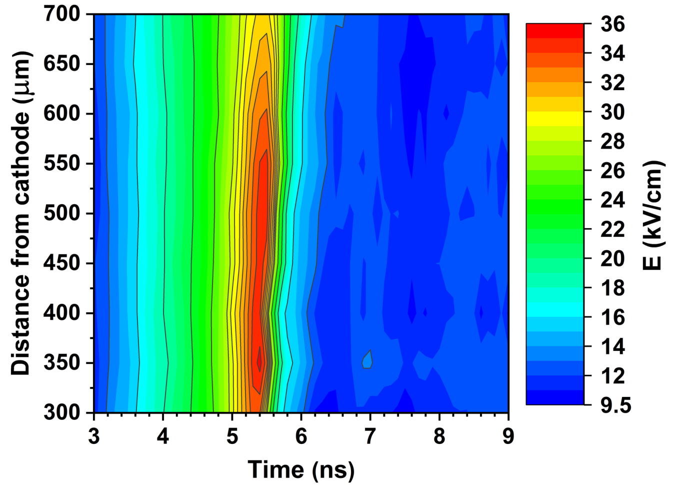


Figure 2. Electric field strength as a function of time and distance from the cathode. He:N_2=5:1 mixture at 900 mbar.

Moreover, after the breakdown the field is uniform in the bulk, see Fig. 2, and does not depend on the duration of the high voltage pulse, see Fig. 3. Remarkably, the bulk electric field in the quasi-DC phase is independent of the amplitude of the applied voltage used to feed the high voltage switch and, consequently, the electric field strength during breakdown, see Fig. 3. Thus, it was concluded that plasma generation - which is almost entirely happening in the breakdown phase - and the subsequent quasi-DC phase are separated and can be controlled independently.

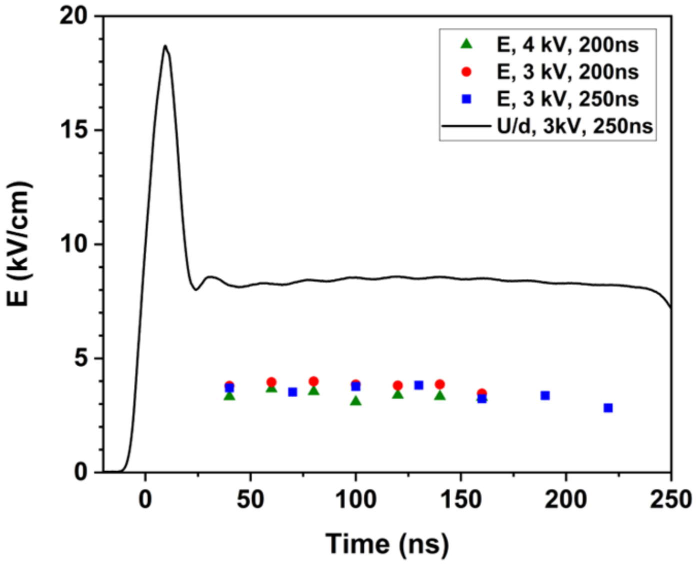


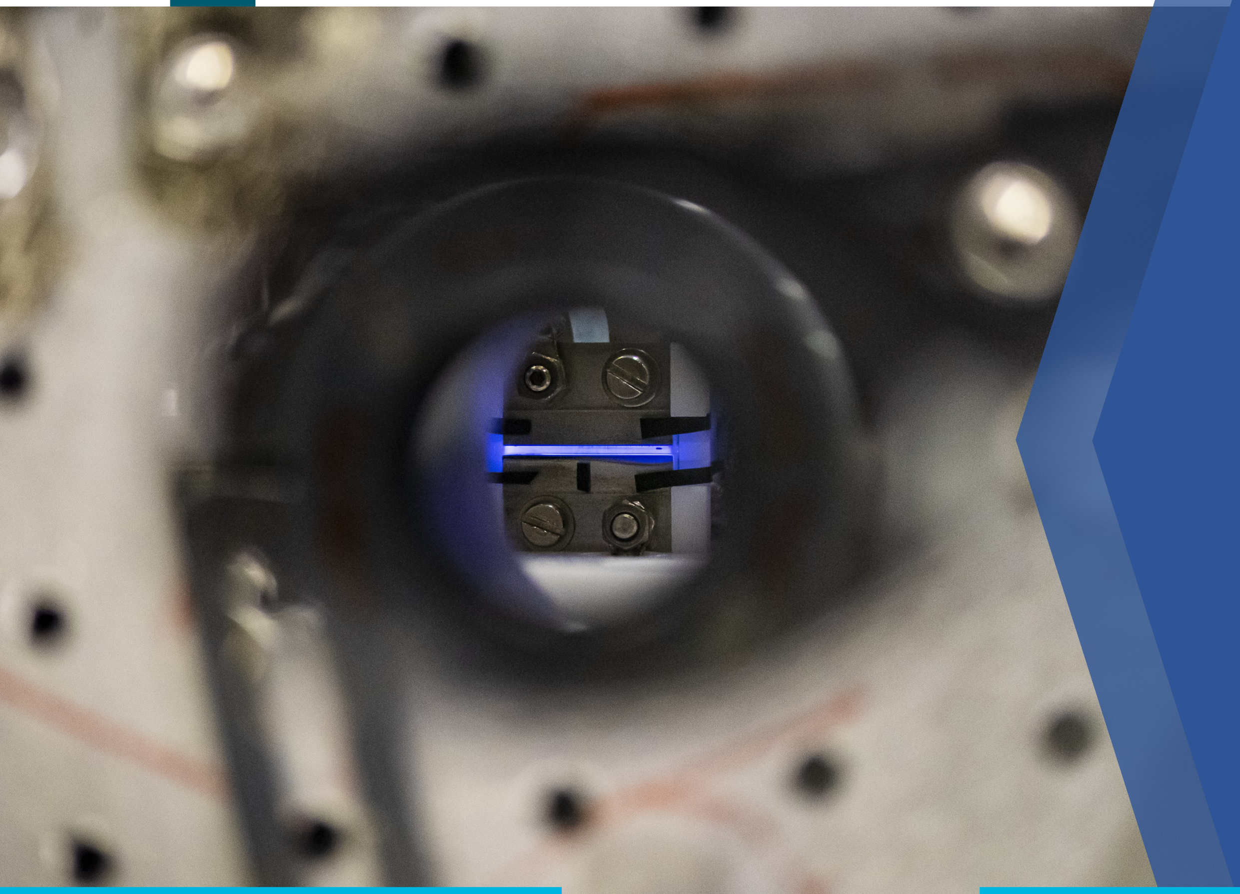
Figure 3. Electric field temporal profile measured by EFISH for different HV pulses compared with the electric field profile calculated as voltage over gap ratio for the 3 kV, 250 ns measurement. As the voltage amplitude during the plateau phase is quite similar for all three measurements only one waveform is shown. Pure N_2 at 200 mbar.

This gives a unique opportunity to adjust the parameters of the discharge: The electron density increases with the applied voltage amplitude, while in a given gas mixture the reduced electric field value in the quasi-DC phase is basically a constant. As a result, a desired yield of active species can be achieved. This approach was used in collaboration with project A2, where vibrational excitation and transfer are studied in an identical discharge as in A1 by Coherent anti-Stokes Raman scattering spectroscopy (CARS). It was shown that the rate of vibrational excitation of N_2 is proportional to the electron density, controlled by the applied voltage, while the fraction of the energy deposited in the plasma bulk spent on the vibrational excitation is close to 100 % throughout due to the "fixed" electric field value. The measured electric field value was used in A2 to model vibrational excitation of N_2 during the discharge. Excellent agreement between the modeling and CARS results has been demonstrated.

[1] N D Lepikhin et al 2021 J. Phys. D: Appl. Phys. 54 055201, https://doi.org/10.1088/1361-6463/abbbb4

[2] J Kuhfeld et al 2021 J. Phys. D: Appl. Phys 54 305204, https://doi.org/10.1088/1361-6463/abfd6b

Nikita Lepikhin, project A1 of the CRC 1316



IMPRESSUM

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