NEWSLETTER

EDITION 12— 12/2021

SFB-TR 87

SFB 1316 Transient Atmospheric Plasmas
from plasmas to liquids to solids

FOREWORD

The new edition of this newsletter reflects the start of many activities in the two CRCs. Researchers attended or hosted seminars, conference visits, or research stays.

We congratulate a number of awardees in both CRCs whose excellent work has received recognition. In detail, Dr. Marco Krewing received the award of the Society of Friends of the RUB (GDF) and Dr. Lukas Mai received the Starck Tungsten award from the GDCh (Society of German Chemists), both are honoured for their outstanding PhD theses. Finally, David Steuer received an award for his Master Thesis .

Both Collaborative Research Centres produced a variety of reports in the new issue of the newsletter. Besides the higher number of meetings, there is also a lot of good news about the extension of CRC 1316 and SFB-TR 87.

In terms of personnel, there have also been some changes since the last issue. Sascha Chur left the public relations project and is now dedicating himself to his PhD in CRC 1316. I would like to thank Sascha for his contribution during more than three years and I am happy to report about his scientific progress here.

As a replacement and ready for upcoming tasks, Maya Krüger is now in the public relations team and will especially support the social media activities. With the implementation of the CRCs' external presentation via social media, the goal is to reach a broader group of interested people.

Marina Prenzel, public relations

CONTENT

DFG APPROVES 2ND FUNDING PERIOD OF THE CRC 1316 & EXTENSION OF THE SFB-TR 87

Plasmas for the systems for species conversion are an important component in the utilization and storage of decentrally generated renewable energies. The Collaborative Research Center 1316 (CRC 1316) "Transient Atmospheric Pressure Plasmas - from Plasma to Liquids to Solids" is dedicated to combining atmospheric pressure plasmas with catalysis to develop the most flexible solutions possible for this species conversion. "They should be scalable, controllable and robust against external influences, such as impurities in the starting materials," explains Prof. Dr. Achim von Keudell, spokesman of the CRC 1316.

After months of preparation with countless requests for statistics and financial statements in the projects, the successful work of CRC 1316 can continue.

In addition to the previous funding period, five new projects have been incorporated B11, B12, B13, INF as well as PR. The three scientific projects will add further focal points in biology and chemistry to the scientific work. The public relations project will be continued here after the SFB-TR 87 is ending to communicate plasmas to the general public, students and scientific colleagues. The INF project will advance the topic of research data management in the CRC.

Due to the pandemic situation, scientific work in the SFB-TR 87 has been delayed. To counteract this situation, a six-month extension of the SFB-TR 87 was approved. The summit meeting will take place in May 2022 at the Eibsee. All SFB-TR 87 members are cordially invited to participate.

adapted from Maike Drießen, RUB & Marina Prenzel, public relations of the SFB-TR 87

SFB-TR 87 MEMBERS CONTRIBUTE TO THE 11TH HIPIMS CONFERENCE

The Eleventh International Conference on Fundamentals and Industrial Applications of HiPIMS was held virtually from 16th - 18th June 2021. The conference had a total of 51 oral presentations each consisting of a 15 min pre-recorded video. The talks were mainly focused on analysis of plasma assisted coatings and surface treatment technologies. Other presentations were concentrated on specific power supply requirements, ion energy distribution functions in HiPIMS, plasma parameter diagnostics and plasma instabilities. A special session introduced a panel of experts who presented their view on the topic of ”How can Surface Engineering remain a pillar of the world manufacturing agenda both academically and industrially?”.

Dr. Julian Held, Rahel Buschhaus and Mathews George represented RUB as a part of the SFB-TR 87 consortium with oral presentations on their latest scientific results. Prof. Dr. Jochen Schneider and Soheil Karimi Aghda, from RWTH who are also fellow members of the SFB TR -87 consortium exhibited their latest results via recorded oral presentations.

Mathews George, project A5 of the SFB-TR 87

2D SPATIALLY RESOLVED O ATOM DENSITY PROFILES IN AN ATMOSPHERIC PRESSURE PLASMA JET: FROM THE ACTIVE PLASMA VOLUME TO THE EFFLUENT

David Steuer, Ihor Korolov, Sascha Chur, Julian Schulze, Volker Schulz-von der Gathen, Judith Golda, Marc Böke

Reactive atomic oxygen and nitrogen species (RONS) are one of the main focuses of recent studies, as they are important for surface treatments and medical applications. The key to these applications is the generation of reactive species within the active plasma volume of µAPPJs by using helium with an admixture (up to a few percent) of molecular gases such as oxygen. To control and optimize the formation of RONS, besides the knowledge of the complex gas composition caused by chemical reactions, also an understanding of the production processes is necessary.

In a collaboration between project A4 and B2, two photon absorption laser induced fluorescence (TALIF) measurements were performed on the COST reference micro-plasma jet to determine 2D atomic oxygen distributions. The observed density profiles are understood based on measurements of the spatio-temporal electron dynamics by phase resolved optical emission spectroscopy (PROES) in combination with basic model calculations.

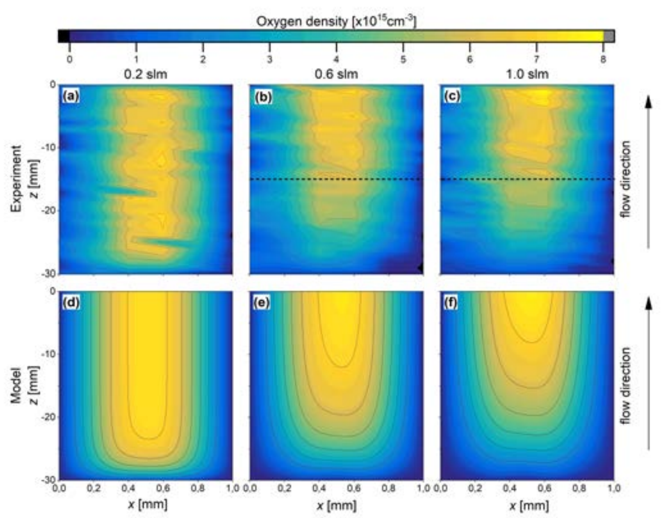


Figure 1: 2D spatial distribution of atomic oxygen inside the COST jet. Discharge conditions: He + 0.5% O_2 admixture at a power of 1 W for different flows.

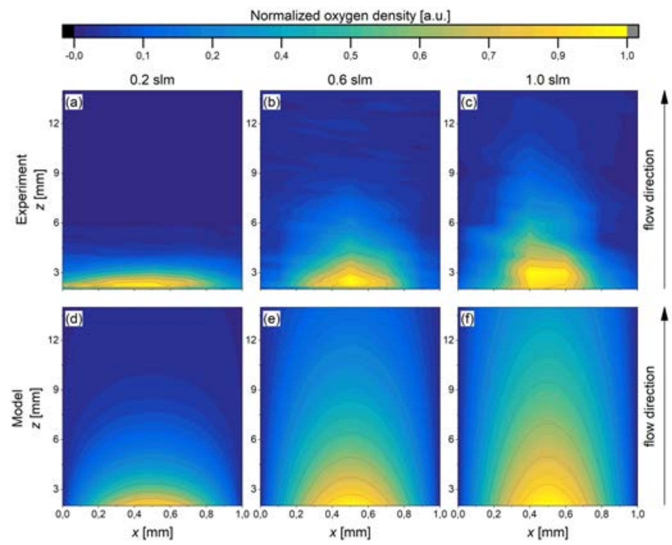


Figure 2: 2D spatial distribution of atomic oxygen in the effluent. Discharge conditions: He + 0.5% O_2 admixture at a power of 1 W and different flows .

The TALIF measurements are in close agreement with the simple model calculations (see figure 1). The oxygen density increases in the direction of the gas flow and reaches a plateau. The increase in density can be influenced by varying the gas flow and thus the residence time through the jet. The results show that the design of the COST jet is optimal for the gas flows used. However, due to the slow density increase at higher flows, the maximum density is not reached, indicating that an extended version of the jet could offer advantages.

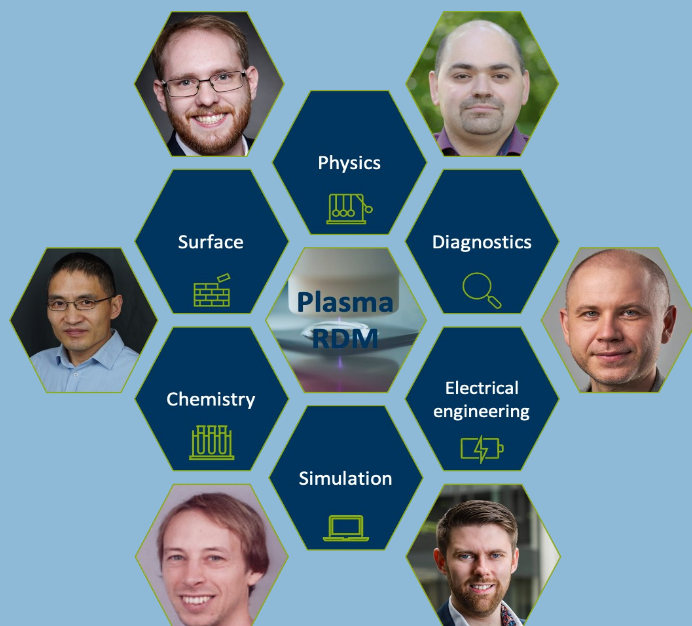
For applications it is especially important to know the density of reactive species also in the effluent. The measurements show that the treatment range can be increased by the gas flow. Furthermore, the atomic oxygen density decreases exponentially in the direction of the gas flow (see figure 2). This can be explained by the absence of electron impact collision sources and the formation of ozone. In contrast to the discharge, differences between measurements and simple model are visible. On the one hand, the treatment range is reduced by Stokes friction. On the other hand, the TALIF signal is quenched at the edges of the effluent, changing the two -dimensional shape of the measurement.

This work demonstrates that treatment distances and treatment times can be optimized for a wide range of applications. The treatment range can be maximized by increasing the gas flow. However, if the flow is too high, the maximum density can no longer be produced. A compromise between sufficient gas flow and optimal oxygen production can be found at 1.0 slm.

This work has been published in the Joournal of Physics D: Applied **54**, 355204 (2021).

David Steuer, project A6 of the CRC 1316

RESEARCH DATA MANAGEMENT



During the preparation of the information infrastructure (INF) project of CRC 1316, various measures for the INF project have already been defined. Through the funding of the second funding period of the CRC, a corresponding number of activities will be carried out. A central aspect is the implementation of *Data Stewards* as responsible persons from each subfield of the CRC 1316.

Furthermore, the exchange with QPQDat (Quality assurance and linking of research data in plasma technology, hosted by INP Greifswald) on metadata schemas will be intensified. Regular meetings on metadata standards development are held online every third Friday of the month at 1pm. During these meetings, various topics are discussed, so different partners from the groups are asked to participate in the meetings.

A first meeting was held on Nov. 26 on the topic of atmospheric pressure discharges. From INP, Nick Plathe, Sarah-Johanna Klose and Robert Bansemer participated under the direction of Markus Becker. From Bochum participated: Wolfgang Breilmann, Sascha Chur, Patrick Preissing, and Marina Prenzel. In the discussion round, necessary parameters for the description of the kinPen® as well as the COST-jet could be worked out, which will be included in the GitHub *Plasma MDS*. In the next weeks a download of json files will be possible, which can be used e.g. in the electronic lab book eLabFTW.

The rdpci repository as a tool for publishing journal data is already in use. All members of CRC 1316 and SFB-TR 87 are asked to upload their data to the repository each time a new publication is made.

As a prototype, an electronic lab book eLabFTW is planned to be hosted by IT.Services of RUB. Further details will follow. Here, the fruitful collaboration with IT.Services at RUB is driving the development.

Marina Prenzel, INF project of the CRC 1316

MODELING OF THE COST-JET IN MIXTURES OF OXYGEN AND NITROGEN

Youfan He, Patrick Preissing, David Steuer, Maximilian Klich, Volker Schulz-von der Gathen, Marc Böke, Ihor Korolov, Julian Schulze, Vasco Guerra, Ralf Peter Brinkmann, Efe Kemaneci

One of the goals of the CRC 1316 is to modify surfaces under the interaction with a specific plasma source to affect the catalytic properties. In this context cold atmospheric pressure plasma jets are one of the sources widely used in the field. However, the jets are not only used for surface modification but also for a wide range of applications such as wound healing, sterilization or greenhouse gas conversion. This is owed to their low (room like) temperature that makes it possible to treat heat sensitive samples, as well as their high efficiency to convert ordinary gases into a cocktail of reactive species that eventually interact with the surface. To control the processes that occur at the surface and to tailor the outcome of the reactive species for certain applications, it is crucial to understand the fundamentals of the plasma physics and the forming mechanism of the relevant chemistry.

In a recent collaboration, the projects A9, B2, A4 and A8 published an article, where a zero dimensional (volume averaged) and a pseudo one-dimensional plug flow (spatially resolved) model were developed. The model calculations were compared to experimental data of different reactive species that are formed in the discharge core of the COST-Jet. For both models the electron energy distribution function is self consistently calculated by coupling the models to the Boltzmann equation under the two-term approximation, to properly account for the electron kinetics. The detailed chemical kinetics have been developed to describe the evolution of the desired species. For example, 138 species and 11799 reactions have been taken into account in the He/ N_2(v<58)/O_2(v<41) plasma.

The simulation results fit quite well to all the experimental data in this study. Most extensively the formation and the influence of external parameters, such as absorbed power, gas flow and different admixtures, on the NO production was studied. The experiments were performed by the projects B2 and A4 and were then compared to the simulation results. Two interesting features were found during the validation of the Nitric Oxide densities. First the densities decrease with increasing helium flow, as a consequence on the shorter residence time in the channel and different power densities. This is contrary to the atomic oxygen density that was found to increase with increasing flows. Another especially interesting feature was found during the validation of the Nitric Oxide densities, where a set of power variations has been performed. Here the rate coefficient for the effective quenching

$N_2(A^3\Sigma,B^3\Pi) + O(^3P) \rightarrow NO + N(^2D)$,

that was used to estimate the influence of multiple higher electronically and vibrationally excited states of N_2 at low power, had to be considered three orders of magnitude higher than the literature value in order to fit the experimental data. Furthermore, it was shown that especially in the high power regime, the vibrationally excited N_2(v≥13) plays a major role in the net NO formation.

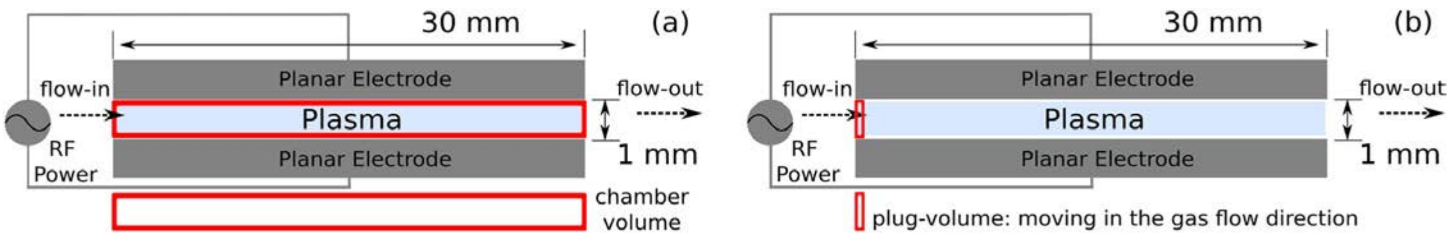


Figure 1: A schematic structure of the COST-jet with a plasma chamber of 1 x 1 x 30 mm^2. (a) The simulation region of the zero-dimensional model: chamber volume, (b) the simulation region of the plug-flow model: plug-volume (moving in the gas direction with time). The figures are not to scale.

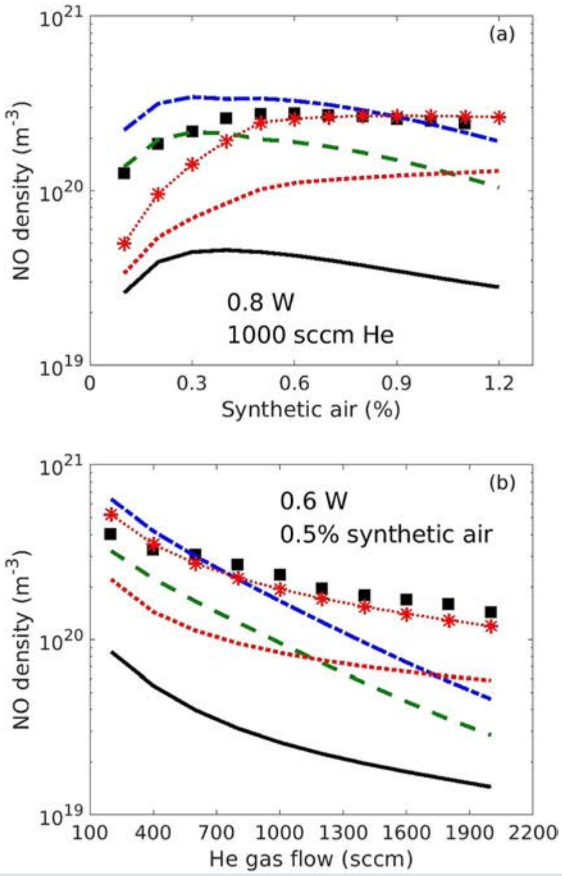


Figure 2: Comparison of the model with different chemical kinetics involved against the experimental data (black squares.) in (a) a variation of the absorbed plasma power can be seen that saturates for high powers. in (b) a variation of the feed gas flow (while the admixture of synthetic air is kept constant at 0.5%) is shown. Here the density decreases with increasing flows due to different power densities and longer residence times in the active plasma region. In both cases it can be seen that the model with the adjusted chemical kinetics and rate coefficients resemble the experimental data well (red stars.)

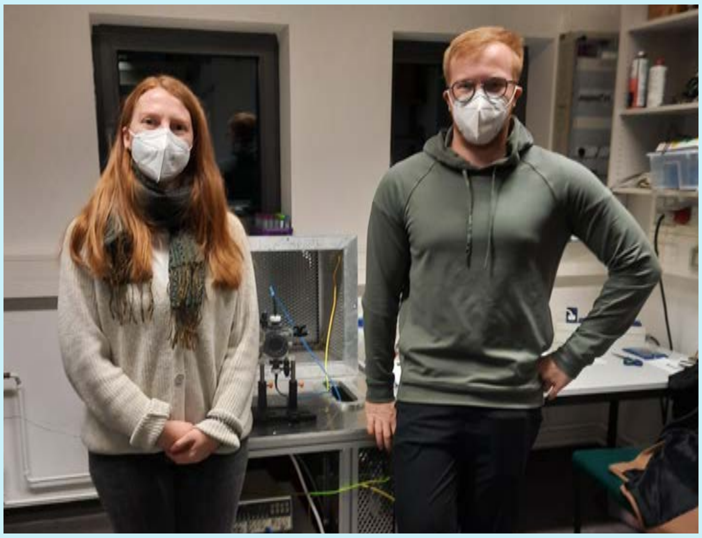
The models were able to recreate the experimental data in both cases, spatially resolved and volume averaged for a variety of species. This is of great importance for the understanding of the creation mechanisms and channels that are responsible for the build up of the interacting species.

The results of this study have been published in the Plasma Sources Science and Technology **30**, 105017 (2021).

Patrick Preissing, project B2 of the CRC 1316

COLLABORATION OF PROJECTS B1 & B7 OF THE CRC 1316

From November 22 until November 26, 2021, the post-docs Philipp and Katharina Grosse from projects B1 (FHI) and B7 (RUB) worked together on the interplay of plasmas in liquids and electrochemistry. The ongoing collaboration of both scientists has already led to several visits and scientific exchanges working on the CO_2 and N reduction reactions (CO2RR und N2RR). They investigated the influence of a µs-pulsed plasma on the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in electrochemical cells. For the future, the projects aim to use a combined cell, consisting



of both an electrochemical and a plasma cell. With this, direct plasma treatment of different electrodes is possible without the transfer between two cells. For the second phase, especially the simultaneous characterization of treated catalytic surfaces at FHI and optical plasma parameters at RUB by using two identical plasma sources will strengthen the collaboration even further.

Katharina Grosse, project B7 of the CRC 1316

UNRAVELLING THE ION-ENERGY DEPENDENT STRUCTURE EVOLUTION AND ITS IMPLICATIONS FOR THE ELASTIC PROPERTIES OF (V,AL)N THIN FILMS

Soheil Karimi, Denis Music, Yeliz Unutulmazsoy, Heng Han Sua, Stanislav Mráz, Marcus Hans, Daniel Primetzhofer, André Anders, Jochen M. Schneider

To understand plasma-surface interactions, the ab initio based ‘thermal spike model’ was developed for metastable (Cr,Al)N to relate plasma energetics with film composition, crystal structure, mass density, stress state, and elastic properties in the second phase of SFB-TR 87 [1]. Within the third phase, this thermal spike model has been expanded to isostructural metastable (V,Al)N. To this end, in a recent publication [2] from project A3, we systematically investigated the ion-energy-dependent defect structure evolution and how the underlying physical mechanisms influence the mechanical properties of (V,Al)N thin films.

(100) preferred orientation for $E_k \geq 104$ eV. Furthermore, the compressive intrinsic stress increases by 336 % to -4.8 GPa as E_k is increased from 4 to 104 eV. Higher ion kinetic energy causes stress relaxation to -2.7 GPa at 154 eV. These ion irradiation-induced changes in the thin film stress state are in good agreement with density functional theory simulations. Furthermore, the measured elastic moduli of (V,Al)N thin films exhibit no significant dependence on E_k. The apparent independence of the elastic modulus on E_k can be rationalized by considering the concurrent and balancing effects of bombardment-induced formation of Frenkel pairs (causing a decrease in elastic modulus) and evolution of compressive intrinsic stress (causing an increase in elastic modulus). Hence, the evolution of the film stresses and mechani-

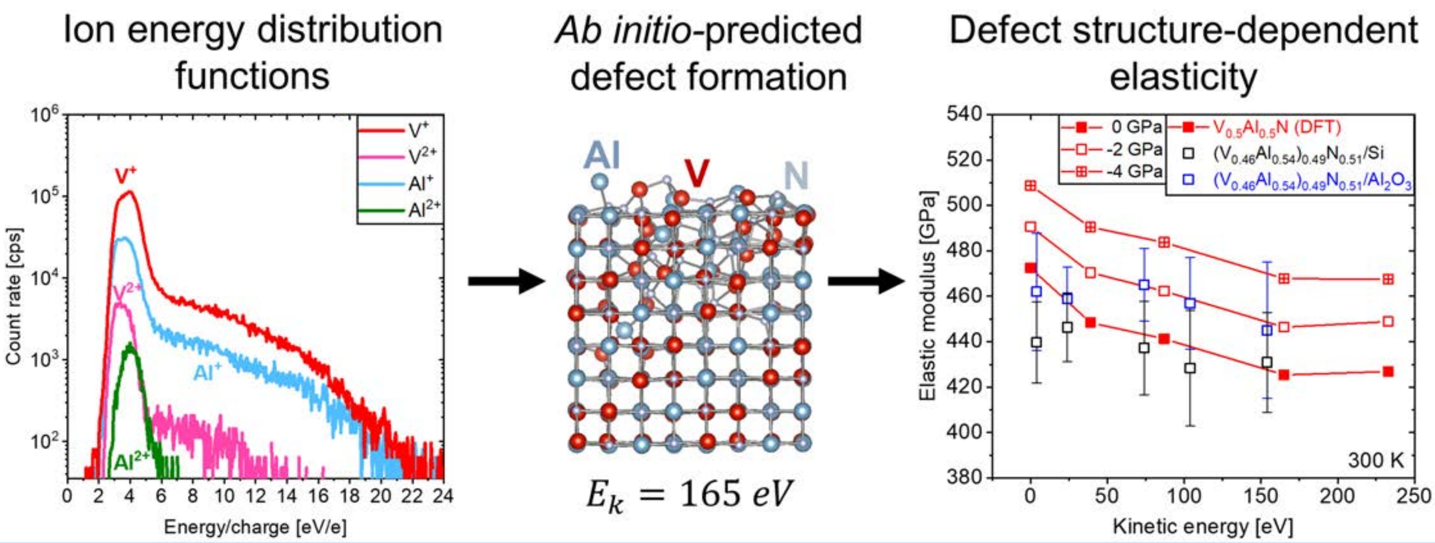


Figure 1: From ion energy distribution functions towards correlating experimental and theoretical investigation of ion energy-dependent defect structure and elasticity evolution of (V,Al)N

Ion irradiation-induced changes in the structure and mechanical properties of metastable cubic (V,Al)N deposited by reactive high power pulsed magnetron sputtering are systematically investigated by correlating experiments and theory in the ion kinetic energy (E_k) range from 4 to 154 eV. Increasing E_k results in film densification and the evolution from a columnar (111) oriented structure at $E_k \leq 24$ eV to a fine-grained structure with

cal properties can be understood based on the complex interplay of ion irradiation-induced defect generation and annihilation. These findings are profoundly in line with the plasma-surface and mechanical model of SFB-TR 87.

Soheil Karimi, project A3 of the SFB-TR 87

[1] D. Music et al. Journal of Applied Physics **121**, 215108 (2017)
[2] S. Karimi Aghda et al. Acta Materialia **214**, 117003 (2021)

H.C. STARCK TUNGSTEN DOCTORAL AWARD 2021 TO DR. LUKAS MAI

Dr. Lukas Mai received a doctoral award for his dissertation, which was written in an interdisciplinary field between chemistry, materials science and engineering science in the Chemistry of Inorganic Materials working group.

Dr. Lukas Mai from the Faculty of Chemistry and Biochemistry receives a prize from the German Chemical Society (GDCh). This is the H.C. Starck Tungsten Doctoral Award 2021 of the GDCh Division Solid State Chemistry & Materials Research. The prize was awarded for Mai's dissertation "*Investigation of Amino-Alkyl Coordinated Complexes as New Precursor Class for Atomic Layer Deposition of Aluminum, Tin and Zinc Oxide Thin Films and Their Application*" for the pioneering contributions to the development of a new Class of precursors for the deposition of atomic layers of binary metal oxides, especially of aluminium oxide, at low temperatures [1]. The two projects SFB-TR 87 and EFRE-FunALD, within which the thesis was written, have provided the ideal platform for this application-oriented research.

The certificate and the prize money of 2,500 euros were awarded at the end of August at the Science Forum Chemistry (WiFo).

Maya Krüger, public relations of the CRC 1316 & SFB-TR 87

[1] https://en.gdch.de/network-structures/divisions/solid-state-chemistry-materials-research/awards-honors/phd-award.html, 16.11.2021

STUDENTS PROJECT WEEK

After a break of two years, the students' project week took place in person at Ruhr University again. In cooperation with the zdi Netzwerk, students grade 8 and 9 could participate in either "World of Plasmas" and "Physics in Medicine" during the first week of the autumn break. During the project week, students gained an insight into different laboratories and could work on a small research project using different diagnostics and apertures to present their findings in a poster session at the end of the week. Next to the research projects, the students visited the Planetarium Bochum, attended a lecture by Prof. Hildebrandt on the weight of the universe and had a session with alumni to ask questions on possible career paths with a degree in physics. The week ended with a common outdoor pizza lunch.

The next project week will take place during the first week of the Easter holiday 2022, offering three workshops to girls in grade 8, 9 and 10.

Maike Kai, public relations of the CRC 1316 & SFB-TR 87

TWO AWARDS FOR CRC RESEARCHERS AT THE RUB ACADEMIC ANNIVERSARY PARTY

David Steuer, project A6 of the CRC 1316

PhD Student **David Steuer** received an award for his exceptional work during his master degree at the Academic Celebration of the Ruhr-University Bochum on the 24th of November 2021. His thesis *Comparative Investigation of Two-Dimensional Oxygen Distributions in Microplasmas by Optical Methods* has been chosen to be the best Master thesis in 2020 from the Faculty of Physics and Astronomy.

Atomic oxygen distributions in the COST-jet and its effluent were measured. The production of reactive species could be controlled and characterized by varying the gas flow and power. Pure oxygen as well as synthetic air was used as gas admixture. A maximization of the dissociation degree could be achieved by tailoring the voltage waveform. The atomic oxygen density could be increased from $2 \cdot 10^{15}\text{cm}^{-3}$ to $8 \cdot 10^{15}\text{cm}^{-3}$. Absolute particle densities could be determined using two-photon laser induced fluorescence spectroscopy (TALIF) and energy resolved actinometry (ERA). Both methods could be extended to two-dimensional measurements in the course of this work, allowing the respective results to be compared and classified. The absolute oxygen densities are higher by a factor of 6.5 with ERA measurements than with comparable TALIF measurements. This deviation can be explained by the uncertainties of the method.

David Steuer, project A6 of the CRC 1316

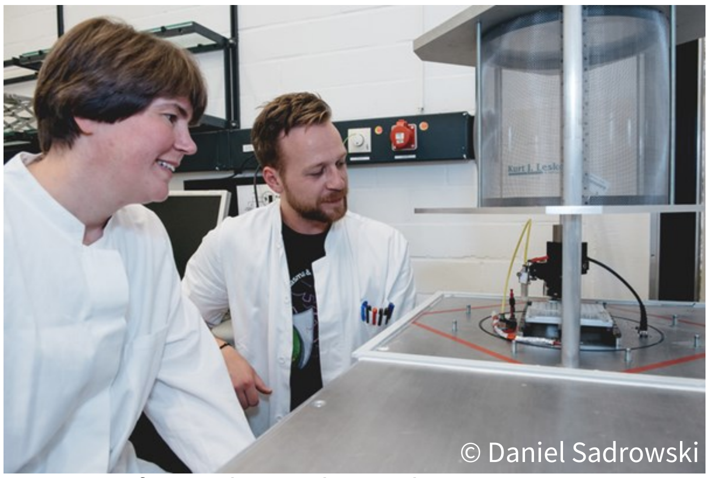
Additionally, **Dr. Marco Krewing** received the GdF-Award (Society of Friends of the RUB) for exceptional interdisciplinary work during his dissertation with the


Dr. Marco Krewing, project B8 of the CRC 1316

title *Impact of low-temperature plasmas on microorganisms and biomolecules*.

His dissertation was written in the field of plasma medicine. Plasmas can not only selectively kill bacteria, viruses and cancer cells, but also promote the growth of healthy human cells and stimulate the immune system. Engineered plasmas are therefore considered a promising complement to conventional therapies to combat modern diseases such as cancer or multi-resistant pathogens.

During his doctorate, Marco Krewing investigated both the interaction of plasmas with individual model proteins in vitro and the effects of plasmas on whole bacterial cells. Particular focus was placed on protein-driven mechanisms that can lead to the development of bacterial resistance to plasma. Multi-resistant germs are a major challenge in modern medicine and although bacteria have an incredible adaptability, a possible bacterial plasma resistance has not yet been considered or denied in the field of plasma medicine. Marco Krewing was



Prof. Dr. Julia Bandow and Marco Krewing

able to identify new cellular processes (e.g. iron-sulphur clusters) that had not been considered before and that contribute in part to the susceptibility of bacteria to plasma treatments. For almost each of these processes, a suitable protective mechanism could be uncovered; for example, the protein Hsp33 delays the harmful aggregation of proteins destroyed by plasma. In relation to the research field of plasma medicine, the first indications are thus given that bacterial plasma resistance is quite possible and can arise in the case of unregulated use of plasmas.

Maya Krüger, public relations of the CRC 1316 & SFB-TR 87

UPCOMING DATES

SPB-TR 87:

16. DEC

Research Seminar:

Dr. Helmut Riedl, Zoom

13. JAN

Project Workshop:

Future Ideas and Directions

16.—18. MAY

Summit Meeting: Garmisch-Patenkirchen

CRC 1316:

7.—11. MAR

Onsite Spring Meeting: Maria in der Aue

MGK Colloquium, Communication Workshop, PI Meeting

JUN / JUL

Onsite Summer Retreat

TO BE SCHEDULED

Onsite Autumn Meeting: RUB

Kiel Visit

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

Research seminar report

HiPIMS: PLASMA DIAGNOSTICS, FILM GROWTH, AND NEW TRENDS & SPUTTERING ONTO LIQUIDS, FROM NANOPARTICLES TO POLYMER NANOCOMPOSITES

Dr. Stephanos Konstantinidis from Université de Mons, Laboratory for Plasma Surface Interactions (ChIPS), gave a two-part seminar on 08 October 2021 via Zoom.

In the first part "High-Power Impulse Magnetron Sputtering: plasma diagnostics, film growth, and new trends" Dr. Konstantinidis started with the introduction of high-power pulse magnetron sputtering (HiPIMS) which generates a highly dynamic plasma. The ions of the target species can promote the ion bombardment at the growing thin film surface and thus modify the film properties such as increasing film density, lowering surface roughness and modifying the films crystallinity. Moreover, he introduced the latest development of bipolar HiPIMS, in which a positive pulse is applied subsequently to the negative pulse. The capability of this technique for tailoring the properties of functional coatings has been demonstrated: TiO_2 and TiN films were deposited by bipolar HiPIMS and the density as well as the hardness of the thin films was enhanced. Besides, characterization by mass spectrometry was used to understand the plasma evolution and control the ion energy in this deposition technique.

In the second part "Sputtering onto liquids, from nanoparticles to polymer nanocomposites" Dr. Konstantinidis presented latest research with respect to magnetron sputtering onto liquids (SoL). Metal nanoparticles (NP) such as Cu, Au, Ag, and Ti can be produced by sputtering the metallic target onto castor oil. Interestingly, the Au NP size is predominated by the growth duration, while the effect of sputtering power and working pressure is less important. In the SoL process, the castor oil can also be substituted by the polyethylene glycol methyl ether acrylate (PEGA480). After undergoing the copolymerization process, a polymer-NP composite was formed. These investigations show the versatility of magnetron sputtering for materials synthesis as well as control of materials properties and were highly relevant for the interaction model of SFB-TR 87.

Yu-Ping Chien, project T1 of the SFB-TR 87

RUBIN SPECIAL ISSUE ON APPLIED PLASMA PHYSICS RESEARCH

This year, the Ruhr-University Bochum has published a RUBIN issue on applied plasma physics research, presenting university-wide plasma research and the application areas of the projects.

The issue covers a wide range of perspectives on the use and understanding of plasmas and their applications, including physical, biological, chemical, technical and medical viewpoints. Experimental studies and simulation studies are also presented.

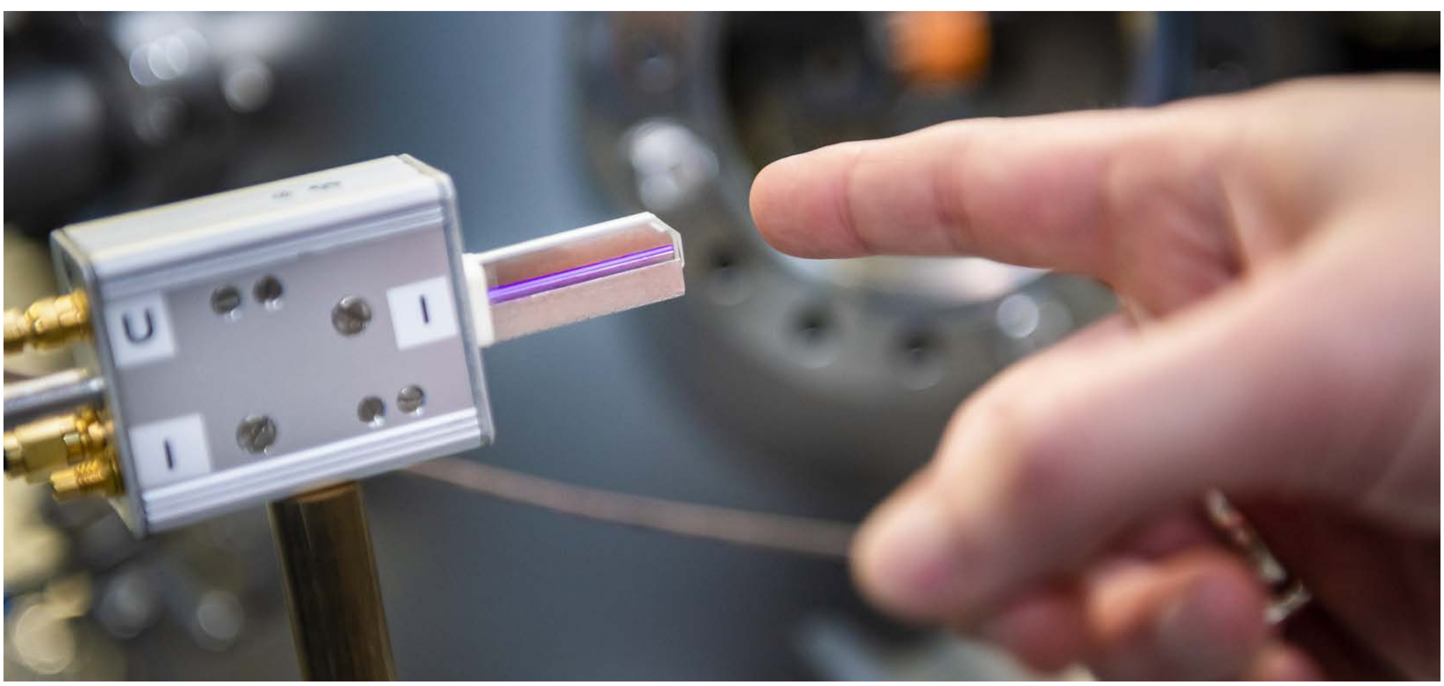
In addition to articles on plasma diagnostics, plasmas in liquids, plasma arrays and many more, the special issue offers a visual impression with many colour photos from the laboratories and of the plasmas.

The special issue is not only aimed at a scientific target audience, but is also intended to inform the wider public. What is a plasma anyway? And what do we need plasmas for? Where are they already used today, and where might they be used in the future? All these questions are answered in a short form and thus provide an easy introduction to the world of plasmas.

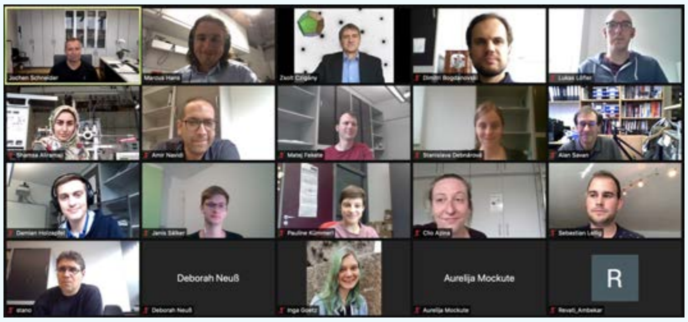
The RUBIN is available online on as single articles as well as a PDF version.

Maike Kai, public relations of the CRC 1316 & SFB-TR 87

https://news.rub.de/dossier/applied-plasma-research



Structure, mechanical properties and thermal stability of nitrides and carbides—insights from transmission electron microscopy



Prof. Zsolt Czigány from the Centre for Energy Research in Hungary, held a two-part-seminar on 30 August 2021 via Zoom. Prof. Czigány is a materials scientist, specialized in transmission electron microscopy of thin films, nanoparticles, nanocomposites and nanostructured materials.

In the first part “Structure and mechanical properties and high temperature stability of binary nitrides and carbides" Prof. Czigány focused on transition metal aluminum nitrides as well as boron carbides. In case of (Ti,Al)N coatings, cathodic arc evaporated macroparticles were found to be predominantly Ti-rich and exhibited a mixture of cubic TiN and hexagonal Ti in the as deposited state. Vacuum annealing at 1000°C induced grain growth within the macroparticle as well as the self -organized formation of a cubic TiN diffusion barrier shell around the Al-rich core of the macroparticle. Thereby, it could be demonstrated that the investigated macroparticles are thermally more stable than metastable cubic (Ti,Al)N. In case of W-B-C, the effect of stoichiometry variations on the growth microstructures were studied. While for high W contents featureless and defect-free compact structures were formed, a reduction in the amount of W resulted in a composite of columnar microstructure with amorphous phase. The highest fraction of crystalline domains was obtained for $W_{40}B_{15}C_{45}$ and the lattice spacing from electron diffraction measurements was in agreement with the formation of a WC_{1-x} phase. These insights were especially interesting for the mechanical model of SFB-TR 87.

In the second part "Transmission electron microscopy - Principles, development and applications" Prof. Czigány discussed the developments which resulted in significant enhancement of spatial resolution such as corrections of spherical and chromatic aberrations. Thermal cathodes and field emission guns were discussed along the lines of different principles of electron sources. Moreover, emphasis was put on the detection methods and sample preparation as the investigated specimens need to be electron transparent. The conventional technique consists of cutting, grinding, polishing and argon ion milling of the specimen and thereby lamellae thicknesses of < 20 nm can be obtained. Nowadays focused ion beam techniques are widely employed due to ease of usability and shorter preparation times. However, focused ion beams based on gallium may cause contamination and in the future, techniques will be developed in order to reduce such beam damage.

Marcus Hans, project A3 of the SFB-TR 87

Insights into initial stages of oxidation of protective coatings from AIMD modelling

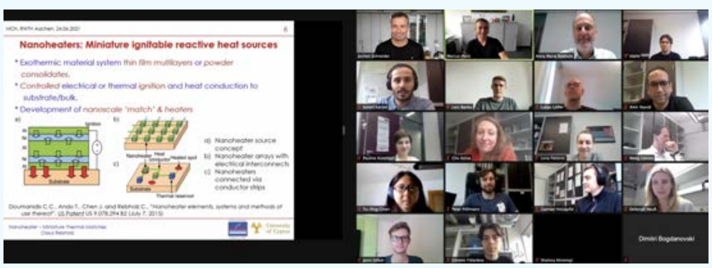
Dr. David Holec from the Montanuniversität Leoben presented a seminar on "Insights into initial stages of oxidation processes of protective coatings from AIMD modelling" on 6 October 2021 via Zoom.

The presentation was focused on a bottom-up approach by ab initio molecular dynamics (AIMD) to understand the oxidation dynamics of transition metal aluminum nitride surfaces exposed to an oxidizing environment. The great capability of the AIMD method is to disentangle the individual mechanisms responsible for the oxidation of different material systems in a time-resolved manner. Firstly, the positive impact of the higher Al content on the oxidation resistance of ternary TiAlN was shown to originate from the formation of aluminum oxide nuclei on the outermost layer of the Al-rich system, rationalizing the experimental observations.

The approach has been extended to the quaternary systems of Ti-Al-X-N (X= V, Hf, Si) to study the impact of alloying elements on the surface layer. The AIMD results revealed that incorporation of Hf and Si facilitates formation of a layered oxide with Ti-rich and Al-rich oscillating layers, enhancing the oxidation resistance at high temperatures. It has been demonstrated that these alloying elements retard the inward diffusion of O atoms and thus promote the oxidation resistance. On the contrary, the addition of V reduces the oxidation resistance of TiAlN. Here, V incorporation leads to the displacement of Ti atoms, resulting in rutile-like TiO_2 formation on the outer layer resulting in the absence of Al-rich protective structure for TiAlVN. These findings were very interesting for the interaction model of SFB-TR 87.

Soheil Karimi, project A3 of the SFB-TR 87

Design of advanced materials and films



Prof. Claus Rebholz from the University of Cyprus gave a workshop on the “Design of Advanced Materials and Thin Films" on 24 June 2021 via Zoom. Prof. Rebholz heads the 'Advanced Coatings Engineering' laboratory and gave insights into different projects from his group.

In the first part, Prof. Rebholz presented the concept of nanoheaters which can be understood as miniature thermal matches. These nanoheaters are realized by a dedicated multilayer architecture with total film thicknesses on the order of 10 µm. Corresponding bilayers consist of systems which exhibit an exothermic reaction upon mixing, for example nickel and aluminum. The exothermic energy release is ignited either thermally or electrically as with a standard nine volts battery. The maximum temperature of > 1500°C as well as the reaction speed are tunable by the bilayer thickness and such nanoheaters can be used for joining of materials.

In the second part, Prof. Rebholz discussed nanoporous carbon-based materials for energy applications. As hydrogen gas occupies a large volume and liquification by compression is energy intensive, the solid state storage of hydrogen by physical adsorption appears very promising. Therefore, stable porous materials are needed and hydrogen adsorption to as well desorption from the pores is controlled by the pressure. Carbon-based materials offer large specific areas, are lightweight and comparably cheap. By employing plasma-based surface modification and decoration of the surface with metals, Prof. Rebholz group could achieve up to 6 wt.% hydrogen uptake at cryogenic temperatures < 80 K.

Finally, combinatorial $(Ti,Al)B_2$ thin films without and with nitrogen additions were discussed. These films were grown in an industrial CemeCon CC800 deposition system and one TiB_2 as well as one TiAl target were combined. While aluminum-rich $(Ti,Al)B_2$ thin films were X-ray amorphous, films with 12% aluminum on the metal sublattice exhibited a nanocomposite structure with 3-4 nm nanocrystals, embedded into an amorphous matrix. The film density was enhanced due to this nanocomposite microstructure and hardness as well as modulus were 35 and 350 GPa, respectively. The addition of 10 at.% nitrogen resulted in a reduction of the hardness to 30 GPa and of the elastic modulus to 300 GPa. However, it was found that the addition of nitrogen caused an enhancement of the oxidation resistance to > 800°C. These insights were especially interesting for the mechanical model of SFB-TR 87.

Marcus Hans, project A3 of the SFB-TR 87

THE CURIOUS SHAPE OF PLASMA WAVES IN MAGNETRON SPUTTERING DISCHARGES

Philipp A. Maaß, Volker Schulz-von der Gathen, Achim von Keudell, Julian Held

One of the main research topics of the SFB-TR 87 is the investigation of magnetron sputtering discharges. Magnetron sputtering sources are used to ignite a plasma and accelerate ions from this plasma onto a surface - a so-called target. The target material is sputtered by the ion bombardment and the sputtered particles condense on other surfaces in contact with the plasma, thus, creating a coating.

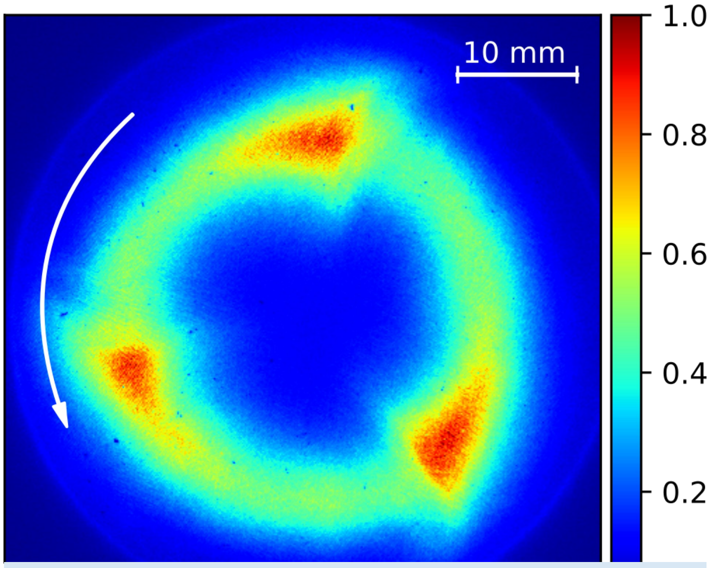


Figure 1: Three spokes rotating in a (high power impulse) magnetron sputtering discharge, in front of the target. The donut-shaped plasma torus is created by the magnetic field configuration, while the three bright spots are the subject of our current research: spokes.

Magnetron sputtering discharges feature magnetic fields, used to confine the electrons to the region close to the target surface. There, they can efficiently ionize the working gas, ensuring a high flux of argon ions onto the target surface. Thus, a large amount of sputtered particles is created, enabling fast coating growth rates.

However, these magnetic fields lead to a discharge configuration with crossed electric (pointing towards the target) and magnetic (parallel to the target surface) field vectors. In such a configuration, plasma waves and instabilities are very common. This is also the case for the magneton sputtering discharges investigated in the SFB-TR 87.

Of particular interest for project A5 is a certain type of plasma wave that has been called "spokes". When the plasma is observed with a very fast camera, these structures appear as bright plasma spots in front of the target surface, rotating along the plasma with velocities in the order of 10 km/s.

Depending on the discharge conditions, spokes can appear to be distinctly asymmetric, as can be seen in figure 1. The triangular shape of spokes has captured the interest of many research groups and over the years, many publications have tried to answer the question of how spokes are created and sustained and what causes this distinctive shape.

Part of the reason that the investigation of spokes has been so difficult, is that the structures appear and disappear at random times and locations in the discharge, rotate along the plasma with a very high velocity, and can then vanish again. This makes the application of traditional plasma diagnostic tools very challenging, since both a good time resolution, as well as synchronization between the measurement tool and the spoke movement are required.

Recently, project A5 of the SFB TR87 has managed to perform optical emission spectroscopy of spokes using a fast camera combined with optical filters, a special synchronization on the spoke movement, and extensive post-processing. This allows to separate out the emission of different types of species in the plasma, showing which part of the distinctive spoke shape is created by which type of light-emitting atom or ion in the plasma.

This can be seen in figure 2, where the general, overall spoke emission (black dotted line) is contrasted with the separated emission of aluminum neutral (Al I), aluminum ions (Al II), or with argon neutrals (Ar I) and ions (Ar II) in figure 2b.

As can be seen from the figure, the leading edge of the moving spoke is mostly made up of aluminum neutral emission (where aluminum is the sputtered target material, in this case). The center of the spoke emission is mostly caused by aluminum ions and argon ions, while the trailing edge of the spoke, where the overall plasma emission drops sharply in the unfiltered images (figure 1), is dominated by argon neutral emission.

spoke, as their density has strongly increased. For argon, for example, the increased emission at the trailing edge of the spoke might indicate increased electron energy, since only highly energetic electrons are able to excite the argon particles to emit the observed light.

Based on these results, we could conclude that the sharp, distinctive edge in the plasma emission (visible in figure 1) is indicative of strong plasma potential variations, which cause a sudden increase in electron temperature which causes an equally sudden increase in light emission. Thus, the spoke images can be used to estimate the strength of the plasma potential variations caused by the spokes, which themselves have important implications for the transport of charged particles inside these plasmas. In turn, the transport of particles determines the performance of magnetron sputtering discharges as coating devices.

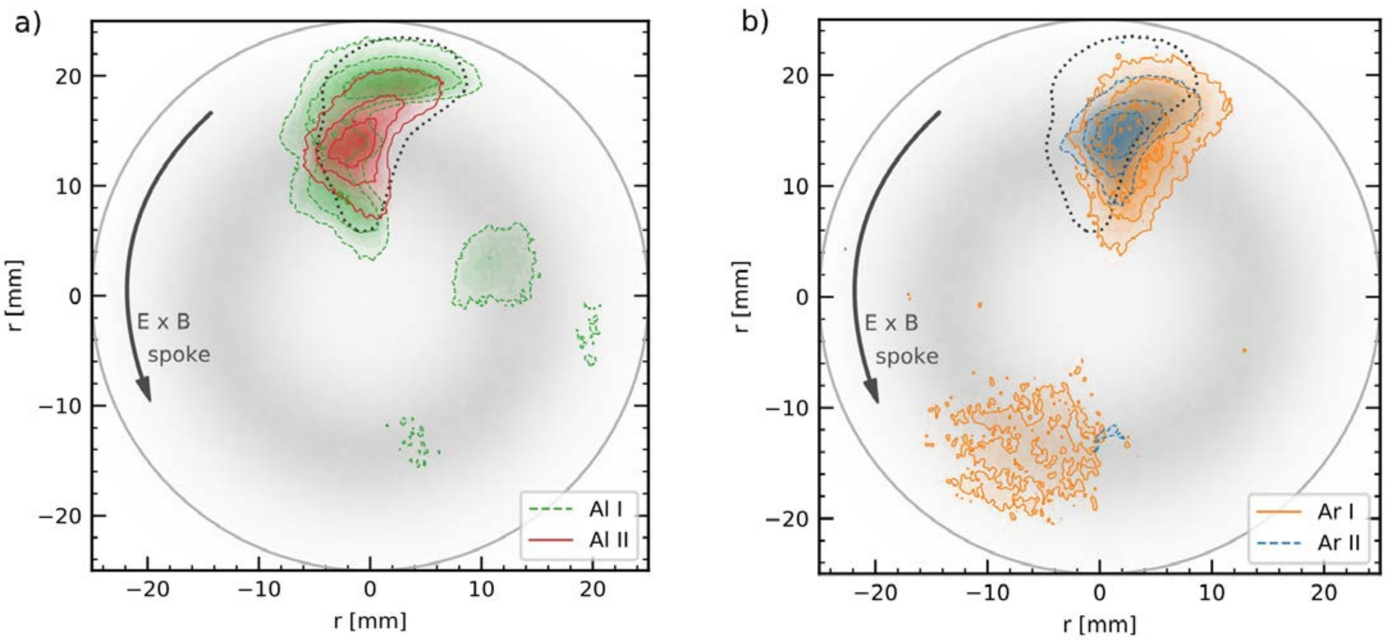


Figure 2: Images of spokes, filtered to separate out the light emission from different species, located at different parts of the spoke. The overall light emission of the spokes is shown as a black dotted outline. a) Aluminium neutrals (Al I) and ions (Al II). b) Argon neutrals (Ar I) and ions (Ar II).

The results seen in figure 2 were obtained for high power impulse magnetron sputtering (HiPIMS), where the plasma is operated at high power pulses and the spokes move in the counter-clockwise direction (the ExB direction of the discharge) at a high velocity of around 10 km/s. The results were compared to measurements performed in the low-powered magnetron sputtering, where the spokes instead move in the opposite direction with a much lower velocity of around 2 km/s.

These results allow inferences about the internal plasma processes inside the spokes: For example, the lack of aluminum neutral emission in the center of the spoke might indicate, that the easy to ionize aluminum neutrals are being completely transformed into ions, which then show an emission maximum in the center of the

The work has been published in Plasma Sources Science and Technology under the name *Synchronising optical emission spectroscopy to spokes in magnetron sputtering discharges*.

Julian Held, project A5 of the SFB-TR 87

CRC 1316—PROJECT AREA A

Dr.-Ing. Sebastian Wilczek successfully completed his doctorate at the Chair of Theoretical Electrical Engineering in 2020. His thesis deals with the influence of nonlocal and nonlinear electron dynamics in capacitive low-pressure plasmas. After his PhD, Sebastian worked on the conversion of CO_2 in radio frequency driven microplasmas within a DFG-RSF collaboration. With the support of 2D fluid simulations (nonPDPSIM), the focus is on the dynamics of the relevant particle species in the COST jet, specifically to investigate the conversion of CO_2.

With the scientific expertise in the field of plasma simulations (Particle-In-Cell Simulations and Fluid-Simulations) Sebastian will support the project A5 of the CRC 1316 in the future.

Mate Vass studied physics at Eötvös Loránd University Budapest, Hungary. His master thesis involved investigating capacitively coupled plasma discharges using Particle-In-Cell/Monte-Carlo Collisions simulations. He has been a PhD student at Ruhr University Bochum since 2020, where he has worked on electron power absorption in capacitively coupled plasmas. He will join the project A4 of the CRC 1316 as a research assistant in January 2022.

In the course of his work, he will perform computer simulations and help develop a 2D hybrid fluid/kinetic framework for capacitively coupled micro atmospheric pressure plasma jets including various chemistries and gridded electrodes.

SFB-TR 87 —PROJECT AREA C

From October 2014 to January 2018, **Dr. Vincent Layes** was employed at the Chair of Experimental Physics II Physics of Reactive Plasmas. His dissertation on "Fundamental surface processes in HiPIMS plasmas: physics and chemistry at the plasma magnetron target interface". Vincent Layes’ defense was held on 16/06/2021.

His scientific work focussed on the in-vacuo characterisation of various surfaces on (composite) targets after sputtering in a High Power Impulse Magnetron Sputtering discharge using X-ray photoelectron spectroscopy. This was complemented by plasma optical characterization techniques such as optical emission spectroscopy and ICCD camera imaging. Among other things, it was shown that the oxidation of the target cannot be readily related to the shape of the current pulse shapes .

After his career at RUB, Vincent Layes started at EPLAN GmbH und Co. KG in Monheim. In October 2021, he took over project management for the entire Software Solutions Business Unit.

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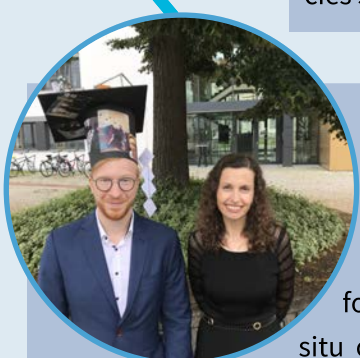
WS

Sascha Chur studied physics at the Ruhr University Bochum. In his master thesis he investigated the two-dimensional atomic oxygen density distribution in the effluent of a COST micro-plasma jet for project B2 within the CRC 1316. Additionally, he was active in the public relations project of the SFB-TR87. He continues in the project B2 as a PhD student from October 2021 on.

The project investigates the interaction of reactive species in the jet effluent with laser induced periodic surface structures (LIPSS) and other laser-surface phenomena. Thus, the project aims to produce more effective and selective catalytic surfaces to be used in electrolysis.

Steffen Schüttler studied physics at Ruhr University in Bochum. As part of his bachelor thesis, he worked on project A3 of CRC 1316 and investigated the influence of catalysts on CO_2 conversion in an atmospheric pressure plasma jet. For his master thesis he switched to project C7 of the SFB TR 87. In this work, he investigated the ion transport in HiPIMS discharges using marker targets.

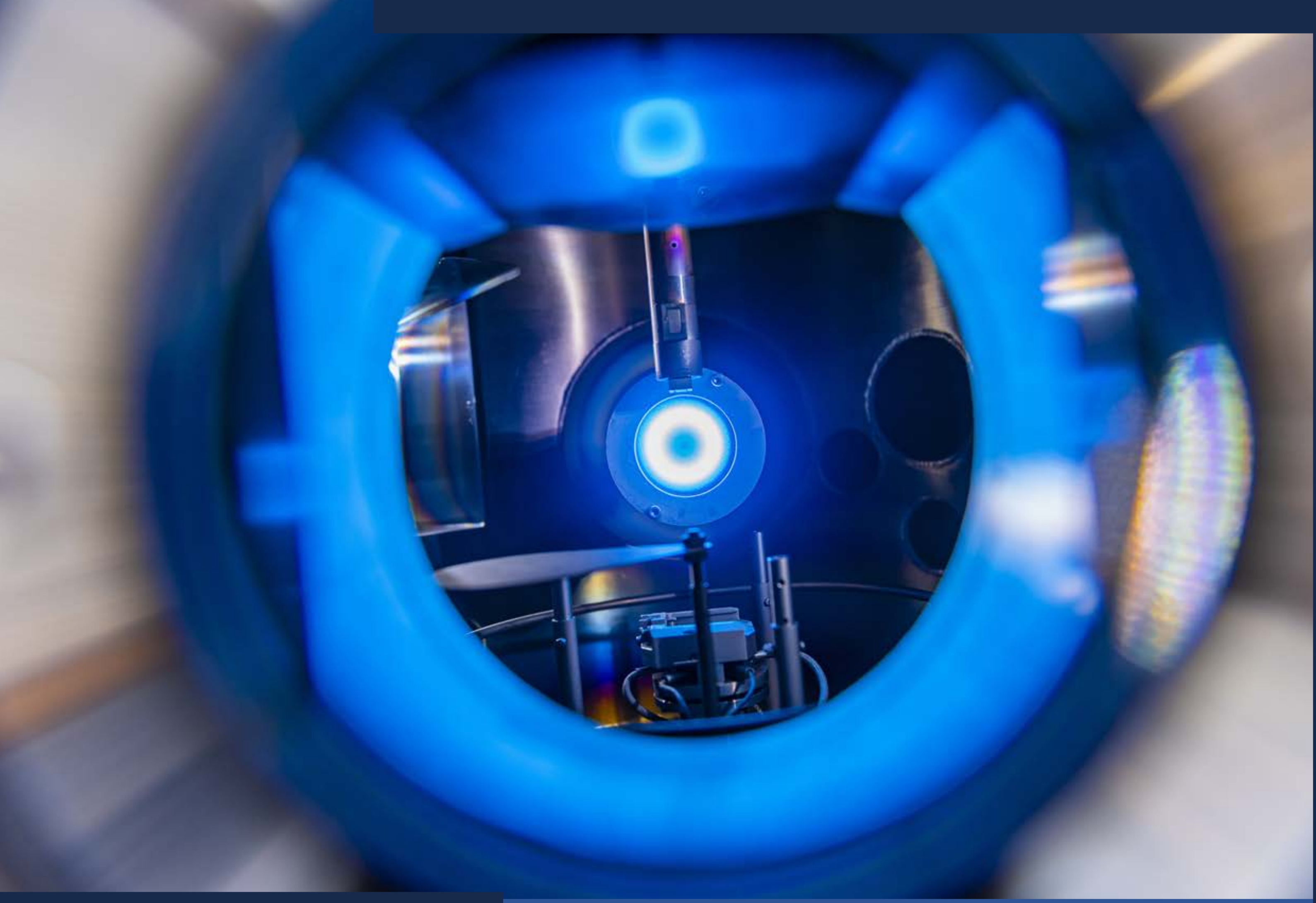
Now he has re-joined CRC 1316 as a PhD student and will cover the plasma physics part of the new interdisciplinary project B11 of the second funding phase. This project deals with the rational tuning of plasma and liquid chemistry for biocatalysis. In the course of his work, he will supply and maintain a plasma source for the biology group of Julia Bandow. His research focus will be the detection of hydrogen peroxide in the plasma and liquid phase as well as other reactive species such as OH.



Dr. Philipp Grosse carried out research on dynamic changes in the morphology and chemical state of copper catalysts for the electrochemical reduction of carbon dioxide.

Philipp was successful at establishing the electrochemical operando atomic force microscopy method within the Roldán group and conducted the first in situ observation of the dynamic changes in the structure of cubic copper precatalysts during the electrochemical reduction of carbon dioxide. Lastly, Philipp investigates the effects of Plasma in liquid on catalyst surfaces under electrochemical reaction conditions. For this, he closely cooperated within the group from Achim von Keudell within the scope of the CRC 1316.

During his PhD Philipp has published seven articles in high impact peer-reviewed journals and two more have been submitted and are currently under review. His recent article has been published in Nature Communications. His combined written dissertation and oral defense were rated Summa Cum Laude.



IMPRESSUM

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