AOFKA 21

conference information · scientific program · abstracts

1st preprint version

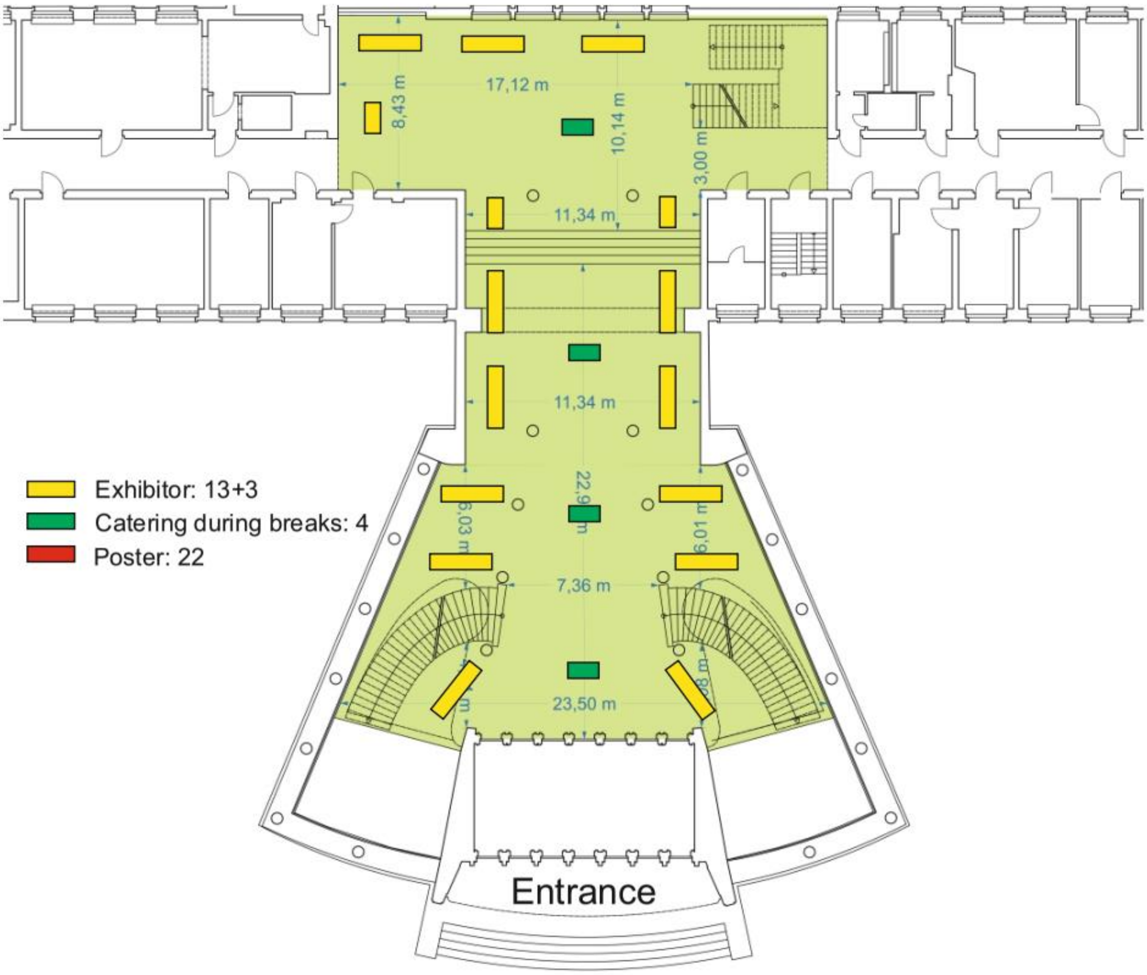
Foto: Jacob Müller

TECHNISCHE UNIVERSITÄT
CHEMNITZ

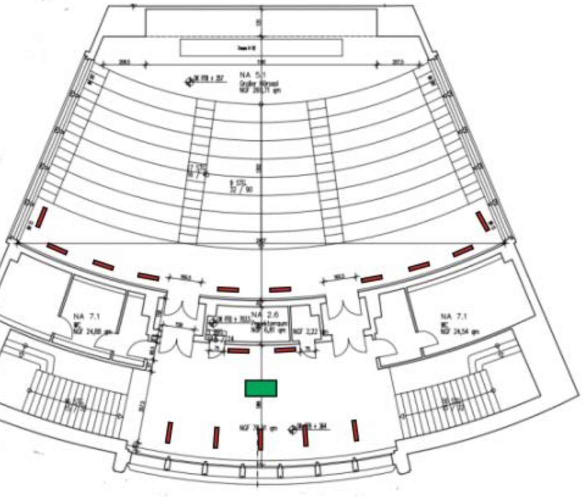
TU BERGAKADEMIE FREIBERG

Clemens Winkler Building
TU Bergakademie Freiberg

Ground level



Lecture Hall level (2nd floor)



Indoor location map of the conference venue

Inhalt

1 Conference information

The AOFKA21 conference on surface and solid state analytics is jointly organized by the FKA and AOFA. It covers all topics related to characterization of solids and their behavior, including both basic research and technological applications. Topics of the conference are:

- **Elemental and compound analysis**: micro- and nano-analysis, surface and interface analysis, trace analysis
- **Structural analysis**
- **Chemical reactions in solids and on solid surfaces**
- **Dynamic behavior of solids**: transport phenomena, diffusion, segregation
- **Application to material science**: metals, semiconductors, ceramics, glasses, polymers, composites, nano-structured materials, biomaterials, functional layer systems (micro/nano-electronics, opto-electronics, photonics, adhesive- and anti-adhesive layers, self-assembled layers)
- **Theoretical and chemometrical aspects**
- **Quality assurance**
- **New instruments & methods**

Besides those general topics, the conference offers hands-on experiments in Raman spectroscopy on Friday afternoon for young researchers and will have a special focus on “Advances in electron microscopy”. The broadband research activities in this field will be demonstrated by invited and contributed lectures as well as poster presentations.

1.1 Local organization committee

- **Prof. Dr. Christoph Tegenkamp**
  Analytics on Solid Surface Analysis
- **Prof. Dr. Thomas Seyller**
  Technical Physics
- **Prof. Dr. Dr. h.c. Dietrich R.T. Zahn**
  Semiconductor Physics

Institute of Physics
Chemnitz University of Technology
Reichenhainer Straße 70, 09126 Chemnitz

- **Prof. Dr. Carla Vogt**
  Institute for Analytical chemistry

TU Bergakademie Freiberg
Leipziger Straße 29
09599 Freiberg

- **Secretaries: Ute Vales**
  Phone: +49 371 531-38034
  Fax: +49 371 531-838034

1.2 Contact information

For up-to-date information about the AOFKA21 please visit the conference website:

https://www.aofka21.de

In case of questions and problems please email us at the official AOFKA address:

aofka21@physik.tu-chemnitz.de

For urgent questions during the conference, you may contact Prof. Tegenkamp by phone: +49 371 531-33103

1.3 Internet access

The eduroam WiFi is available in the area of TU Bergakademie Freiberg. All participants with eduroam access via their home institution may use this network for internet access. Furthermore, guest accounts for the local WiFi will be available for participants without eduroam access. Corresponding login details can be obtained at the conference office.

1.4 Hygiene concept

1. Status quo:
According to the Corona Protection Ordinance of the State of Lower Saxony of June 22, 2021 (https://www.coronavirus.sachsen.de/amtliche-bekanntmachungen.html), §14 permits the holding of our scientific meeting in presence again if the seven-day incidence falls below the threshold of 100. However, testing is still required for indoor meetings, conventions, and trade shows. If the incidence is below 50, the use of catering establishments is possible according to §12 indoors with a hygiene concept and contact recording.

2. Participation in the event:
The basis for participation in our events is that the hygiene regulations and distances are observed. All our employees, team members, speakers and participants are bound to comply with these regulations. Persons with pre-existing conditions or belonging to other risk groups are asked to consult a doctor if necessary; the responsibility for this lies with everyone. The decision about the final participation in the event is also the responsibility of the participants. If it is not possible for participants to wear a medical mask (surgical mask) for reasons certified by a doctor, you can contact us before registering.

3. Before the event:
Only participants who have registered and agreed on this hygiene concept before the start of the event will be admitted, so that any follow-up questioning or contact tracing

by the health department can be made possible. The actual attendance will be documented on site (attendance lists at the reception). Due to regulatory requirements, it is mandatory to provide a contact telephone number. In the event of an infection, the data will be requested from the responsible health office. This is necessary for reasons of traceability of infection chains. This data will be treated confidentially and will be destroyed by us 4 weeks after the end of the event (9 November 2021). We recommend all external participants to contact their hotel in advance to enable a telephone check-in if necessary. This will reduce the waiting time at the hotel and the stay at the reception will be shortened to the shortest possible time.

4. Your arrival:
The participants are responsible for their own arrival. The applicable distance regulations and hygiene conditions (during that time) must be observed. At present, the wearing of a respiratory protection mask (FFP2) is obligatory when using public transport. If you arrive by car, parking spaces are usually available at the hotels we recommend. Please inform yourself in good time about alternatives, should the parking spaces of the hotel be occupied. For our scientific event will take place in the Clemens-Winkler Building of the TU Bergakademie Freiberg, Leipziger Straße 29, 09599 Freiberg. It is therefore recommended to use public transport to get to the conference venue. Many of the recommended hotels are also located about 1km away from the conference venue.

5. Prerequisite for participation in the AOFKA21 event is:
A negative test, i.e. a certificate of a negative test from an approved test center, not older than 48 hours. In addition to the municipal test centers in Freiberg https://tu-freiberg.de/corona/corona-test-zentrum-der-stadt-freiberg-in-betrieb, the test center Mensa of the TU Bergakademie Freiberg can also be used.
or
an immunization and the absence of typical symptoms of an infection, i.e. a complete vaccination (at least 14 days ago) or a certificate of a survived Covid-19 infection, at least 28 days and max. 6 months ago (recovery certificate needed).

Test results or immunizations will be noted on the contact tracking sheet and destroyed after 4 weeks. Hands must also be washed thoroughly before entering the conference venue. Disinfectants are also available at the meeting site.

6. During the conference:
Keep distance: The different areas, such as conference office, checkroom, exhibitors' area, poster session, catering stations as well as the lecture hall are distributed in the Clemens-Winkler Bau (CWB) to avoid crowding (see layout plan). Table and seating arrangements may not be changed arbitrarily.
Conference Office and Cloakroom: Registration and tracking data will be taken in advance to ensure a quick check-in. While observing the distances with a waiting area in front of the Clemens-Winkler building (CWB), the participants will be admitted in a one-way-street principle and guided to the checkroom by information signs.
Exhibitor area: the exhibitors will be located in the foyer of the Clemens-Winkler building and compliance with spacing and disinfection rules (see 6.3 below).
Poster session: Two poster sessions will be held in the second level of the CWB according to the side map.

Coffe and cake stations: Beverages will be available at several serving stations during breaks. Along with 30-minute break times, crowding will be kept to a minimum.
Lecture Hall: Lectures will be held in the lecture hall of the Clemens-Winkler building. Seating is arranged to maintain the specified minimum distance. destroyed within weeks. Hands must also be washed thoroughly before entering the conference venue. Disinfectants are also available at the meeting site.

Wear masks: Depending on the actual rules during the time of the event, wearing a medical mask (surgical mask) or a higher-quality mask (respirator mask FFP2) might be mandatory in all rooms occupied by us, the corridors and toilets of the CWB, because the distance rules cannot necessarily be observed there. If there is a risk of "grouping" in any area, the appropriate spacing must be maintained. The medical mask (surgical mask or higher quality) must be worn tightly over the mouth and nose at all times and changed when wet through; it should not be touched in the filter area while being worn or when being put on or taken off. The obligation to wear a medical mask (or higher quality) exists regardless of compliance with a minimum distance throughout the event. Speakers are exempt from the obligation during the lecture activity if the distance to the persons in the room is maintained.

Testing: For the safety of all participants, it is recommended to be tested once a day. If a test shows a positive result for participants or speakers, there is an obligation to take a PCR test as soon as possible and to inform the conference office immediately about the result. The event will be cancelled immediately. All participants/speakers must go into quarantine and inform their local health authorities.
Further information on ensuring distance rules and hygiene conditions will be explained on site by organizers and staff of the conference office.

6.1 Exceptions:

Exceptions to these regulations are only possible according to point 2. Refusal to wear at least a medical mask (exception only according to point 2) or to perform the tests properly will result in immediate exclusion from the event, with the full costs being charged. The conference office must be informed.

6.2 Ventilations:

Regular ventilation of the rooms, if possible shock ventilation/cross ventilation with wide open windows, is generally carried out to improve the air quality. This must be done taking into account possible accident hazards. Ventilation at the beginning/end of a lecture session is possible, for example. Organizers of the event are responsible for this. Air exchange must take place. The time required for this depends on the spatial conditions, e.g. the possibility of cross-ventilation. If the rooms are externally ventilated (air conditioning, etc.), it can be assumed that there is sufficient air exchange and no further measures need to be taken.

6.3 Maintenance cleaning and disinfecting cleaning of surfaces :

Regular cleaning of rooms and surfaces with which participants may regularly come into contact is carried out according to the respective cleaning schedule of TU Bergakademie Freiberg. This cleaning is carried out at least within the framework of the official requirements.

6.4 Food and beverages :

For the provision of food and beverages at the event location, in the mensa and restaurant, there are extensive requirements on the part of the authorities. In the run-up to the event, the organizers and staff of the conference office will explain the most important points in this regard and address the local conditions.

2 Sponsors & Exhibitors

The following companies and societies support the AOFKA21 conference:

neaspec
see the nanoworld

BRUKER

Gesellschaft der Freunde der TU Chemnitz e.V.

HIDEN
ANALYTICAL

HORIBA
Scientific

IONTOF

JEOL

Leybold

PFEIFFER VACUUM

PREVAC

RENISHAW®

apply innovation™

scientaomicron

SPECS™

ThermoFisher
SCIENTIFIC

VAT
PASSION. PRECISION. PURITY.

WITec
focus innovations

3 Venue, accomodation, and travel

AOFKA21 is held from 06-08 October 2021 at the TU Bergakademie Freiberg. The conference venue is the “Clemens-Winkler-Bau”, which belongs to the faculty of chemistry and physics. It’s address is:

TU Bergakademie Freiberg
Clemens-Winkler-Bau
Leipziger Straße 29
09599 Freiberg.

An indoor location map of the conference site is shown on the inside of the front cover.

About Freiberg

The university town Freiberg is a nice midsize town with around 40k inhabitans in the middle of Saxony between Dresden and Chemnitz. With the Bergakademie Freiberg founded in 1765, it is the seat of the oldest still existing technical and mining science university in the world. The entire historic city center is listed under monument conservation and always worth a look. Together with local monuments of mining history such as the Reiche Zeche, it has been a UNESCO World Heritage Site of the Ore Mountains Mining Region (Montanregion Erzgebirge) since 2019. Until 1969, the city was shaped by mining and the iron and steel industry for around 800 years. In the last few decades there has been a structural change to a high-tech location in the field of semiconductor manufacturing and solar technology, making Freiberg part of Silicon Saxony.

About Chemnitz

Chemnitz is the third largest city in saxony with around 250.000 citizans and has an impressive history of groundbreaking inventions in mechanical engineering and textile industry, as well asbold entrepreneurs such as Richard Hartmann, Carl Gottlieb Haubold and Louis Schönherr.

Chemnitz is today one of the German cities with the strongest growth. The city is still a technological centre specialising in the automotive and supplier industries, information technology, mechanical engineering and microsystems technology. The Chemnitz University of Technology as an intellectual centre, research institutions such as the Fraunhofer Institutes and a large number of successful medium-sized companies, largely made up of family businesses, together create the ideal conditions for an economic success story.

Moreover, Chemnitz offers plenty of museums and theaters to discover. The Chemnitz Art Collections or the Gunzenhauser Museum, for instance, houses one of the most impressive collections of classical modernism. Meanwhile, the Saxon Museum of Industry depicts history and the present day. The City Theatre with the Robert-Schumann-Philharmonie draws audiences from across Germany.

3.1 Travelling to Freiberg

Freiberg is a nice midsize town 40km from Chemnitz with a great mining history. The name TU Bergakademie Freiberg refers to that. It is situated in the middle of Saxony and can be reached by train, bus, car or plane.

By train: Freiberg train station is connected to the regional and long-distance trains (RB, RE) from Dresden and Chemnitz. Trains run here every half hour.

By bus: City and regional transport Freiberg: to the route and timetable information

By car: Arrival via Autobahn from Frankfurt, Munich, Berlin, Dresden, Leipzig, Chemnitz: Autobahn A4 - Exit Siebenlehn - B 101 direction Freiberg
Arrival via Autobahn from Prague: Autobahn A17 – Exit Kesselsdorf – B 173 direction Freiberg

By plane: from Dresden Airport: 54 km; from Leipzig/Halle Airport: 112 km

3.2 Accomodation

Below you find a selection of possible hotels:

- **Hotel am Obermarkt**
  Waisenhausstraße 2, 09599 Freiberg
  Distance: 1.5 km
- **Hotel Blaue Blume**
  Donatsgasse 25, 09599 Freiberg
  Distance: 2 km
- **Hotel Maucksches Gut**
  Hornstraße 20, 09599 Freiberg
  Distance: 2 km
- **Altstadt-Hotel Freiberg**
  Donatsgasse 3, 09599 Freiberg
  Distance: 2 km
- **Hotel Regenbogenhaus**
  Brückenstraße 5, 09599 Freiberg
  Distance: 2.5 km

4 Scientific & social programm

4.1 Invited speakers

- **Ute Kaiser** (Uni Ulm)
  “Properties of low-dimensional materials by low-voltage TEM”
- **Eva Olsson** (Chalmers Göteborg)
  “High resolution correlation between atomic structure and properties using advanced transmission electron microscopy”
- **Christian Papp** (FAU Erlangen)
  “Catalysis with liquid metal alloys”
- **Dietrich R.T. Zahn** (TU Chemnitz)
  “Exploiting Enhancement Effects in Raman Spectroscopy”
- **Andreas Undisz** (Uni Jena)
  “New insights into the early oxidation stages of metallic materials by transmission electron microscopy”
- **Klaus Danzer** (em. Uni Jena)
  “The Way of Chemometrics”
- **Renato Zenobi** (ETH Zürich)
  “Tip-enhanced Raman Spectroscopy for Nanoscale Chemical Analysis of Sensitive 2D Materials”

4.2 Talk sessions

During the AOFKA21, 9 talk sessions will be held. Three types of talks are included in these sessions:

- **Invited talks** are scheduled for a duration of 25 minutes + 5 minutes for questions.
- **Contributed talks** are scheduled for a duration of 12 minutes + 3 minutes for questions.
- **Company presentations** are scheduled for a duration of 10 minutes.

We kindly ask all speakers to observe the times for their talks.

4.3 Poster sessions

Two poster sessions will be held on the first and second conference day. The posters may be mounted at any time during the day of the respective poster session and should be removed directly after the session.

4.4 Special focus: Advances in electron microscopy

For each edition of the FKA conference we would like to solicite contributions on highly relevant current research topics. In 2021 this focus will be put on “Advances in electron microscopy”. All contributions related to this topic ranging from theory to experiments covering fundamental and application-related aspects are particularly welcomed, and will be matched by the program committee with the other topics of the conference and the whole program.

The special focus sessions are scheduled on the afternoon of the first conference day and are framed by three invited talks given by Ute Kaiser, Eva Olsson, and Andreas Undisz.

4.5 Hands-on workshop: Raman spectroscopy

We offer also this time a hands-on workhop for young scientists. **The topic for the AOFKA21 is Raman spectroscopy**. The workshop will be held on Friday afternoon (around 3pm for 2-3 hours). After an introduction given by Prof. Dietrich Zahn, the students will have the opportunity to practise their knowledge regarding solid state analytics. We will arrange a shuttle service to Cemnitz. Further instructions will be announced during the conference.

4.6 Poster award & logo contest

During the AOFKA21 two poster sessions will be held. A jury will evaluate all presented posters and award a prize for the best poster.
Besides this poster award, a second contest is announced to find a logo for the new AOFKA conference. We encourage you to participate in this logo contest and email your suggestion to logo_contest_aofka21@physik.tu-chemnitz.de. If you allow, we will publish your suggestion on the conference website in advance. The committee will evalutate your suggestions during the meeing and will present the final three during our social event, where all participants are invited for voting. The winner of the logo contest will get a prize money.

4.7 Social event

The evening of the second conference day is reserved for social activities. At moment we plan to visit the terra mineralia in Freiberg. It's a beautiful collection of minerals from all over the world. In parallel, we offer also an enjoyable City tour through.
After these activities, a conference dinner will be held at the Ratskeller Freiberg. During this banquet the winners of the poster award and the logo contest will be announced and awarded.

5 Conference schedule & abstracts

The AOFKA21 conference features 9 talk sessions and 2 poster sessions. Contributions from the multi-faceted fields of surface and solid state analytics are complemented by invited talks and company presentations.
An overview of the conference program is printed on the back cover of this book. The detailed schedule for all sessions is shown on the following pages together with the respective abstracts.

5.1 Session I — Wednesday, October 6th

08:50 – 09:20	**Christian Papp (invited)** Catalysis with Liquid Metals
09:20 – 09:35	**Andreas Borgschulte** Cataluminescence in Er-substituted perovskite oxides
09:35 – 09:50	**Florian Schrenk** Influence of exsolved nanoparticle size on the catalytic activity during methane dry reforming
09:50 – 10:05	**Gilbère Mannie** Chemical reactions, corrosion, electrochemistry and biological materials - routine operando studies with Near Ambient Pressure XPS
10:05 – 10:20	**Emanuel Billeter** Hydrogen pressure composition isotherms of TiHx by electron spectroscopy
10:20 – 10:30	**Company presentation 1**

Catalysis with Liquid Metals

Christian Papp

Physical Chemistry 2, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Supported catalytically active liquid metal solutions (SCALMS) are deactivation-resilient and highly active dehydrogenation catalysts for short alkanes, based on binary transition metal Gallium alloys. The remarkable properties of these catalysts, especially their good resiliency towards deactivation, are attested to the atomic dispersion of the active transition metal in liquid Gallium nano-droplets and the dynamics at the liquid metal/gas interface. The concept was pioneered at FAU and over the recent years we published findings on PdGa [1], PtGa [2] and most recently RhGa [3, 4] alloys.

Herein, we report XPS studies on macroscopic alloy droplets and model catalyst particles, including in situ heating and comparative near ambient pressure oxidation studies for Pd-, Pt- and RhGa alloys. In all cases, enrichment of the transition metal in sub-surface layers is observed. Despite their similarity in the concentration gradient and high catalytic activity, the development during the oxidation however suggests significant differences for the transition metals. For Platinum [5] and Rhodium [4], we deduce an incorporation of the transition metal into the oxide film, for Palladium the data points towards an enrichment at the Gallium/Gallium oxide interface. The results are supported by high resolution TEM and EDX results. Our obtained spectroscopic results were interpreted with the aid of DFT based molecular dynamics and theoretically obtained XPS binding energy shifts.

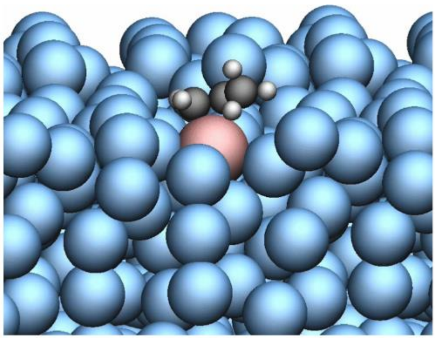


Fig. 1: Snapshot from a molecular dynamics calculation showing a single transition metal atom bound to a propane molecule at the surface of a liquid gallium slab.

[1] Taccardi, N., et al., Nature Chemistry, 2017. 9: p. 862-867.

[2] Grabau, M., et al., Chemistry-a European Journal, 2017. 23: p. 17701-17706.

[3] Raman, N., et al., ACS Catalysis, 2019. 9: p. 9499

[4] Wittkämper, et al. J. Chem. Phys., 2020.153: 104702 1-13.

[5] Grabau, M., et al., Surface Science, 2016. 651: p. 16-21.

Cataluminescence in Er-substituted perovskite oxides

Andreas Borgschulte,[1,2] Olga Sambalova,[1,2] Andrea Sterzi,[1] Jana Niggli[3], Bastian Welte[3], and André Heel[3]

[1]*Laboratory for Advanced Analytical Technologies, Empa - Swiss Federal Laboratories for Material Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

[2]*Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057, Zürich, Switzerland*

[3]*Institute of Environmental and Process Engineering (UMTEC), OST – Eastern Switzerland University of Applied Sciences, Oberseestrasse 10 CH-8640 Rapperswil, Switzerland*

Thermophotovoltaic devices are promising for various energy conversion applications. However, currently, the conversion efficiency is very low due to the low efficiency of chemical energy to light limited by the process of heat from the chemical reaction released as black body radiation [1]. From a fundamental point of view, the direct conversion of chemical energy into light without the detour is possible in principle. For the first time, we demonstrate this so called cataluminescence [2] from methanol combustion over Er-substituted $SrTiO_3$ with high efficiency. The catalytically active quaternary perovskites $Er_xSr_{1-x}Ti_{0.95}Cu_{0.05}O_{3-d}$ are non-conducting in oxidized state, but exsolute metallic Cu particles onto the surface upon reduction at high temperatures [3]. Thus, we are able to manipulate the metallic state and investigate its influence on the catalytic as well as luminescent properties. Coincidentally, the fuel to air ratio ('lambda ratio') around the stoichiometry point corresponds to the tipping point between reducing and oxidizing conditions altering the surface properties as evidenced by operando optical spectroscopy and post mortem X-ray diffraction and X-ray photoemission. Cataluminescence takes place under oxidizing conditions (lean fuel to air mixture) on the Er-perovskite with a strong selective IR- emission, while under reducing conditions Cu-nanoparticles develop, which emit black body radiation.

[1] T.J. Coutts, A review of progress in thermophotovoltaic generation of electricity, Renew. Sustain. Energy Rev. 3 (1999) 77–184.

[2] M. Aras, V., M. Breysse, B. Claudel, L. Faure, M. Guenin, Chemiluminescence during Catalysis - Part 2, J. Chem. Soc., Faraday Trans. 1 (1977) 1039–1047

[3] Ohhun Kwon, Sangwook Joo, Sihyuk Choi, Sivaprakash Sengodan, and Guntae Kim, Review on exsolution and its driving forces in perovskites, J. Phys. Energy 2 032001 (2020).

Influence of exsolved nanoparticle size on the catalytic activity during methane dry reforming

Schrenk Florian[1], Lorenz Lindenthal[1], Hedda Drexler[1], Raffael Rameshan[1], Christoph Rameshan[1]

[1] Institute of Materials Chemistry, Technische Universität Wien, Austria

Perovskite oxide type catalysts have shown great potential regarding CO_2 utilization in reactions such as MDR (**M**ethane **D**ry **R**eforming)[1]. One of the reasons for that is exsolution, a process in which sinter- and coke-resistant nanoparticles are formed on the surface of the catalyst[2]. A deep understanding of the exsolution process is a fundamental building block for an intelligent design of perovskite catalysts. In this study we examined the exsolution behavior of different perovskite oxide type catalysts with the general formula $Nd_{0.6}Ca_{0.4}Fe_{1-x}B'_xO_3$ with the two dopants Ni (x = 0.03, 0.05) and Co (x = 0.03 and 0.10) as well as an undoped version (x = 0.00). Therefore, the catalysts were analyzed with *in-situ* NAP-XPS (**N**ear **A**mbient **P**ressure **X**-ray **P**hotoelectron **S**pectroscopy), *in-situ* XRD (**X**-**R**ay **D**iffraction) and SEM (**S**econdary **E**lectron **M**icroscopy) to assess the formation of nanoparticles during MDR as well as during a reductive pretreatment. Additionally, the influence of the formed nanoparticles was investigated with catalytic tests in a fixed bed reactor. The experiments showed that all catalysts were capable of exsolving the dopant while maintaining their perovskite structure. However, the exsolved nanoparticles differed in size, distribution, and amount and therefore, influence on MDR performance. Despite forming nanoparticles during the reaction, most catalyst did not improve their catalytic activity during the reaction. The bigger nanoparticles formed during the reductive pretreatment however, always increased the catalytic activity, leading to the conclusion that the exsolved particles need a minimum size to catalyze the reaction and to enhance the activity.

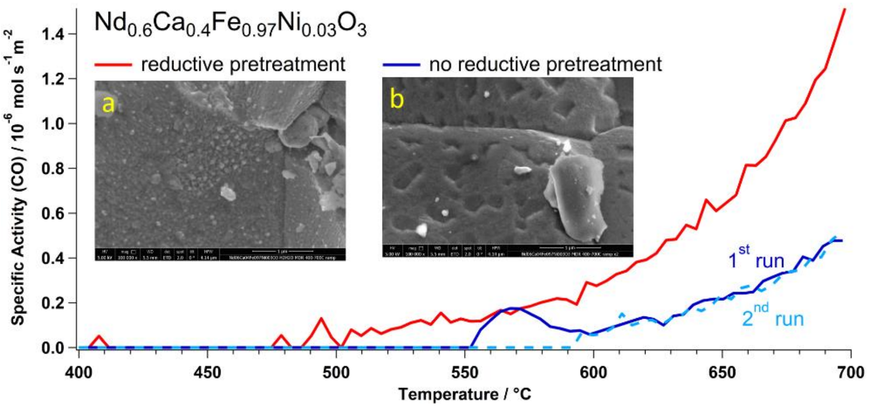


Figure 1: Comparison of the catalytic activity for the 3 % Ni-doped catalyst. The pre-reduced sample (red) shows higher activity and bigger nanoparticles (a), than the sample which was not reduced before the reaction (blue/b).

References:

1. Barbero, J.; Pena, M. A.; Campos-Martin, J. M.; Fierro, J. L. G.; Arias, P. L., *Catalysis Letters* **2003,** *87* (3-4), 211-218.
2. Neagu, D.; Oh, T. S.; Miller, D. N.; Menard, H.; Bukhari, S. M.; Gamble, S. R.; Gorte, R. J.; Vohs, J. M.; Irvine, J. T. S., *Nature Communications* **2015,** *6*.

Corresponding author: Florian Schrenk (florian.schrenk@tuwien.ac.at)
This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement n° 755744 / ERC - Starting Grant TUCAS)

Chemical reactions, corrosion, electrochemistry and biological materials – routine operando studies with Near Ambient Pressure XPS

Paul Dietrich [1], Gilbère Mannie [1], and Andreas Thissen [1]

[1] *SPECS Surface Nano Analysis GmbH, Voltastraße 5, 13355 Berlin, Germany*

Over the last decades XPS under Near Ambient Pressure (NAP) conditions has demonstrated its promising potential in a wide variety of applications. Starting from operando studies of surface reactions in catalysis, the applications soon have been enhanced towards studies of processes at liquid surfaces, mainly using freezing/melting cycles, liquid jets or liquid films on rotation disks or wheels. Since more than 15 years, the need for basic studies of the fundamental chemistry at solid-liquid interfaces has attracted growing interest. Dip-and-pull experiments at synchrotrons finally also demonstrated, that in-situ and operando XPS in electrochemical experiments can be realized, mainly using synchrotron beams, significantly contributing to the basic understanding of modern energy converting or storing devices, like batteries, fuel cells, etc.

The development of pure laboratory NAP-XPS systems with optimized sample environments, like special sample holders, Peltier coolers and operando liquid cells combined with full automation and process control provides possibilities for the preparation and analysis of a multitude of liquid samples or solid-liquid interfaces on a reliable daily base.

During the presentation several physical chemistry topics will be highlighted to illustrate the impact to NAP-XPS: gas interaction monitoring with metal-organic frameworks (MOFs), interface interaction between organic solvents with semiconductors, operando corrosion studies and operando electrochemistry in a classic three-electrode set-up. In all of these examples NAP-XPS will prove to be the ideal technique to investigate physical and chemical changes in the materials studied.

So far little attention has been paid to the potential of XPS as a method applied to biological materials. Until now, bacteria characterised with conventional XPS requires tedious sample preparation usually involving freeze drying, a treatment that may degrade biological sample constituents. By studying biological samples in their native wet states, new insight about composition, absorption and transport of drugs through cell membranes and extracellular polymeric substance (EPS) layers can be obtained. Both artificial model-films of exopolysaccharides and biofilms of Escherichia Coli have been characterised at pressures ranging from ultra-high vacuum to 15 mbar. By applying antimicrobials to model biofilms, some of which are known to be resistant towards the antimicrobial in question, the distribution of antimicrobials in biofilms has been studied.

Finally an outlook is given on the future perspective of applications and scientific contributions of routine operando XPS.

Hydrogen pressure composition isotherms of TiH_x by electron spectroscopy

Emanuel Billeter,[1,2] Andreas Borgschulte [1,2]

[1] *Laboratory for Advanced Analytical Technologies, Empa - Swiss Federal Laboratories for Material Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

[2] *Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057, Zürich, Switzerland*

The interaction of hydrogen with solids is of fundamental interest regarding a future renewable energy scenario, where hydrogen is one of key building blocks. Hydrogen affects the physical properties of metals at concentrations from the ppm range to high stoichiometries, where metal hydrides are formed. TiH_2 is predicted to be superconductive at high pressures [1], Ti catalyzes the hydrogen ab- and desorption of alanates and related compounds for hydrogen storage [2] and Ti-H is model system for hydrogen embrittlement [3]. The measurement of pressure composition isotherms at relevant temperatures is inhibited by ever-present surface contaminations due to the reactive nature of titanium. Traditional surface science methods, delivering electronic structure information, can overcome this problem but they are incompatible with the hydrogen pressure required for hydride formation. We solve this problem by disconnecting the chemical potential from pressure using a membrane approach [4]. We demonstrate the reversible hydrogenation of titanium as followed by REELS (Reflected Electron Energy Loss Spectroscopy), AES (Auger Electron Spectroscopy) and XPS (X-ray Photoelectron Spectroscopy) up to 1 bar hydrogen pressure. This enables the construction of pressure-composition isotherms from spectroscopic data and the calculation of standard thermodynamic variables.

[1] D. V. Semenok et al., *Curr. Opin. Solid. St. M.*, **24** (2020), 100808

[2] B. Bogdanovic and M. Schwickardi, *J. Alloy. Compd.*, **253-254** (1997), 1-9

[3] D. S. Shih et al., *Acta Metall.*, **36** (1988), 111-124

[4] R. Delmelle et al., *Rev. Sci. Instr.*, **86** (2015), 053104

5.2 Session II — Wednesday, October 6th

10:55 – 11:10	**Maximilian Weiss** Online Laser Ablation of solids in Liquids (LASIL) as a versatile tool for quantitative thin film analysis
11:10 – 11:25	**Johannes Pedarnig** Detection of Zn in aqueous solution by LIBS using liquid-solid matrix transfer and internal reference element
11:25 – 11:40	**Hartmut Leipner** Signal modification in glow discharge optical emission spectroscopy with a pulsed radio-frequency powered source
11:40 – 11:50	**Company presentation 2**
11:50 – 12:00	**Company presentation 3**
12:00 – 12:10	**Company presentation 4**

Online Laser Ablation of solids in Liquids (LASIL) as a versatile tool for quantitative thin film analysis

Maximilian Weiss[1], Christoph Riedl[2], Helmut Riedl[3], Johannes Frank[4], Paul Heinz Mayrhofer[3], Jürgen Fleig[2] and Andreas Limbeck[1]

[1] *TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-I²AC, 1060 Vienna, Austria*
[2] *TU Wien, Institute for Chemical Technologies and Analytics, Getreidemarkt 9/164-EC, 1060 Vienna, Austria*
[3] *TU Wien Institute of Materials Science and Technology, Getreidemarkt 9, 1060 Wien, Austria*
[4] *TU Wien, Joint Workshop Technical Chemistry, Getreidemarkt 9, 1060 Wien, Austria*

The recently introduced online Laser Ablation of solids in Liquids (online-LASIL) technique [1] allows to combine the advantages of direct solid sampling with those of liquid measurements. In LASIL the sample is ablated by a laser beam in a flow of a liquid medium, the ablated material is carried by the fluid into the sample inlet of an ICP-MS or ICP-OES. As liquid standards can be injected into the carrier solution, it is possible to assess the composition of the sample without the need of matrix matched standards. A further advantage is that the depth resolution accessible with LASIL is better than with conventional nanosecond laser ablation. This benefit is demonstrated by analysis of two different samples from the field of material science.

The first is the quantification of the surface platinum concentration on a mixed ionic electronic conductor (MIEC). These materials serve as cathode materials for solid oxide fuel cells (SOFC). Recently it was shown [2] that the deposition of platinum nanoparticles on the surface can increase the electrochemical performance of lanthanum strontium iron oxide (LSF). As these samples not only have platinum on their surface but contain also a current collector made of platinum beneath the MIEC, an analytical method with a sufficient depth resolution is required to separate these two layers of platinum. It is shown that online-LASIL is capable of performing this task and provides the required information about the deposited amount of platinum. Moreover, imaging experiments were performed to monitor the homogeneity of the platinum decoration.

As second example serve boride based hard materials, which were used as protective coatings to enhance the erosion resistance of cutting and machining tools. [3] As the properties of the applied coating changes substantially with composition, reliable analysis of the materials stoichiometry is necessary to ensure the aspired protective effect. Here the flexibility of online-LASIL allows to determine the exact composition of several material systems without the need for matrix matched standards.

1. M. Bonta, J. Frank, S. Taibl, J. Fleig and A. Limbeck, *Anal Chim Acta*, 2018, **1000**, 93-99.
2. C. Riedl, A. Schmid, A. Nenning, H. Summerer, S. Smetaczek, S. Schwarz, J. Bernardi, A. Optiz, A. Limbeck and J. Fleig, *Journal of The Electrochemical Society*, 2020, **167**.
3. C. Fuger, B. Schwartz, T. Wojcik, V. Moraes, M. Weiss, A. Limbeck, C. A. Macauley, O. Hunold, P. Polcik, D. Primetzhofer, P. Felfer, P. H. Mayrhofer and H. Riedl, *Journal of Alloys and Compounds*, 2020, DOI: 10.1016/j.jallcom.2020.158121.

Detection of Zn in aqueous solution by LIBS using liquid-solid matrix transfer and internal reference element

Johannes D. Pedarnig[1], Peter Gschwandtner[1], Florian Rudinger[1], Stefan Trautner[1], Georg Hölzl[2],
Christoph Ramsauer[2], Thomas Röder[2]

[1] *Institute of Applied Physics, Johannes Kepler University, A-4040 Linz, Austria*

[2] *Lenzing AG, A-4860 Lenzing, Austria*

The subject of this work is the detection of Zn in aqueous solutions using laser induced breakdown spectroscopy (LIBS) with a focus on possible industrial applications. State of the art measurement methods for Zn quantification in solutions use time extensive chemical processes which do not allow real time measurements in a production process. LIBS measurements are fast, however, measurements directly in the liquid produced poor results regarding sensitivity and repeatability. In order to bypass these problems, a liquid-solid matrix transfer is applied. Commercially available filtration paper is soaked in the sample liquid, then dried, and finally measured using LIBS (560 measurements at different positions per paper sample). The intensities of Zn lines at the different positions are strongly varying (Fig. 1). However, the spatially averaged Zn intensity is very reproducible from sample to sample. This method quickly produced encouraging results, including suitable calibration curves ($R^2 \geq 0.99$) to determine the Zinc concentration in unknown liquids. To further improve the accuracy of the Zn calibration the sample solutions are spiked with a reference solute containing Mg. We measure the spiked solutions by single-pulse and double-pulse LIBS and analyze the intensities of various Zn, Mg and C lines. Our results indicate that the limit of detection (LOD) for Zn is reduced when using Mg as internal reference element.

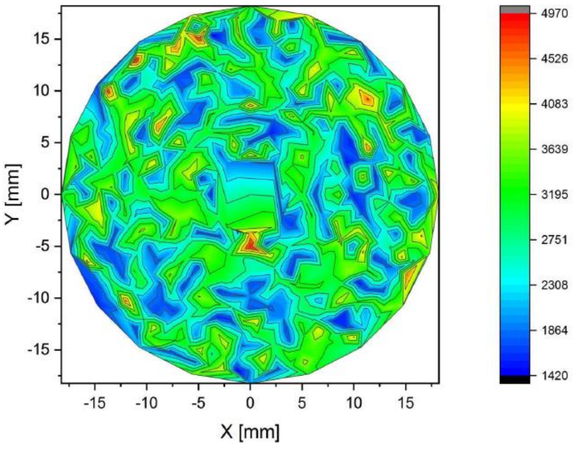


Fig. 1: Spatial distribution of Zn on filtration paper measured by LIBS (Zn I, 334.5 nm).

Acknowledgements: Financial support by the Austrian Research Promotion Agency FFG is gratefully acknowledged (K-project PSSP 871974).

Signal modification in glow discharge optical emission spectroscopy with a pulsed radio-frequency powered source

Frank Heyroth[1], Jean Jamil[1], Hartmut S. Leipner[1]

[1] *Interdisziplinäres Zentrum für Materialwissenschaften,*
Martin-Luther-Universität Halle–Wittenberg, D-06099 Halle

Using pulsed glow discharge for surface analysis of solid materials is a relatively new technique compared to studies involving continuously powered glow discharges. The advantage of this method is on the one hand the lower heating of the sample and on the other hand for detectors with a slow readout time – like a CCD – the increased depth resolution. Studying the effects of the pulse width on the signal in glow discharge optical emission spectroscopy, an additional intensity gain in the CCD signal has been found. The experiments have been done using a GDA 750 HR device manufactured by Spectruma Analytik GmbH. It is equipped with a CCD detector for the optical signal and a pulsed radio frequency powered source with variable pulse frequency and duty cycle.

As an example, the experimental results for a brass sample analyzed using different pulsing frequencies are presented and discussed. One example is given in figure 1. The deviation of the intensity as a function from the duty cycle from a linear behavior increases with increasing pulse frequency. However, the measured crater depth has a linear relationship to the duty cycle, independent of the pulse frequency. So for the same amount of material sputtered from the sample, a higher signal can be generated for higher pulse rates.

The cause of this effect is the afterglow of the plasma [1]. Combining the results from different duty cycles and frequencies measurements, the amount and time constant of this afterglow can be determined. In addition, for daily work, this result indicates that a change in pulse rate or duty cycle requires a recalibration.

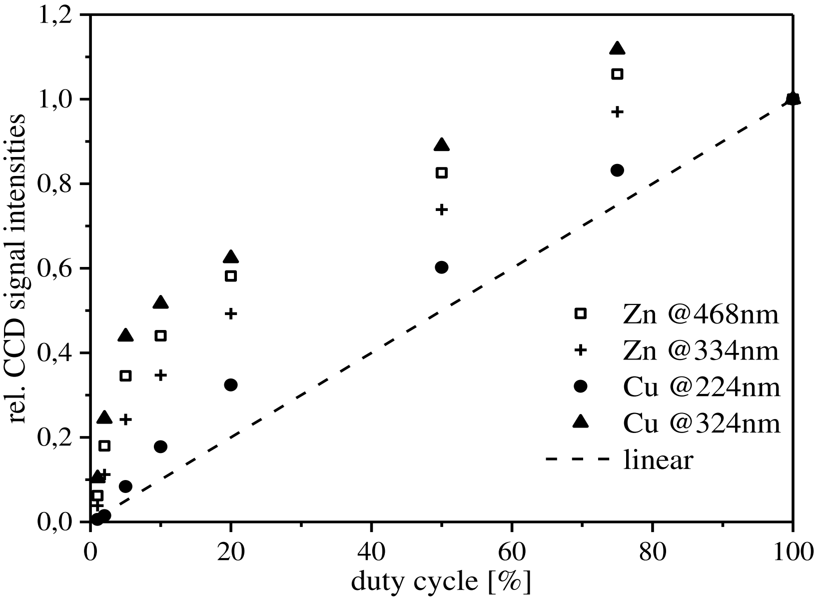


Fig. 1: Plot of the relative CCD signal intensities vs. duty cycle for copper and zinc spectral lines using a rf source at a pulse frequency of 2223 Hz with 800 V operating voltage und 3 hPa argon gas pressure. The intensities are normalized to the unpulsed ones.

[1] A. Bogaerts, J. Anal. At. Spectrom., 502, 22 (2007).

5.3 Session III — Wednesday, October 6th

Focus session “Advances in electron microscopy”

13:00 – 13:30	**Eva Olsson (invited)** High resolution correlation between atomic structure and properties using advanced transmission electron microscopy
13:30 – 13:45	**Manuel Ederer** Imaging the spatial distribution of π* states in graphene
13:45 – 14:00	**Christian Schwalb** In-situ Correlative Analysis of Electrical and Magentic properties of 3D Nanostructures by combination of AFM,SEM and FIB
14:00 – 14:15	**Markus Gruschwitz** Imaging Charge Densities at Interfaces with TEM
14:15 – 14:25	**Company presentation 5**
14:25 – 14:35	**Company presentation 6**

Imaging the spatial distribution of π^* states in graphene

M. Ederer[1,*], M. Bugnet[2,3,4], V. Lazarov[5], Q. M. Ramasse[2,3], D. M. Kepaptsoglou[2,5], and S. Löffler[1]

[1] TU Wien (Vienna, Austria), [2] SciTech Daresbury Campus (Daresbury, United Kingdom),
[3] University of Leeds (Leeds, United Kingdom), [4] Université de Lyon (Lyon, France),
[5] University of York (York, United Kingdom), [*]manuel.ederer@tuwien.ac.at

Electronic states are the basis for the description of nearly all macroscopic material properties. Despite this, directly mapping electronic orbitals in bulk specimens in real space remains a challenge. Only recently has orbital mapping been proven possible using electron microscopy together with electron-energy loss spectroscopy (EELS) [1]. This is achieved by recording electrons having lost a certain energy corresponding to the transition to a specific unoccupied final electronic state in the sample, thus allowing these states to be mapped in real space.

In this work, we focus on the spatial distributions of π^* states in layers of quasi free-standing 'epitaxial' graphene grown on 6H-SiC. We accompany the EELS measurements with state of the art simulations [2], applying a multislice electron probe propagation algorithm coupled with inelastic scattering probabilities based on DFT calculations [3].

In order to be able to differentiate between the π^*- and σ^*-orbitals the optical axis is chosen along the crystallographic [210] axis, parallel to the carbon atomic planes. Both the π^* and σ^* maps display higher intensity at the atomic column positions, which can partly be attributed to electron channeling effects. While the σ^* orbitals are mostly confined to the carbon planes, the π^* orbitals extend noticeably farther in between the planes. This behavior is even more pronounced for the π^*/σ^* ratio maps when compared to the HAADF map. The π^*/σ^* maxima correspond perfectly to minima in the HAADF signal, demonstrating the different real space distributions of the two states. The inelastic scattering calculations allow us to predict the effect of the specimen thickness on the orbital maps by repeating the simulations for various thicknesses.

The excellent agreement between the simulations and the experiments shows the potential of orbital mapping and opens up the way for broad applicability on interfaces and crystal defects in the future.

[1] Löffler et al., Ultramicroscopy, 26, 177 (2017)

[2] Löffler et al., Ultramicroscopy, 39, 131 (2013)

[3] Blaha et al., The Journal of Chemical Physics, 074101, 152 (2020)

[4] The authors gratefully acknowledge funding from the Austrian Science Fund (FWF) under grant nr. I4309-N36. Experiments were performed at the SuperSTEM Laboratory (UK) with support from the Engineering and Physical Science Research Council (EPSRC).

In-situ Correlative Analysis of Electrical and Magnetic properties of 3D Nanostructures by combination of AFM, SEM and FIB

C.H. Schwalb[1], J. Hütner[1,2], R. Winkler[3], P. Frank[2], M. Wolff[1,2], and H. Plank[3]

[1] *Quantum Design Microscopy GmbH, Darmstadt, Germany*
[2] *GETec Microscopy GmbH, Vienna, Austria*
[3] *Institute for Electron Microscopy and Nanoanalysis, Graz Univ. Technology, Graz, Austria*

Combining different analytical methods into one instrument is of great importance for the simultaneous acquisition of complementary information. In this work, we present the in-situ combination of scanning electron and ion microscopy (SEM/FIB) and atomic force microscopy (AFM).

We will present a variety of case studies to highlight the advantages of interactive correlative in-situ analysis for different materials. We show results for *in-situ* electrical characterization of 2D materials (Figure 1) as well electrostatic force microscopy (EFM) of piezoceramic films. In addition, we will present first results for the in-situ characterization of magnetic nanostructures by combination of SEM and magnetic force microscopy (MFM). SEM enables to identify grain boundaries in, e.g., duplex steel samples, where the magnetic properties at the grain boundaries can be directly analyzed via MFM to characterize the magnetic properties with nanometer resolution (see Figure 2).

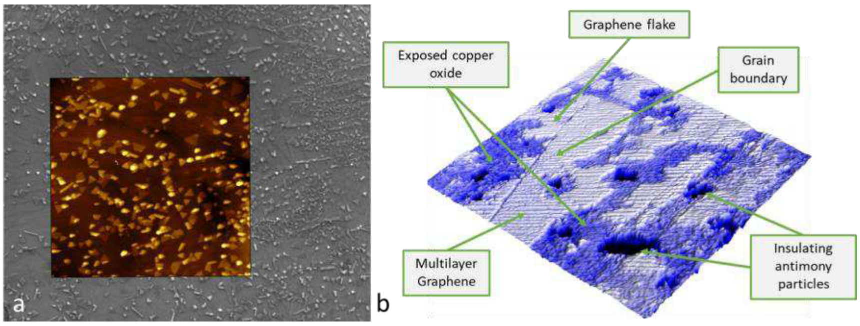


Figure 1: Conductive AFM measurements done using AFSEM® nano a) Correlative SEM and AFM image of on Cu/Graphene/Antimony sample. b) 3D topography overlaid with conductivity signal showing distinct regions. (Light regions correspond to high current and dark regions correspond to low current)

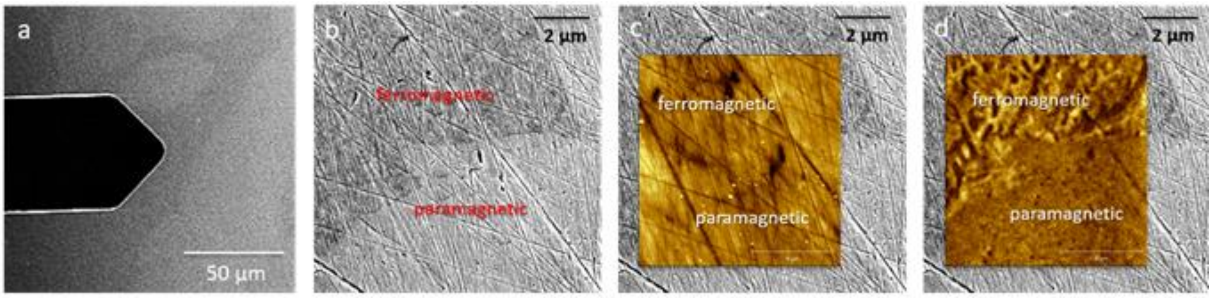


Figure 2: Correlative AFM & SEM measurements of duplex steel sample provided. (a) SEM guidance allows the positioning of the cantilever on the region of interest. (b) SEM image with increased contrast shows ferromagnetic and paramagnetic phases. (c) Topography and (d) MFM signal.

[1] D. Yablon *et al.*, Microscopy and Analysis **31(2)** 14-18 (2017)
[2] J. Kreith *et al.*, Rev. Sci. Instr. **88** 053704 (2017)
[3] S.H. Andany *et al.*, Beilstein J. Nanotechnol. **11**, 1272-1279 (2020)

Imaging Charge Densities at Interfaces with TEM

Markus Gruschwitz[1], Steffen Schulze[1], Herbert Schletter[1], Christoph Tegenkamp[1]

[1] *Analytik an Festkörperoberflächen, TU Chemnitz, Reichenhainer Str. 70, 09126 Chemnitz*

As early as 40 years ago the use of a four-quadrant detector geometry in the scanning electron microscope was proposed to get differential phase contrast (DPC) [1]. This contrast mechanism heavily depends on the local electrical (or magnetic) fields in the sample, which induce a deflection of the transmitted electron. By utilizing segmented detectors, the shift of the center of mass of the CBED pattern can be detected. Recent developments in conjunction with aberration corrected scanning transmission electron microscopes (STEM) demonstrated the ability to achieve atomically resolved DPC images [2]. The evaluation of such images allows an estimation of local charge densities.

The technique is applied to epitaxial monolayer graphene on 6H-SiC(0001) (Fig. 1a). The exceptional transport properties of this well-defined 2D system are limited by substrate-based charge transfer [3]. Thus, imaging the local charge density is of great interest (Fig. 1c). In the buffer layer and graphene layer, defined spots of positive charges (carbon atomic cores) are surrounded by a delocalized loud of π-electrons. By using the pristine substrate SiC to calibrate the charge densities, we approach the system quantitatively and discuss deviations due to screening effects and influences of the protective capping layer.

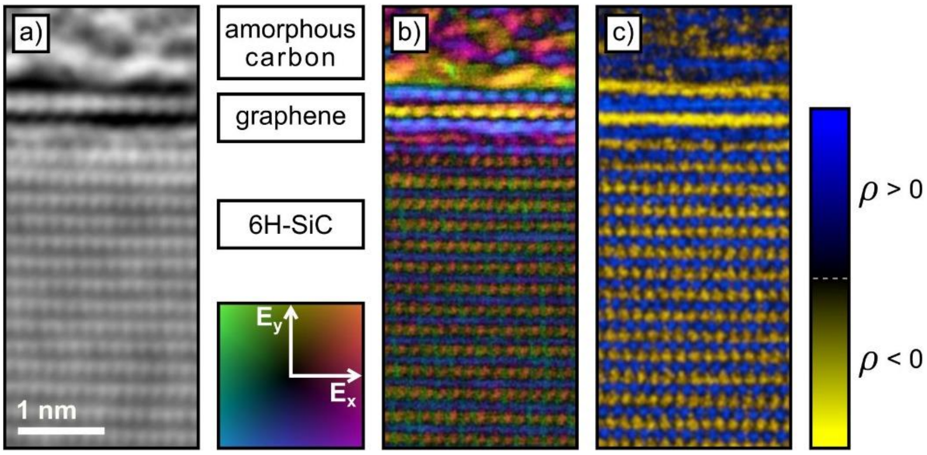


Fig. 1: (a) Integrated DPC-image. (b) Colour-coded visualisation of the vector. The wide range of 2D colour distribution necessary for this image makes a direct interpretation difficult. (c) Charge density derived from the DPC data. With only two colour gradients, the image yields an intuitive visualization of the charge density. [3]

[1] H. Rose, Ultramicroscopy, 251, Volume 2 (1976)
[2] N. Shibata, S. Findlay, Y. Kohno, H. Sawada, Y. Kondo, Y. Ikuhara, Nature Phys., 611, Volume 8 (2012)
[3] J. Ristein, S. Mammadov, T. Seyller, Phys. Rev. Lett., 246104, Volume 108 (2012)
[4] S. Schulze, M. Gruschwitz, H. Schletter, I. Alexandrou, M. Hietschold, C.Tegenkamp, Imaging & Microscopy, 34, 3/2020 (2020)

5.4 Session IV — Wednesday, October 6th

Focus session “Advances in electron microscopy”

15:05 – 15:35	**Ute Kaiser (invited)** Properties of low-dimensional materials by low-voltage TEM
15:35 – 15:50	**Gary Säckl** Quantification of the carbon content of single grains in martensite-ferrite dual phase steel by UHV-EDXS
15:50 – 16:05	**André Reck** Insights and challenges of transmission Kikuchi diffraction (TKD) analysis for ferroelectric HfO2 ultra-thin films for semiconductor applications
16:05 – 16:20	**Alexey Minenkov** Unraveling the phase formation and stability of the Ge-Sn nanosystem via in situ TEM
16:20 – 16:35	**Heiko Groiss** Strain and phase analysis of magnetic nanocrystals in GaδFeN/AlxGa1-xN heterostructures investigated by precession electron diffraction
16:35 – 17:05	**Andreas Undisz (invited)** New insights into early oxidation stages of metallic materials by transmission electron microscopy

Properties of low-dimensional materials by low-voltage TEM

Ute A. Kaiser

Central Facility Electron Microscopy. Materials Science Electron Microscopy, Ulm University, Albert-Einstein Allee 11, 89081 Ulm, Germany, ute.kaiser@uni-ulm.de

Two-dimensional materials exhibit properties, which can differ strongly from those of the bulk counterparts. They offer unique opportunities for new and miniaturized electronic and optical devices [1], which properties may even alter with changes of single atom's positions at surfaces and interfaces. In situ electron microscopy nowadays can provide experimental data on the level of the single atom, as it has seen extremely rapid developments in recent years owing to ground-breaking advances in electron optics, electron detectors, sample preparation and manipulation, and highly versatile *in situ* setups can simultaneously while imaging also functionalizing the material under study. Here we present recent results using our unique chromatic and spherical aberration-corrected *SALVE* instrument both in imaging and spectroscopy modes [2].

We first discuss the formation of defects in two-dimensional inorganic and organic crystals. For transition metal di-chalcogenides (TMDs) we present results at electron energies below the knock-on threshold in the range between 20-80kV and understand the role of electronic excitations. We show that the formation of vacancies is possible at electron voltages nearly half of the knock-on threshold and quantify the damage. We demonstrate that indeed there is an additional channel for defect production with a threshold energy well below the knock-on value [3,4]. Further, we analyse in-situ structural and chemical modifications of different freestanding transition metal phosphorus tri-chalcogenides (TMPTs). We predict the displacement thresholds, electronic properties, and the displacement cross-section of single vacancy S and P in all materials by ab-initio calculations and using these results, the observed structural changes are understood. Moreover, our results provide insight into layer-number-dependent changes in the electronic properties as result of lowering the dimensionality and thus it is a new tool to exactly determine the numbers of layers. As the TMPTs are often very oxygen-sensitive, they were prepared with the help of our newly-developed polymer-assisted sample preparation method [5]. We also present studies on the structure of two-dimensional polymer crystals and characterize on the molecular level the defect structure [6]. Furthermore, we present in-situ studies of a miniaturized electrochemical cell, where reversibly single-crystalline bilayer graphene is lithiated and delithiated in controlled manner using an electrochemical gate confined to a device protrusion [7]. On the more fundamental base we show that differentiating between the bond nature between two metal atoms is now possible [8].

[1] A. Hashemi et al. (2017). J. Phys. Chem. C 121, 27207
[2] M. Linck, et al. 117 (2016) 076101.
[3] S. Kretschmer, et al. submitted
[4] T. Lehnert et al. ACS Appl. Nano Mater. 2 (2019) 3262-3270
[5] J. Köster et al. (2021). Nanotechnology 32, 075704
[6] H.Qi et al. (2020), Science Advances 6, eabb5976
[7] M. Kühne et al. (2018), Nature 564, 234, [8] K. Cao, (2020), Science Advances 6, eaay5849

Quantification of the carbon content of single grains in martensite-ferrite dual phase steel by UHV-EDXS

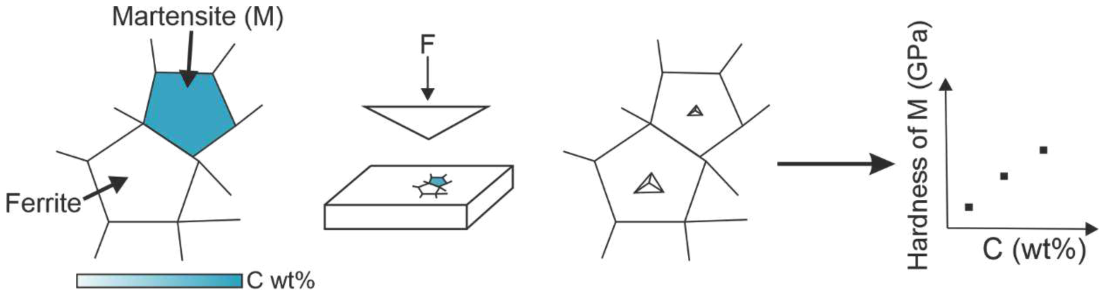
Gary Säckl[1,2], Martin Arndt[5], Jiri Duchoslav[2,3], Heiko Groiss[4], Katharina Steineder[5], Gernot Wallner[1,6], David Stifter[2]

[1] *Christian Doppler Laboratory for Superimposed Mechanical-Environmental Ageing of Polymeric Hybrid Laminates (CDL-AgePol), Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria*
[2] *Center of Surface and Nanoanalytics (ZONA), Johannes Kepler Universität Linz, Altenberger Straße 69, 4040 Linz, Austria*
[3] *Centre for Electrochemistry and Surface Technology GmbH (CEST), Stahlstraße 2-4, 4020 Linz, Austria*
[4] *Christian Doppler Laboratory for Nanoscale Phase Transformations, Center of Surface and Nanoanalytics (ZONA), Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria*
[5] *voestalpine Stahl GmbH, voestalpine-Straße 3, 4031 Linz, Austria*
[6] *Institute of Polymeric Materials and Testing (IPMT), Johannes Kepler Universität Linz, Altenberger Straße 69, 4040 Linz, Austria*

Ferrite and martensite in dual phase steel differ in hardness, local dislocation density and in the carbon content. A conventional method for the distinction of the two phases is electron back scatter diffraction (EBSD). Even though martensite and ferrite show a similar crystal structure, the quality of electron back scatter pattern differs for the phases. Hence, we estimated the martensite volume fraction, which determines the hardness of the grains, with the help of EBSD.

The carbon content of the steel grains were obtained by measurements with a scanning Auger electron microscope. While Auger electron spectroscopy did not lead to satisfactory results, chemical mappings of carbon obtained by novel ultra high vacuum energy dispersive X-ray spectroscopy (UHV-EDXS) showed a clear correlation to the distribution of ferrite and martensite. The ultra high vacuum of the scanning Auger microscope in combination with a customized windowless EDXS detector resulted in a minimization of hydrocarbon contamination and maximization of the sensitivity for the detection of light elements. These conditions resulted in a measurement which even enabled us to quantify the carbon content of individual grains. Furthermore, nano-hardness tests were performed on the exact same grains which were evaluated with UHV-EDXS and EBSD for samples with varying martensite volume fraction. An increase of hardness of the ferrite grains and decrease of hardness of martensite grains with increasing martensite fraction could be observed. We were able to confirm that the decrease of the hardness of the martensite grains is associated with the carbon content of the grains.

Graphical abstract:



Insights and challenges of transmission Kikuchi diffraction (TKD) analysis for ferroelectric HfO$_2$ ultra-thin films for semiconductor applications

André Reck[1*], Maximilian Lederer[1], Kati Biedermann[1]

[1] Fraunhofer Institute for Photonic Microsystems (IPMS) – Center Nanoelectronic Technologies;
An der Bartlake 5, 01109 Dresden, Germany

**andre.reck@ipms.fraunhofer.de*

In most recent years transmission Kikuchi diffraction (TKD) became a valuable tool for the analysis of ultra-thin films like ferroelectric HfO$_2$, which is of special interest in the application of e.g. non-volatile memories or pyroelectric sensors [1]. Particularly the detailed microstructural insights possible due to local crystallographic phase and orientation mapping and grain analysis enables the assessment of annealing regimes or local stresses and textures. Furthermore, phase fraction and distribution of the metastable orthorhombic phase (Pca2$_1$) can be determined, which contributes to the overall evaluation of the ferroelectric properties of HfO$_2$ [2]. With utilization of an optimized flat detector head geometry TKD analysis targets a stronger signal yield, higher resolution as well as less pattern distortion due to a central pattern center. Investigations of nanostructured materials with grain sizes down to 5-10 nm and scaled thin films for semiconductor applications < 10 nm are possible. On the contrary, sample preparation with focused ion beam (FIB) or dimpling becomes more difficult, complex and sensitive to parameters like ion implantation, contamination or sample thickness. The present work shows and summarizes the recent results obtained on HfO$_2$ ultra-thin films for dimpled samples as well as samples prepared by FIB. Both approaches demonstrate successful TKD analysis and reveal distinct influences of higher annealing temperatures, strong out-of-plane textures and high orthorhombic phase fractions, which in turn results in excellent ferroelectric behavior of HfO$_2$.

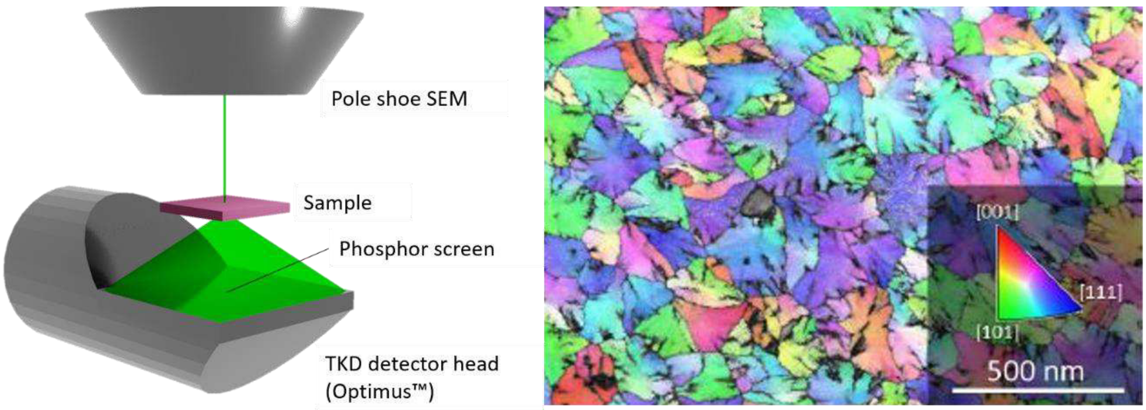


Fig. 1: Visualization of the TKD analysis with inverse pole figure map (IPF) of a sample with ferroelectric HfO2 ultra-thin film annealed at 650°C

[1] T. Mikolajick, U. Schroeder, S. Slesazeck, and T. Mikolajick, IEEE Trans. Electron Devices 67, 1–10 (2020).
[2] M. Lederer, A. Reck, K. Mertens, R. Olivo, P. Bagul, A. Kia, B. Volkmann, T. Kämpfe, K. Seidel and L.M. Eng, Appl. Phys. Lett. 118, 012901 (2021).

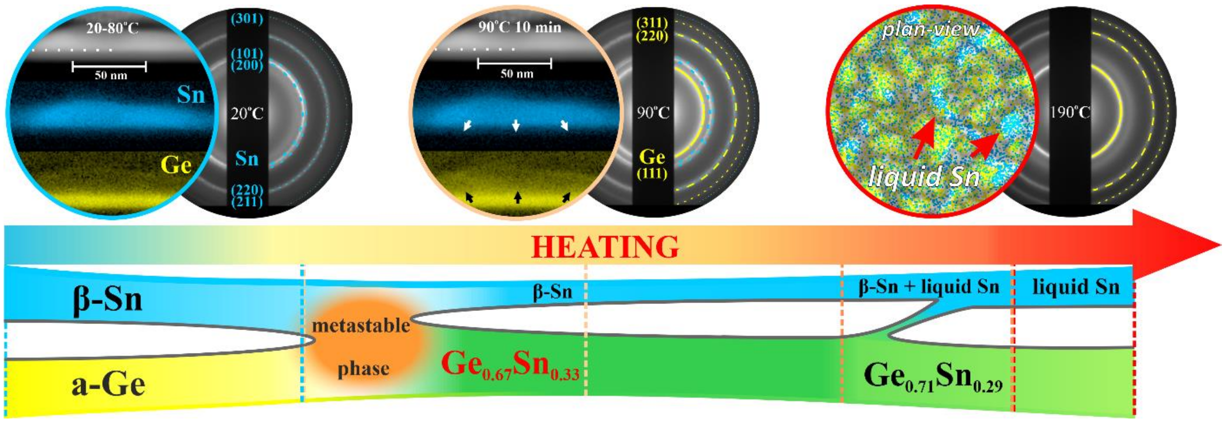
Unraveling the phase formation and stability of the Ge-Sn nanosystem via *in situ* TEM

Alexey Minenkov*, Heiko Groiss

Christian Doppler Laboratory for Nanoscale Phase Transformations, Center of Surface and Nanoanalytics, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria

*oleksii.minienkov@jku.at

The fundamental scientific interest and applicational prospects of Ge-Sn nanoscale alloys stem from the fact their bandgap can be engineered all the way from a semiconductor to a semimetal [1]. A recent demonstration of optical gain in this system with Sn concentration of 10 at.% [2] confirmed the superior properties, but also outlined the challenges. Because of the extremely limited equilibrium solid-state solubility of Sn in Ge and the low Sn melting point, heat-treatment leads to efficient phase separation and decomposition processes [1,3]. Our knowledge of these peculiarities is still scarce. In this regard, *in situ* TEM could provide dynamic observation of the material evolution in response to external stimuli such as temperature. We have utilized 25 nm thick binary Sn-Ge layered thin films formed via PVD as a suitable model object for studying phase evolution at the nanoscale. Experiments were conducted in Jeol JEM-2200FS TEM equipped with in-column Ω-filter and fitted with the MEMS-based Wildfire heating holder from DENSsolutions. Our approach allows the continuous direct observation of interfacial interactions, including a Ge-Sn solid solution formation with Sn concentration up to 33 at.% by metal-induced crystallization and melting-crystallization phase transitions during controlled heating-cooling cycles. Morphological and structural changes were rigorously traced and filmed. Combining complementary *in situ* microscopic techniques (HRTEM, HAADF STEM, SAED, EDXS), plain-view and cross-sectional specimens we have unraveled the crucial role of metastable and stable Sn-rich liquid phases in the alloy thermal stability and also proposed the general phase evolution diagram [3]. The suggested stages of observed complex interphase interactions would be presented and discussed in detail.



[1] Jessica Doherty et al., Chem. Mater. 4383–4408, 32, 11 (2020).

[2] S. Wirths et al., Nat. Photonics, 88–92, 9, 2, (2015).

[3] Alexey Minenkov, Heiko Groiss, Journal of Alloys and Compounds, 157763, 859, 2021.

Strain and phase analysis of magnetic nanocrystals in GaδFeN/$Al_xGa_{1-x}N$ heterostructures investigated by precession electron diffraction

H. Groiss[1], T. Truglas[1, 2], V. Bauernfeind[1], A. Navarro-Quezada[3], A. Bonanni[3]

[1] *Christian Doppler Laboratory for Nanoscale Phase Transformations, Center for Surface and Nanoanalytics, Johannes Kepler University Linz, Altenberger Str. 69, 4040 Linz, Austria*

[2] Tietz Video and Image Processing Systems GmbH, Eremitenweg 1, 82131 Gauting, Germany

[3] *Institute of Semiconductor and Solid-State Physics, Johannes Kepler University Linz, Altenberger Str. 69, 4040 Linz, Austria*

Precession electron diffraction (PED) is a robust transmission electron microscopy method generating pseudo-kinematic, straightforward interpretable diffraction results, which can be used for phase and orientation maps, as well for detailed lattice and strain analysis. Here, a relevant spintronic system, namely phase-separated GaδFeN containing ordered arrays of embedded Fe_yN nanocrystals (NCs)[1], is investigated. The samples are grown by metalorganic vapor phase epitaxy on *c*-sapphire substrates and consist of $Al_xGa_{1-x}N$ buffers with $0 < x < 0.41$ Al, on which the GaδFeN layers are deposited and host two different ferromagnetic phases, ε-Fe_3N and γ-Fe_4N. Using a TVIPS-manufactured universal scan generator, nanobeam PED patterns are recorded on a fast 4k×4k CMOS camera while scanning the beam over the NCs area. The PED maps are analyzed by extracting the positions of diffraction discs automatically through image processing, and subsequently discriminating between the reflexes originating from the GaN matrix and those from the Fe_yN nanocrystals. The direct recording and evaluation allows phase identification and the detection of the highly localized, in-plane strain fields originating from the embedded NCs. Overview maps are presented in Fig. 1. The crystallographic orientation and the distribution of the two phases in the GaN matrix point to the formation of hexagonal ε-Fe_3N NCs elongated along the growth direction as origin of the magnetic anisotropy observed by magnetometry. These findings highlight the power of analytic PED methods for investigating phase-separated magnetic systems.

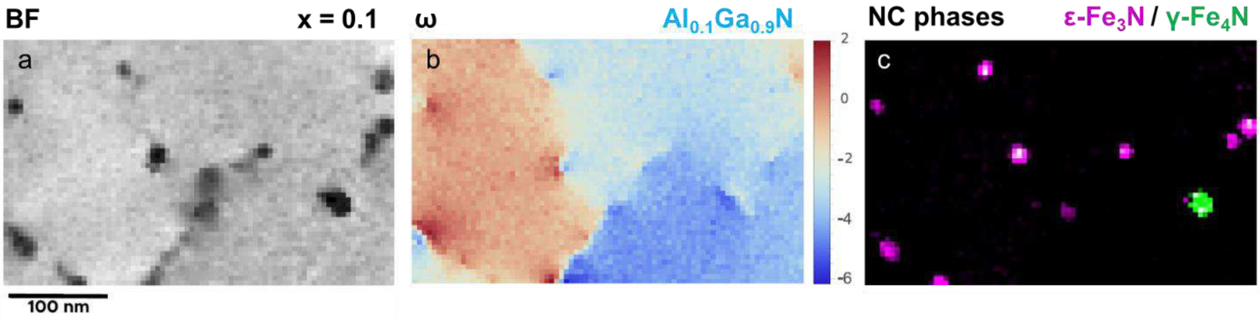


Figure 1: (a) Bright field image of a $x = 0.1$ sample calculated from the PED direct beam. (b) Map of the rotational strain component highlighting different crystal domains slightly misoriented and separated by dislocations. (c) Identified Fe_yN phases at the dislocation positions.

[1] A. Navarro-Quezada, T. Truglas, V. Bauernfeind, W. Ginzinger, M. Matzer, A. Ney, H. Groiss, and A. Bonanni, Materials 13, 3294 (2020).

New insights into early oxidation stages of metallic materials by transmission electron microscopy

Andreas Undisz

Technische Universität Chemnitz, Institut für Werkstoffwissenschaft und
Werkstofftechnik (IWW), Erfenschlager Straße 73, 09125 Chemnitz

The property profile of metallic materials is determined not only by the bulk but also by its surface. This is of particular importance when considering metallic materials in corrosive environments or under thermal stress. A widely researched and routinely applied alloy in such context is austenitic stainless steel 316L. Apparently, the oxide on 316L formed during short oxidation time is complex regarding the distribution of elements and formed oxide phases. Double, dual and triple layers, enriched by chromium or iron were reported to form under similar conditions, either in corundum-type or spinel-type structure. In this presentation, austenitic stainless steel is chosen as an example for demonstrating the benefits of state-of-the-art transmission electron microscopy for giving new insights into early oxidation stages of metallic materials.

A first challenge is the preparation of electron transparent samples while preserving the usually only a few nanometers thin oxide [1]. In case of 316L, the thickness of the oxide was measured to ~15 nm after annealing for 1h at 400°C. Although this corresponds to only a few dozen times the usual lattice parameters, the application of STEM-EDX was able to clearly detect concentration differences of chromium and iron in the thin oxide in the form of layers parallel to the material surface [2, 3]. The concentration difference of chromium and iron in the layers may be as high as ~30 at.%. Whereas a two-layered oxide formed during annealing at 400°C, a three-layered oxide was observed after annealing at 800°C.

Remarkably, the inhomogeneous distribution of chromium and iron was observed to have formed within single oxide grains. In contrast to various results in the literature on basis of grazing-incidence X-ray diffraction, the oxide grains were identified as corundum-type structure, using nanobeam electron diffraction in the TEM. HR-TEM at the transition of the layers inside the oxide grains did not show crystal defects. The local interplanar spacing was evaluated and found to correlate with the local concentration of chromium and iron, exhibiting larger values for higher iron concentrations and vice versa. Implications of these new observations regarding the property profile of 316L will be discussed.

[1] K.E. Freiberg, R. Hanke, M. Rettenmayr, A. Undisz, Practical Metallography 53, 193-205 (2016).

[2] R. Wonneberger, M. Seyring, K. Freiberg, A. Carlsson, J. Rensberg, B. Abendroth, H. Stöcker, M. Rettenmayr, A. Undisz, Corrosion Science 149, 178-184 (2019).

[3] R. Wonneberger, S. Lippmann, B. Abendroth, A. Carlsson,M. Seyring, M. Rettenmayr, A. Undisz, Corrosion Science 175, 108884 (2020).

5.5 Poster session I — Wednesday, October 6th

P I.01	**Rudolf Holze** Performance of graphene oxide nanoflakes synthesized by facile two-step synthesis in a supercapacitor electrode
P I.02	**Rudolf Holze** Morphological and Elemental Analysis of Green Synthesized Pt-Pd Nanoparticles
P I.03	**Chitran Ghosal** STM Characterization of Bismuth deposited on Epitaxial Graphene
P I.04	**Conny Becht** Spatial and Temperature variation of the Huang-Rhys factor in InGaN quantum wells
P I.05	**Agnieszka Anna Wiciak** Characterization of Ge needle-like nanostructures grown by Reactive Ion Etching towards nanotechnology applications
P I.06	**Maximilian Weiss** LIBS analysis of Fluorine in solid samples via measurement of molecular emission bands
P I.07	**Dina Friebel** Characterization of soil quality parameters and element contents in soils as a contribution to precision farming
P I.08	**Annika Morgentern** Solvent based deposition and growth mode of nanosized amino acid functionalized bismuth oxido clusters on gold surface
P I.09	**Ronald Hesse** Improved Estimation of the Spectrometer-Transmission Function with UNIFIT 2022
P I.10	**Ronald Hesse** UNIFIT 2018 - the Improved Spectrum Processing, Analysis and Presentation Software for XPS, AES, XAS and RAMAN Spectroscopy
P I.11	**Bowen Zhang** Correlative electron microscopy and probe microscopy study of two-dimensional crystalline polymers for organic electronics
P I.12	**Johan Persson** In situ TEM applications of sample drive lasers and fast-switching deflectors
P I.13	**Franziska Schölzel** Polymer-Assisted Sublimation Growth of Graphene on 4H-SiC(000-1)
P I.14	**Peter Richter** Polymer-Assisted Sublimation Growth of Graphene on 4° off-axis 4H-SiC(0001)
P I.15	**Adrian Schütze** Growth and characterization of WS2 on epitaxial graphene on SiC(0001)

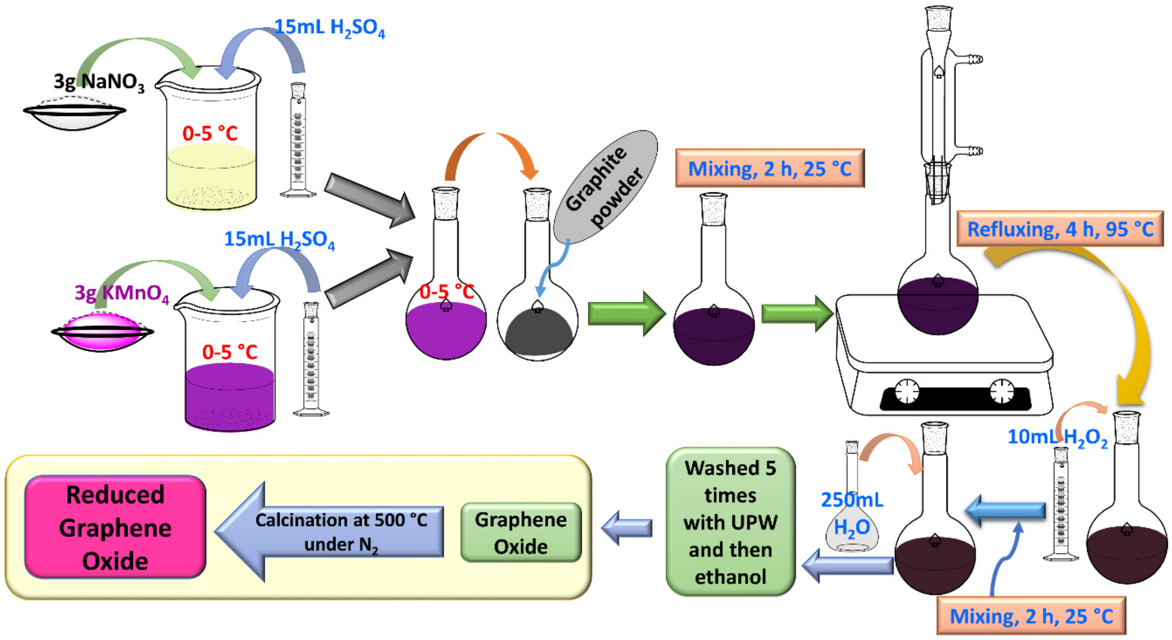
P I.16	**Korbinian Heimler** Application of well-defined multilayer inhouse standards as model systems for the performance-related verification of a 3D-µXRF spectrometer
P I.17	**Kevin Kraft** Influence of laser wavelength and pulse duration on depth resolved stoichiometric analysis of Li/Mn ratio in LiMn2O4 thin films using Laser Ablation
P I.18	**Ashley Maloney** In situ, high spatial resolution chemical mapping of freshly exposed FIB faces using AES
P I.19	**Mamiyev Zamin** Enhancing long-range order in 1D atomic gold chains by selective doping
P I.20	**Muhammad Awais Aslam** Universal approach towards bottom-up fabrication of 2D material nanoribbon based field-effect devices
P I.21	**Lorenz Lindenthal** Controlling Size and Nature of Nanoparticles Exsolved from Perovskite Oxides
P I.22	**Anika Rogoll** Distribution of trace elements in plants – quantification strategies for 2D-µXRF and Laser ablation ICP-MS measurements
P I.23	**Nikolaos Giannakaris** Chemical imaging and analysis by Femtosecond LIBS with micrometer spatial resolution
P I.24	**Philip Schädlich** Graphene on Copper Foil: Stacking Relations and Substrate Interaction

Performance of graphene oxide nanoflakes synthesized by facile two-step synthesis in a supercapacitor electrode

Md. Ikram Ul Hoque[1,2,3] and Rudolf Holze[4,5,6]

[1]Discipline of Chemistry, The University of Newcastle, University Drive, Callaghan, NSW 2308, Australia
[2]Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane, QLD 4072, Australia
[3]Department of Chemistry, Dhaka University of Engineering & Technology, Gazipur, Gazipur-1700, Bangladesh
[4]Saint Petersburg State University, Institute of Chemistry, St. Petersburg, 199034, Russia
[5]State Key Laboratory of Materials-oriented Chemical Engineering, School of Energy Science and Engineering, Nanjing Tech University, Nanjing, 211816, Jiangsu Province, China
[6]Chemnitz University of Technology, Institut für Chemie, AG Elektrochemie, D-09107 Chemnitz, Germany

Reduced graphene oxide rGO showing superior performance in a supercapacitor electrode has been synthesized by a facile two-step process based on a modified Hummers' process. In the first step oxidation of graphite yielded graphene oxide (GO); in the second step in a carbonization process reduction of the graphene oxide proceeded to rGO nanoflakes of ≈ 500 nm size and ≈ 5 nm thickness.



Scheme: The two step synthesis of rGO. The white background refers to the first step involving oxidation of graphite whereas the yellow background refers to the second step with the carbonization process.

The specific capacitances of the rGO were found to be 1248.46, 897.38, 783.34, 735.54, 691.30, 523.40, 430.75, 345.39 and 243.32 F/g at scan rates 1, 2, 5, 10, 20, 50, 100, 200 and 500 mV/s, respectively. The cyclic performance tests show that rGO was stable after completion of the initial 20 cycles.

Morphological and Elemental Analysis of Green Synthesized Pt-Pd Nanoparticles

Fredrick Mwazighe[1] and Rudolf Holze[2,3,4]

[1]University of Nairobi, College of Biological and Physical Sciences, School of Physical Sciences, Department of Chemistry, P.O. Box 30197, 00100, Nairobi, Kenya
[2]Saint Petersburg State University, Institute of Chemistry, St. Petersburg, 199034, Russia
[3]State Key Laboratory of Materials-oriented Chemical Engineering, School of Energy Science and Engineering, Nanjing Tech University, Nanjing, 211816, Jiangsu Province, China
[4]Chemnitz University of Technology, Institut für Chemie, AG Elektrochemie, D-09107 Chemnitz, Germany

For electrochemical detection of pyrene, a polycyclic aromatic hydrocarbon suggested by environmental authorities for monitoring, a glassy carbon electrode was modified with Pt-Pd nanoparticles (NPs) and multi-walled carbon nanotubes (MWCNTs) The Pt-Pd NPs were synthesized using metal salt precursors and an aqueous extract of *E. grandis* leaves. This offered an alternative synthesis route that eliminates use of conventional hazardous reductive chemicals. The size of the NPs was optimized by varying the proportions of the Pt and Pd ions in the precursor solutions. Square wave voltammetry and cyclic voltammetry were used in the electrochemical analysis of pyrene. The electrode modification resulted in an increase of the peak current for pyrene oxidation by up to 200 %. Pt-Pd NPs from a green process could be used together with MWCNTs to modify an electrode for relatively sensitive electrochemical detection of pyrene. An increase in the separation between the oxidation peaks of pyrene and anthracene at the modified electrode provides a slight improvement in selectivity. The size of Pt-Pd NPs was optimized by varying the ratio of Pt to Pd ions in the precursor. The NPs were synthesized using an aqueous extract from *E. grandis* as the reducing and capping agent. TEM and SEM analysis of the NPs revealed that the size of the NPs varied with the ratio of Pt to Pd ions in the precursors. The precursors with a high amount of Pd ions resulted in relatively smaller particles. The precursor with 1:3 ratio of Pt to Pd ions formed the smallest particles with a size of about 10 nm. This can be explained using Lamer's nucleation theory of particle growth or Ostwald ripening. Pd ions reduced easily to Pd^0 which formed centers of particle growth onto which the Pt^0 from Pt ions that reduced later, migrated to grow the particles. A high concentration of Pt ions in the precursor solution resulted in more Pt^0 migrating to grow the particles resulting in larger particles. XPS analysis of the particles proved that Pd formed the core of the particles because it could hardly be quantified in the larger particles.

STM Characterization of Bismuth deposited on Epitaxial Graphene

C Ghosal, C Tegenkamp[1]

[1] *Institut für Physik, Technische Universität Chemnitz*

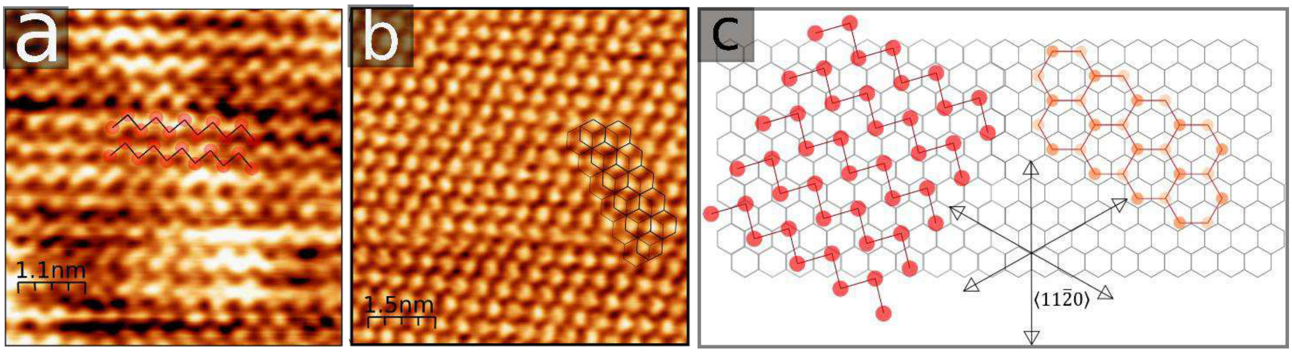


Fig1: (a) atomic resolution of Bi(110) islaqnd on epitaxial graphene (10mV,1.5nA), (b) atomic resolution of Bi(111) structure on epitaxial graphene (100mV, 1.0nA), (c) models describing the epitaxial geometry between the Bi(110) and Bi(111) phases w.r.t the graphene substrate

The semimetal Bi still attracts a lot of interest because of its unique electronic properties such as a low carrier concentrations and large carrier motilities. The mesoscopic Fermi wavelength gives rise to pronounced quantum confinement effects, e.g the semimetal to semiconductor transition. The surface states on Bi(111) reveal strong spin polarization and ultrathin Bi films are topologically non-trivial. Therefore, proximity coupling of Bi nanostructures to graphene may be used to tune the transport properties of the 2D relativistic electron gas.

In this work we studied the growth of the Bi on epitaxial graphene on SiC (0001) by means of LEED and STM under UHV conditions, which are strongly triggered by quantum size effects. While for low coverages, Bi (110) are formed with anisotropic growth along the $< 11\bar{2}0 >$ direction on the surface of epitaxial graphene, Bi (111) structures were found to grow in the high coverage regime on the surface of the Bi (110) structures. This allotropic transition starts to compete for dominance after around 9 monolayers (~3 nm) and significantly larger than the transition reported on Si (111) [1]. Moreover, experimental evidence supporting the "black phosphorous" like allotrope was also found during the scanning procedure, where-in a preference for an even number of layers of Bi(110) was found growing on some preferred basal structures. Subsequent annealing of the substrate showed a complete transition of the Bi (110) structures to the Bi (111) structures with edges with zigzag termination directed along the three-fold symmetric $< 11\bar{2}0 >$ directions of epitaxial graphene/SiC.. The delicate interplay between vertical and lateral confinement effects and strain against the background of allotropic transition and topology is further corroborated by spatially resolved STS measurements.

[1] T. Nagao, et al. Phys. Rev. Lett, 93, 105501 (2004).

Spatial and Temperature variation of the Huang-Rhys factor in InGaN quantum wells

C. Becht[1], M. Baggash[1], U.T. Schwarz[1,*], M. Binder[2], R. Zeisel[2], J. Off[2], M. Tauer[2], A. G. Iglesias[2], H. Wang[2], M. Straßburg[2]

[1]*Institute of Physics, Chemnitz University of Technology, 09126, Chemnitz, Germany*
[2]*OSRAM Opto Semiconductors GmbH, Leibnizstr. 4, 93053 Regensburg, Germany*
*email: ulrich.schwarz@physik.tu-chemnitz.de

Photoluminescence (PL) in InGaN quantum wells (QW) show a pronounced spatial variation of intensity, wavelength shift, and linewidth. Several origins like dislocations, point defects, QW thickness, strain variation and Indium content fluctuations are leading to observable changes in PL spectra. Experimental methods for spatially resolved characterization of carrier recombination and transport are micro-photoluminescence (µPL) [1,2,3,4], micro-electroluminescence [5], cathodo-luminescence [6,7], and scanning near-field microscopy [8].

With µPL, we observe a variation of the Huang-Rhys factor between 0.1 to 0.3. Similar values for the Huang-Rhys factor have been observed in previous researches [1,2]. The Huang-Rhys factor is a measure for the coupling strength of the electronic interband transition to the longitudinal optical phonon due to the Fröhlich interaction [4]. The factor changes with the spatial electron-hole separation. The observed variation shows a strong correlation with the µPL intensity variation. One factor influencing the Huang-Rhys factor is the localization of excitons, with stronger localization leading to an increase in the Huang-Rhys factor. The observed correlation in our experiment would then lead to the conclusion that localization is stronger in the darker areas of the QW.

To investigate this further, we made µPL scans of the same area at different temperatures between $T = 10$ K and $T = 150$ K, i.e. in the typical temperature range of the S-shape of the photoluminescence wavelength. We observe an S-shape behavior for the Huang-Rhys factor in the bright area of the sample. There, the Huang-Rhys factor rises from $S= 0.1$ to above $S= 0.2$ in the temperature range from $T= 10$ K to $T= 80$ K, and then falls again to $S= 0.1$ at $T= 150$ K. In contrast to this, the Huang-Rhys factor is nearly constant at $S= 0.2$ up to $T= 120$ K in the dark area, and rolls off to $S= 0.13$ at $T= 150$ K.

In summary, our experiment shows that the spatially resolved measurement of the Huang-Rhys factor, indicating electron-phonon coupling, might help understanding recombination processes and localization of electron-hole pairs in InGaN QWs.

References

[1] P.P. Paskov, P.O. Holtz, B. Monemar, S. Kamiyama, M. Iwaya, H. Amano, and I. Akasaki, Phys. Stat. Sol. **234**, 755 (2002).

[2] S.M. Olaizola, W.H. Fan, D.J. Mowbray, M.S. Skolnick, P.J. Parbrook, A.M. Fox, Superlattices and Microstructures **41**, 419 (2007).

[3] J. Danhof, U.T. Schwarz, A. Kaneta, Y. Kawakami, Phys. Rev. B **84**, 035324 (2011).

[4] X.B. Zhang, T. Taliercio, S. Kolliakos and P. Lefebvre, J. Phys.: Condens. Matter **13**, 7053 (2001).

[5] S. Cao, X.-M. Wu, J.-L. Liu, F.-Y. Jiang, Chin. Phys. Lett. **36**, 028501 (2019).

[6] Y. Estrin, D.H. Rich, S. Keller, and S.P. DenBaars, J. Phys.: Condens. Matter **27,** 265802 (2015).

[7] G. Schmidt, M. Müller, P. Veit, F. Bertram, J. Christen, M. Glauser, J.-F. Carlin, G. Cosendey, R. Buttée, N. Grandjean, Appl. Phys. Lett. **105**, 032101 (2014).

[8] A. Hangleiter, F. Hitzel, C. Netzel, D. Fuhrmann, U. Rossow, G. Ade, and P. Hinze, Phys. Rev. Lett. **95**, 127402 (2005).

Characterization of Ge needle-like nanostructures grown by Reactive Ion Etching towards nanotechnology applications

A. A. Wiciak[1], W. M. Klesse[1], B. Kuck[1], W. Koczorowski[2], D. Spirito[1]

[1] IHP–Leibniz-Institut für innovative Mikroelektronik, Im Technologiepark 25, 15236 Frankfurt (Oder) (Germany)
[2] Faculty of Materials Engineering and Technical Physics, Poznan University of Technology, Piotrowo 3, 60-965 Poznań (Poland)

In microelectronics manufacturing *Reactive Ion Etching* (RIE) is a widespread method for the fabrication micro and nanostructures. This etching process is based on two surfaces phenomena; (1) high energy ion sputtering and (2) chemical reactions of dissociated etchant gas species. Importantly, for each targeted application dedicated processes must be developed to achieve high-level process control in terms of anisotropy, selectivity against the etch mask, and etch rates), requiring a detailed understanding of the complex processes which take place at the substrate surface. For example, dense needle-like surface structures ("grass") are known to occur as a result of not controlled RIE processes of silicon (Si) and germanium (Ge) (see figure 1). In fact such "grass" formations observed in Si have found application in optoelectronics, due to their high optical absorption from UV to IR [1]. However the Ge case, despite its similar chemical structure to Si, has been less investigated.

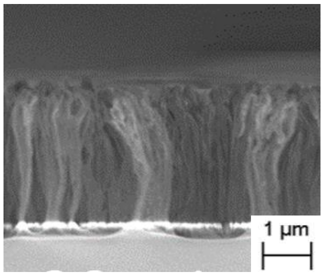


Figure 1 SEM image of fully formed Ge grass after RIE processing

Here, we present our recent experimental studies towards unraveling the underlying physical-chemical mechanisms leading to these grass-like structures in Ge. The three complementary techniques X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and scanning electron microscopy (SEM) provide new insights on the formation and morphological properties of "grass"-like nanostructures, fabricated via RIE in fluorine based plasmas on thin Ge films grown epitaxially on Si substrates. In line with literature [2-3] we verify that the "grass" formation is the result of µm-sized clusters (micro-masks) which, under certain RIE conditions, form on the surface, impeding locally the etching of the substrate Using XPS we identify the chemical nature of these clusters as oxides or carbides, indicating that they are formed as by-products of the reaction between etchant gas species, the Ge surface and possible residues from the reactor walls [3]. Furthermore, using AFM and SEM, we detail the various stages of the formation of the "grass" as a function of different etch parameters as well as determine its morphology. We show that the shape of the grass is independent of the chemistry of the micromask, but can be controlled in density and size by adjusting the etching power and time. In particular, increasing time and power results in higher density of smaller structures.

[1] Chih-Hung Hsu, et al., Materials Science in Semiconductor Processing, 2-17, 35 (2014)
[2]T.P. Chow, et al., Soc. 134, 1281 (1987)
[3] G.S. Oerlein, et al., Surface Interf. Anal. 8, 243 (1986)

LIBS analysis of Fluorine in solid samples via measurement of molecular emission bands

Maximilian Weiss[1], Zuzana Gajarska[1], Hans Lohninger[1], Georg Ramer[2], Bernhard Lendl[2] and Andreas Limbeck[1]

[1] *TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-I²AC, 1060 Vienna, Austria*

[2] *TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-UPA, 1060 Vienna, Austria*

In recent years, fluorine analysis has become increasingly important due to its applications in high performance polymers, membranes, surfactants and pharmaceuticals, as well as due to the potential environmental harm of its compounds. Despite its importance, its accessibility by analytical techniques remained limited. One of the techniques showing a potential for the fluorine detection is LIBS (laser induced breakdown spectroscopy), however, the high excitation energy of this element limits the sensitivity of the analysis and its possible applications. Nevertheless, this limitation can be circumvented by a well-established method of detecting the molecular emission of the element of interest instead of detecting the atomic line itself. In LIBS, such molecules are formed by recombination of atoms upon the plasma cooling. For analytical purposes, either an element naturally occurring in the sample or an element intentionally added to the sample can be used as a partner for the molecular formation. In the literature, several approaches of the latter are reported, including spiking of a powdered sample with an additive [1] or introduction of a nebulized liquid standard on the sample surface during the LIBS analysis[2].

As these approaches allow only for the bulk analysis of the sample, we would like to present a novel method for the introduction of the element acting as a molecule building partner for the fluorine detection, opening up the possibility of its imaging. The proposed methodology is based on sputter coating, allowing to apply homogenous films with a thickness in the nano- to micrometer range on the solid surface. Our work includes the investigation of several candidate elements as well as the optimization of the film thickness and LIBS measurement parameters.

Finally, we demonstrate the applicability of the developed procedure for actual research tasks, in particular the quantitative measurement of fluorine in polymer samples, and the mapping of the fluorine distribution in polymers.

1. L. Nagli, M. Gaft and Y. Raichlin, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2020, **166**.
2. C. Alvarez-Llamas, J. Pisonero and N. Bordel, *Journal of Analytical Atomic Spectrometry*, 2017, **32**, 162-166.

Characterization of soil quality parameters and element contents in soils as a contribution to precision farming

Dina Friebel[1], Saskia Stopp[1], Miriam Kreher[1], Thomas Vogt[1], Carla Vogt[1]
[1] TU Bergakademie Freiberg, Institute of Analytical Chemistry, Leipziger Str. 29, 09599 Freiberg

Soils can be seen as the most important sink of CO_2 in the atmosphere and are of existential importance as a substrate for plant growth.[1,2] The targeted use of fertilizers can increase the growth of plants. In order to achieve a balanced supply of nutrients, needs-based fertilization with mineral and organic fertilizers is necessary. Online characterization of the most important soil parameters is required in order to avoid negative consequences from overfertilization. The analysis of nutrients such as nitrogen, potassium, calcium, magnesium, phosphorus and sulfur as well as the analysis of organic carbon (humus), inorganic carbon (carbonate) and water content are necessary to be able to examine the quality of soil.[2,3,4]

A fast and direct method for the analysis of solids is required for the direct characterization of the element contents.[5] As a robust surface-sensitive solid sample method, the Laser-induced breakdown spectroscopy (LIBS) is found to be qualified. The influences of various parameters, such as grain size, water content or the use of an inert gas, on the analytical figures of merit were analyzed. A suitable strategy for evaluating the data using various normalizations also needed to be optimized for each element.

Infrared spectroscopy (IR), especially the attenuated total reflection technique (ATR), can be used to analyze the water and carbonate contents. These parameters can be determined by quantitative evaluation of the spectra. In addition, clayey and sandy soils may be differentiated using the corresponding absorption bands, which makes it possible to adapt the calibration of the water content to the respective soil type. It was observed that the quantification of the carbonate content is in turn dependent on the water content.

The superordinate aim is to combine LIBS and IR spectroscopy in an appropriate way and to attach them to farming vehicles for online characterization of the soil parameters so the analyzation process can be accomplished directly in the field. The experimental data were validated by established methods such as combustion analysis, XRF and standard methods for determining the water content. Furthermore, ETV-ICP-OES was used as a direct solid sampling technique for the multi-element analysis of solid samples.

References:

[1] M. W. I. Schmidt, M. S. Torn, S. Abiven, T. Dittmar, G. Guggenberger, I. A. Janssens, M. Kleber, I. Kögel-Knabner, J. Lehmann, D. A. C. Manning et al., Nature, 49, 478 (2011).

[2] H.-P. Blume, G. W. Brümmer, R. Horn, E. Kandeler, I. Kögel-Knabner, K. Strahr, B.-M. Wilke, Lehrbuch der Bodenkunde, Spektrum Akademischer Verlag, Heidelberg (2010)

[3] M. Bertau, A. Müller, P. Fröhlich, M. Katzberg, Industrielle anorganische Chemie, Wiley-VCH Verlag, Weinheim (2013).

[4] A. Finck, Pflanzenernährung und Düngung in Stichworten, Gebrüder Borntraeger Verlagsbuchhandlung (2007).

[5] F. J. Pierce, P. Nowak in Advances in Agronomy (Ed.: D. L. Sparks), Academic Press, 1, 67 (1999).

Solvent based deposition and growth mode of nanosized amino acid functionalized bismuth oxido clusters on gold surface

A. Morgenstern[1], R. Thomas[2], M. A. Hoffmann[3], O. Selyshchev[1], I. Milekhin[1], M. Rahaman[1], A. Sharma[1,] S. Gemming[1,4], D.R.T. Zahn[1,4], M. Mehring[2,4] and G. Salvan[1,4]

[1] *Institute of Physics, Chemnitz University of Technology, 09126 Chemnitz, Germany*
[2]*Institute of Chemistry, Chemnitz University of Technology, 09126 Chemnitz, Germany*
[3]*Center for Microtechnologies, Chemnitz University of Technology, 09126 Chemnitz*
[4]*Center for Materials, Architecture, and Integration of Nanomembranes (MAIN),*
Chemnitz University of Technology, 09126 Chemnitz, Germany

It is well known that bismuth shows an extremely structurally rich cluster chemistry.[1] For example, starting from bismuth nitrate the hydrolysis under various conditions leads to different condensation products composed of bismuth oxido clusters of varying composition, historically called bismuth subnitrates. Due to relatively low toxicity and interesting properties, bismuth oxido clusters and, in general, bismuth-based nanomaterials are suitable for applications in electronic devices, catalysis or medicine.[2] The understanding of film formation is the fundamental importance for further developments in these fields. Our interest in bismuth oxido clusters significantly increased after selective ligand exchange for clusters such as $[Bi_{38}O_{45}(NO_3)_{24}]$ was successful. This opens a promising direction in the research of atomically precise metal oxido nanoclusters since changes in the cluster periphery can lead to significant changes in the reactivity, electronic properties and solubility. So far, there is only one study focusing on the deposition of a bismuth oxido cluster, $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]$ on a metal surface from its solution.[3] The growth of organically modified nanoclusters on surface is significantly affected by a number of parameters such as type of solvent, temperature, concentration, environment, substrate topography etc. Among these, the solvent is the most critical parameter because solubility, dispersity and evaporation rate are governed by solvent choice. Here we study the influence of various solvents on the deposition of $[Bi_{38}O_{45}(Boc\text{-}Phe)_{24}(DMSO)_y]$ from the liquid phase on to a metal surface and the film growth mechanism. A set of organic solvents with different polarity, viscosity, and evaporation temperature were used for depositing thin films of amino acid functionalized bismuth oxido nanoclusters on Au-coated silicon substrates using three solution based methods, *i.e.* spin, drop and dip coating. The samples were characterised using X-Ray diffraction (XRD), infrared (FTIR), Raman and X-ray photoelectron (XPS) spectroscopies to probe the eventual structural and chemical changes in the nanoclusters and their crystalline packing induced by the solvent based deposition. The growth mode of nanocluster films on the Au surface was monitored and analysed using optical and atomic force microscopy (AFM) techniques.

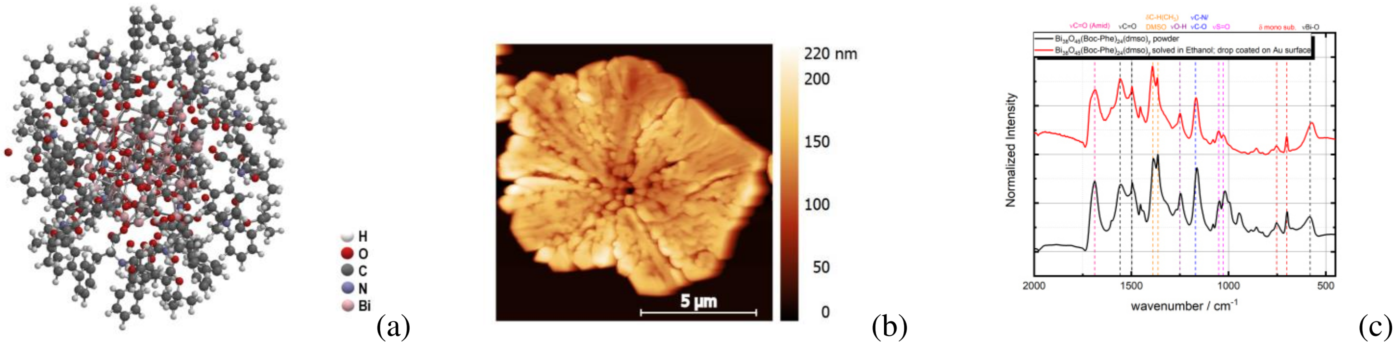


Fig. 1 (a) Chemical structure of $[Bi_{38}O_{45}(Boc\text{-}Phe)_{24}(DMSO)_y]$ (simulation), (b) AFM images of $[Bi_{38}O_{45}(Boc\text{-}Phe)_{24}(DMSO)_y]$ (solved in Ethanol) agglomeration after dip coating (c) FTIR spectroscopy of $[Bi_{38}O_{45}(Boc\text{-}Phe)_{24}(DMSO)_y]$ powder compared with dip coated film.

1 S. Dehnen*, Ed. Springer International Publishing*, 2017, **46**, 201-268

2 M. Mehring, *Coordination Chemistry Reviews*, 2007, **251**, 974-100

3 M. Hofmann, *Chemistry Open*, 2020, **9**, 277-284

Improved Estimation of the Spectrometer-Transmission Function with UNIFIT 2022

. Hesse*[1], J. Radnik[2], R. Denecke[1]

[1] *Universität Leipzig, Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie,*
Linnéstr. 2, 04103 Leipzig, Germany
[2] *Bundesanstalt für Materialforschung und -prüfung (BAM), Fachbereich 6.1 „Oberflächenanalytik und Grenzflächenchemie", Unter den Eichen 44-46, 12203 Berlin, Germany*

Quantitative analysis of the elemental and chemical composition in the analysis area is one of the main aims of x-ray photoelectron spectroscopy (XPS). Mainly, three approaches are common to achieve reliable quantitative results: the use of (i) experimentally determined relative sensitivity factors, (ii) specific reference samples or (iii) theoretically derived sensitivity factors. For all these methods and for a reliable comparison between instruments reliable transmission functions of the spectrometer are crucial. Unfortunately, no standards exist for a consistent procedure of the determination of the spectrometer transmission function.

Some years ago two different methods for the determination of the transmission functions were implemented in the software package UNIFIT 2004 [1]. The so-called survey-spectra approach (SSA) uses the reference spectra from the NPL and approximates the transmission function by fitting a model function. Another approach is using quantified peak areas (QPA) of specified peaks, e.g. from Ge, Cu, Ag and Au, covering a suitable kinetic energy range. This method is much more flexible in terms of excitation energies, spectrometer modes and reference materials which enhance the useful-ness for the determination of the transmission function. It can be applied for different spectrometer modes, at synchrotron sources and with other suitable reference materials like ionic liquids [2].

These points are of great importance due to the developments in the last years. For achieving best signal-to-noise ratios and maximum lateral resolutions the electro-optic lens systems of the spectrometers have become more and more sophisticated. This positive development has led to more complex transmission functions which complicate their approximation to reference spectra. Furthermore, especially the hard x-ray energy region has become more popular. In particular, the introduction of lab-based HAXPES (Hard-Energy X-ray photoelectron spectroscopy) spectrometer will lead to a further dissemination of such instrumentation.

To meet this need UNIFIT 2022 has been developed. The re-worked QPA method uses a improved fitting routine and allows the visualisation of the relative peak areas of the reference peaks and the fitted transmission function in one frame. Thus, a quick check of the quality of the fit for the transmission function is possible. Additionally, the options for the definition of the iteration procedure were extended. The new features and test results demonstrating the good performance are presented.

References:

[1] R. Hesse, P. Streubel, R. Szargan, Surf. Interface Anal., 51, 618-626, (2005)

[2] M. Holzweber, A. Lippitz, R. Hesse, R, R. Denecke, WSM Werner, WES Unger, J. Electron. Spectrosc. Rel. Phenom. 233, 51-56, (2019)

UNIFIT 2018 - the Improved Spectrum Processing, Analysis and Presentation Software for XPS, AES, XAS and RAMAN Spectroscopy

R. Hesse, R. Denecke

Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie,
Universität Leipzig, D-04103 Leipzig

Corresponding author: rhesse@uni-leipzig.de

UNIFIT is a well-established specialized software for data analysis and presentation of photoelectron spectroscopy, Auger electron spectroscopy and X-ray absorption spectroscopy data. Now new additions and improvements are presented. In order to have more linking options for the fit parameters the fit procedures were improved (e.g. to be able to describe multiplet structures from intermediate-coupling Eu $3d_{5/2}$ and Eu $3d_{3/p}$ spin-orbits components for the divalent Eu+ compounds). The selection of the master peaks of the peak fit with relative fit parameters was extended. Now every peak-fit component can be defined as master peak. The parameters of slave peaks with a succeeding component numbers can be linked to the parameters of the corresponding master peak. The main-memory used by UNIFIT was strongly reduced. The UNIFIT 2018 software needs more than 30% less main-memory with respect to UNIFIT 2017. The large parameter arrays were redefined. The peak identification for XP spectra was expanded by an automatic option. The peak-finding procedure can be approached by defining of ΔE (energy separation), ΔI (peak height) as well as a check with a data set of main lines. The annotation list may be shown directly. A fourth spectroscopic method was implemented in the new software. The improved software offers the data analysis of photoelectron spectra (XPS), Auger electron spectra (AES), X-ray absorption spectra (XAS) and RAMAN spectra. The peak fit of RAMAN spectra gives a considerably better analysis of the studied sample with respect to the traditional analysis of untreated data. Two new 3D plots 'XY 3D 45° Colour Profile' and 'XY 3D -45° Colour Profile' were implemented in the batch processing subroutines.

The selectable processing results for the generation of XY-3D presentations were enhanced. Now, all fit parameters, the position of the maximum and minimum can be selected additionally.

Three new options for the selection of standard windows for easier handling of large data sets were implemented: i) all windows with a defined X position, ii) all windows with a defined Y position, iii) all windows with a χ^{2*} greater than a defined χ^{2*} (after a peak fit to detect incomplete fit results). Additionally, the number of the selected windows is displayed.

We will demonstrate the additional feature using typical applications.

Correlative electron microscopy and probe microscopy study of two-dimensional crystalline polymers for organic electronics

Bowen Zhang[1, 2], Martin Mičulka[1,3], Zhongquan Liao[1], Wei Li[4], Peng Zhang[4], T. Sikola[3], Ehrenfried Zschech[1]

[1] Fraunhofer Institute for Ceramic Technologies and System (IKTS), Maria-Reiche-Strasse 2, 01109 Dresden, Germany

[2] Faculty of Electrical and Computer Engineering, Technische Universität Dresden, 01062 Dresden, Germany

[3] Faculty of Mechanical Engineering, Brno University of Technology, Technická 2896, Brno-Královo Pole, Czech Republic

[4] Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany

**e-mail: bowen.zhang@ikts-extern.fraunhofer.de*

Abstract

Flexible electronics have been widely considered as next-generation electronics in sensing, displaying and memorizing [1], incorporating all functionalities of conventional electronics. The most crucial factor in flexible electronics is the robustness of the active layer under mechanical deformation. Two-dimensional (2D) crystalline polymers are among the most promising candidates for flexible active layers due to their intrinsic low bending modulus and their adjustable electronic properties [2]. Although synthesis and electronic properties of 2D crystalline polymers have been intensively investigated [3], it is still a lack of studies on the intrinsic mechanical and local electronic properties. We report a study of the effect of an external load and respective deformation on the microstructure and functionality of 2D crystalline polymers. Elastic properties, fracture strengths and local conductivities of novel free-standing 2D crystalline polyimine and q2D crystalline polyaniline films were systematically measured using a scanning probe microscope (LiteScope, Nenovision) integrated in a scanning electron microscope (NVision40, Carl Zeiss). The effect of external load on the microstructure of the materials was characterized at molecular level using high-resolution transmission electron microscopy (Libra200, Carl Zeiss). This correlative materials characterization indicates that 2D crystalline polymers are mechanically suitable for flexible electronics.

Acknowledgements

The authors thank Josef Horák and Veronika Hegrová (Nenovision Brno, Czech Republic) for assistance. Bowen Zhang thanks for the financial support from China Scholarship Council (CSC).

[1] T. Sekitani, T. Someya, Advanced Materials, 22(20): 2228-2246 (2010).
[2] X. Feng, AD. Schlüter, Angewandte Chemie International Edition, 57(42): 13748-13763 (2018).
[3] H. Sahabudeen, et al, Angewandte Chemie International Edition, 59(15): 6028-6036 (2020).

In situ TEM applications of sample drive lasers and fast-switching deflectors

Speaker: Johan Persson, PhD, JEOL (Germany) GmbH

1. Introduction

In situ TEM is a powerful tool for revealing fundamental nanoscale processes in physics, biology, and materials science. Thanks to advances in both instrumentation and technique, this is true now more than ever. This talk will explore the possibilities for studying laser-driven processes with the help of electrostatic deflection systems that can switch states on the nanosecond scale. To set the stage, we will review recent results showing laser-driven sintering, dewetting, and coarsening in nanostructured gold at kHz frame rates [1]. These results will serve both as examples of current capabilities and as motivation for the core of the talk: new developments involving electrostatic beam blankers, programmable high-speed timing systems, and advanced automation and data analysis.

2. Objectives

We wish to examine and elucidate the synergy of using high speed beam blanking in conjunction with laser illumination of the specimen for in situ studies of nanomaterial dynamics. We demonstrate the use of post specimen sub-framing systems to achieve extremely high frame rates during observation of laser driven material processes.

3. Materials & methods

A recently developed laser module, “Luminary Micro” (JEOL/IDES), facilitates direct focused laser-sample interaction. This has previously successfully been used to show dewetting of gold on a surface, sintering of nanoparticles and more [1], and has now been developed into a mature product [2]. Two electrostatic optical systems have been developed that can be precisely synchronized with the laser. The first of these, a pre specimen electrostatic dose modulator (EDM), works with a timing control system, “Synchrony” (JEOL/IDES), to enable nanosecond precision definition of electron beam temporal profiles. The second, a post specimen camera subframing system, “Relativity”, (JEOL/IDES) has previously been shown to provide kHz scale fame rates with similarly precise timing control [3]. Particles were produced using standard techniques.

4. Results

It is shown that the high-speed timing system in coordination with the advanced data analysis system give a benefit to in situ experiments. The methodology is validated through the demonstrated ability to record high-frame-rate details of well understood material processes, thus paving the way for future experiments on material systems and processes with completely unknown dynamics.

5. Conclusion

Together the systems described here, a compact sample laser, a pre-specimen EDM, a post specimen camera subframing deflector, and a precision timing controller enable users to craft scriptable experiment definitions to control all timing aspects of a laser driven in situ experiment. From dose rate to heating profiles to camera frame rate, users can decide how their experimental conditions will evolve with nanosecond precision.

6. References

[1] B. W. Reed, A. A. Moghadam, R. S. Bloom, S. T. Park, A. M. Monterrosa, P. M. Price, C. M. Barr, S. A. Briggs, K. Hattar, J. McKeown, and D. J. Masiel, *Struct. Dyn.* **6**, 054303 (2019)
[2] https://www.jeol.co.jp/en/products/detail/LuminaryMicro.html
[3] B. W. Reed, S. T. Park, R. S. Bloom, and D. J. Masiel, *Microsc. Microanal.* **23 (Suppl 1)**, 84 (2017)

Polymer-Assisted Sublimation Growth of Graphene on 4H-SiC(000-1)

Franziska Schölzel[1,2], Philip Schädlich[1,2], Thomas Seyller[1,2]

[1] Technische Universität Chemnitz, Institut für Physik, 09126 Chemnitz
[2] Center for Materials, Architectures and Integration of Nanomembranes (MAIN), 09126 Chemnitz

The growth of epitaxial graphene on the Si-face of SiC, i.e. SiC(0001) has been achieved on a large scale with a reproducible high quality [1]. Although graphene grown on this side shows a lower electron mobility compared to the C-face, i.e. SiC($000\overline{1}$), fewer studies have been conducted on the latter one [2,3]. That is due to the high growth rate and the consequently difficult thickness control. Recently, the polymer-assisted sublimation growth (PASG) on SiC(0001) has opened a novel routine towards ultra-smooth graphene films with outstanding thickness control [4].

In this study graphene synthesis via PASG was investigated on the SiC($000\overline{1}$) surface. Optimization of critical parameters such as growth temperature and annealing time led to monolayer graphene films as deduced from XPS core level analysis. LEED investigations reveal a preferential relative rotation around 0° and 30° with respect to the SiC lattice. In addition, multiple SiC surface reconstructions such as a (2x2) and a (3x3) reconstructions are observed during the growth process. AFM shows that the PASG approach prevents step bunching during the growth process such that the initial SiC morphology is conserved.

[1] K. Emtsev et al., Nature Mater, 203-207, 8 (2009).

[2] C. Berger et al., Science, 1191, 312 (2006).

[3] W. A. de Heer et al., Solid State Communications, 92, 143 (2007).

[4] M. Kruskopf et al., 2D Mater, 041002, 3 (2016).

Polymer-Assisted Sublimation Growth of Graphene on 4° off-axis 4H-SiC(0001)

Peter Richter[1,2], Philip Schädlich[1,2], Thomas Seyller[1,2]

[1] *Technische Universität Chemnitz, Institut für Physik, Chemnitz, 09126 Chemnitz*
[2]*Center for Materials, Architectures, and Integration of Nanomembranes (MAIN), 09126 Chemnitz*

Epitaxial graphene (EG) on SiC [1] has proven to be a suitable substrate for the synthesis of different 2D materials such as hBN or TMDCs [2]. However, the high symmetry of monolayer EG enables the nucleation of multiple crystallographic domains, leading to polycrystalline films [3]. Off-axis SiC surfaces with a high step density exhibit a lower symmetry and therefore might be a promising substrate for single-crystal growth. The high growth temperature of epitaxial graphene growth drives the step bunching process, effectively reducing the number of steps, and increasing the size of the substrate terraces.

In this study we used 4H-SiC(0001) substrates with a nominal miscut angle of 4°. Optimizing the parameters of hydrogen etching and the polymer-assisted sublimation growth [4], it was possible to reduce the step bunching to a minimum step height of 3 nm. ARPES data show replicas of the graphene band structure in the ΓM direction, which are unique to graphite layers grown on off-axis SiC [5], indicating the presence of facets. LEEM measurements reveal a homogeneous coverage, with undesired buffer layer and bilayer graphene areas representing less than 10% of the surface.

[1] K. Emtsev et al., Nature Mater, 203–207, 8 (2009)

[2] A. Rossi et al., 2D Mater., 031013, 3 (2016)

[3] S. Forti et al., Nanoscale, 16412–16419, 9 (2017)

[4] M. Kruskopf et al., 2D Mater., 041002, 3 (2016)

[5] T. Seyller et al., Surface Science, 600, 18 (2006)

Growth and characterization of WS_2 on epitaxial graphene on SiC(0001)

Adrian Schütze[1], Philip Schädlich[1], Constance Schmidt[1], Florian Speck[1], Dietrich R.T. Zahn[1], Thomas Seyller[1]

[1] Technische Universität Chemnitz, Institut für Physik, 09126 Chemnitz

2D materials such as, for example, graphene, hexagonal boron nitride or transition metal dichalcogenides have recently received much interest as building blocks for electronic devices. For a successful integration of these materials, scalable growth methods are essential. Here we investigate the growth of WS_2 by metal organic molecular beam epitaxy (MOMBE) [1] on epitaxial graphene. In that process $W(CO)_6$ is used as a precursor in conjunction with sulfur vapor produced by decomposition of FeS_2 in a thermal evaporator. Using MOMBE we were able to grow ultra-thin films of WS_2 on epitaxial graphene which were characterized by a combination of X-ray photoelectron spectroscopy (XPS), angle resolved photoemission spectroscopy (ARPES), low-energy electron diffraction and microscopy (LEED, LEEM), atomic force microscopy (AFM) and Raman spectroscopy. The ultra-thin films, which had thicknesses between one and two monolayers, were observed to consist of triangular domains. We discuss the influence of the growth parameters on the structural and electronic properties of the layers.

[1] S. Tiefenbacher et al., Surf. Sci. 318 (1994) L1161.

Application of well-defined multilayer inhouse standards as model systems for the performance-related verification of a 3D-µXRF spectrometer

Korbinian Heimler, Carla Vogt

TU Bergakademie Freiberg, Institute of Analytical Chemistry, 09599 Freiberg, Germany

Tabletop 3D-µXRF unites have been introduced only recently and are the subject of studies by various research groups during the last years. The in-depth sensitivity of the spectrometer is based on a defined three-dimensional probing volume which is formed by the confocal arrangement of two polycapillary lenses in the excitation and the detection channel (Fig. 1A). The spectrometer used in this study is a modified commercial tabletop µXRF spectrometer (M4 TORNADO) by *Bruker Nano GmbH*, the setup is based on research results obtained by the Kanngießer group at TU Berlin.[1] The spectrometer is equipped with a 30 W Rh micro focus tube, operating up to 50 kV and 600 µA. The commercial µXRF setup is equipped with a polycapillary lens with a spot size ≤ 20 µm (Mo Kα) for X-ray focusing and a 30 mm^2 silicon drift detector. Due to the modification a second polycapillary lens was installed perpendicular to the first one in front of a 60 mm^2 silicon drift detector.

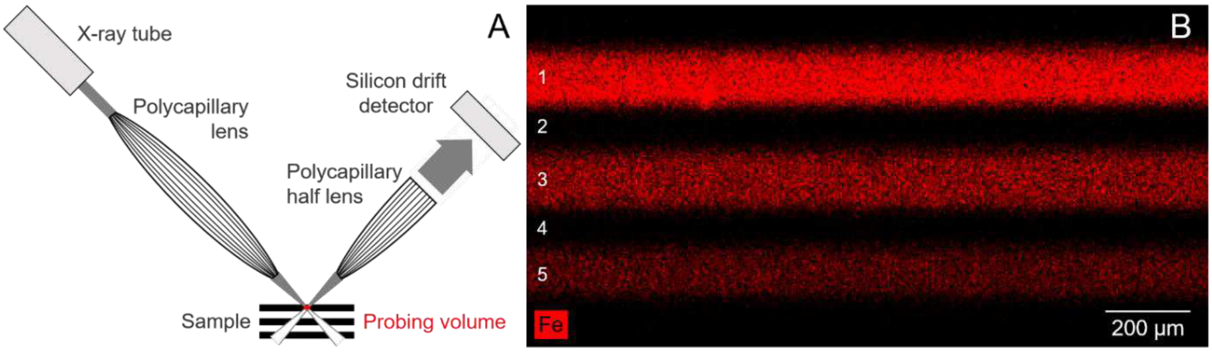


Figure 1. Schematic representation of the perpendicular arrangement of the polycapillary lenses and the thereby formed probing volume (A). Elemental distribution image of a stratified polymeric inhouse standard with Fe_2O_3 as additive in layer one, three and five (B).

Stratified polymeric inhouse standards with well-defined elemental contents have been used for model-studies in order to identify the capability of the 3D-µXRF spectrometer setup and to overcome the lack in availability of suitable certified reference materials. Concerning the application of those stratified systems, various parameters, such as the base-polymer ratio, additive addition, selection of suitable elemental fillers with regard to homogeneity, dispersing or realization of different layer thicknesses, had to be considered. Considering the performance-related verification of the 3D-µXRF setup, the elements Ca, Fe and Ce were added into the polymeric mixture in order to achieve an analytical diversity due to vastly different fluorescence energies and lines of the selected elements. Furthermore, various stratified standards consisting of five polymeric layers were fabricated with varying elemental contents and layer sequences (see example in fig. 1B). For the final validation of the 3D-µXRF setup different parameters, like penetration depth, matrix effects, absorption effects and probing volume dimension, have been evaluated.

References:

[1] I. Mantouvalou, T. Wolf, C. Seim, V. Stoytschew, W. Malzer, B. Kanngießer, Anal. Chem., 9774-9780, 86 (2014).

Influence of laser wavelength and pulse duration on depth resolved stoichiometric analysis of Li/Mn ratio in $LiMn_2O_4$ thin films using Laser Ablation

Kevin Kraft[1,2], Matthias Trottmann[1], Adrian Wichser[1], Davide Bleiner[1,2]

[1] Laboratory for Advanced Analytical Technologies, Swiss Federal Institute for Materials Science and Technology Empa, Überlandstrasse 129, 8600 Dübendorf, Switzerland
[2] Department of Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

The cubic spinel $LiMn_2O_4$ could potentially replace the curent cathode material $LiCoO_2$ of lithium ion batteries and thus replace the use of toxic and expensive cobalt, making the batteries cheaper and more environmentally safe without reducing the capacity.[1] The deposition of Li manganates is straightforward by means of pulsed laser deposition (PLD).[2] Unfortunatelly, the atomic mass difference between Li and Mn leads to different behaviour during the deposition process, which alters the stoichiometry of the produced thin film.[2] An accurate and precise stoichiometric tuning of the Li/Mn ratio is essential, in order to grow thin films that have the same Li/Mn stoichiometry as the target material.[2] Common methods for the analysis, such as rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) are hampered by a large error range for light elements such as Li and give only accurate results in thick films respectively.[2] The aim of this study was to develop a new method and quantification strategy, using self made matrix matched standard materials with different Li/Mn ratios, to make use of the broad detection range of LA-ICP-MS for the analysis of $LiMn_2O_4$ thin films, while preserving local information.[3]

Using LA-ICP-MS the ablation spot as a function of the laser energy was investigated from 0.1-1.0mJ and 2-50 pulses, with a Nd:YAG 532nm laser and pressed pellet samples of $LiMn_2O_4$. With selfmade matrix matched standard materials, having different Li/Mn ratios and using an RPa threshold for Li and Mn to overcome oversaturation through the Mn from the bulk, a LOD for Li from 0.004µg/g (1mJ) to 0.06µg/g (0.1mJ) and 0.001µg/g (1mJ) to 0.02µg/g (0.1mJ) for Mn was achieved. The determined stoichiometric Li/Mn ratio of 0.5mol/mol was constant over the investigated laser intensity. The ratio of the measured intensity was also constant over the laser intensity range of 0.1mJ to 1mJ with 0.55 ± 0.5 cps/cps.

The study showed that the calibration strategy, using homemade matrix matched standard materials, the stoichiometric ratios of $Li_{(1-x)}Mn_{(2+x)}O_4$ thin films can be quantified by LA-ICP-MS. The stoichiometric ratio of Li/Mn will be further investigated using different wavelengths to study the effect of elemental fractionation, essentially repeating the experiments before using wavelengths of 1064nm, 266nm and 213nm.

[1] D. Albrecht, H. Wulfmeier, and H. Fritze, “Preparation and Characterization of c-LiMn2O4 Thin Films prepared by Pulsed Laser Deposition for Lithium-Ion Batteries,” *Energy Technol.*, vol. 4, no. 12, pp. 1558–1564, 2016, doi: 10.1002/ente.201600117.

[2] A. Ojeda-G-P, C. W. Schneider, M. Döbeli, T. Lippert, and A. Wokaun, “The importance of pressure and mass ratios when depositing multi-element oxide thin films by pulsed laser deposition,” *Appl. Surf. Sci.*, vol. 389, pp. 126–134, 2016, doi: 10.1016/j.apsusc.2016.07.003.

[3] S. Smetaczek *et al.*, “ Spatially resolved stoichiometry determination of Li 7 La 3 Zr 2 O 12 solid-state electrolytes using LA-ICP-OES ,” *J. Anal. At. Spectrom.*, pp. 972–983, 2020, doi: 10.1039/d0ja00051e

In situ, high spatial resolution chemical mapping of freshly exposed FIB faces using AES

Ashley Maloney, Dennis Paul[1]

[1] *Physical Electronics USA, Chanhassen, MN 55317*

Auger Electron Spectroscopy (AES) is a powerful analytical tool that provides quantitative elemental information from surfaces of solid materials. The average depth of analysis for an AES measurement is approximately 5 nm with lateral spatial resolution as small as 8 nm. The information AES provides about surface layers or thin film structures is important for many industrial and research applications where surface or thin film composition plays a critical role in performance including: nanomaterials, photovoltaics, catalysis, corrosion, adhesion, semiconductor devices and packaging, magnetic media, display technology, and thin film coatings used for numerous applications.

In this presentation, defect sites present on a Ti passivated Al sheet sample were identified and analyzed using a PHI 710 scanning Auger nanoprobe equipped with a 25kV Schottky field emission electron gun and a coaxial Cylindrical Mirror Analyzer (CMA). We demonstrate the use of AES in conjunction with a focused ion beam (FIB) to produce site specific imaging of microscale features. The combination of the two techniques allows for high spatial resolution analysis of buried particles and defects in an ultra high vacuum environment. This information can be very useful in helping to determine important parameters such as the origin of defects, corrosion mechanisms, coating problems, etc. Energy dispersive x-ray spectroscopy (EDS) is also a powerful complementary technique to Auger analysis as it provides information from much deeper in the sample surface (few µm). With the combination of AES, FIB, and EDS, we show that buried metal particles can be first located and characterized with EDS, followed by the subsequent FIB milling and Auger spectroscopy of the particles.

Enhancing long-range order in 1D atomic gold chains by selective doping

Zamin Mamiyev[1,2*], Christoph Tegenkamp[1,2], Herbert Pfnür[2]

[1]Institut für Physik, Technische Uni Chemnitz, Reichenhainer Str. 70, 09126 Chemnitz, Germany

[2]Institut für Festkörperphysik, Leibniz Uni Hannover, Appelstraße 2, 30167 Hannover, Germany

Metal-induced atomic wires on semiconductor surfaces are the ultimate limit of long-range ordered one-dimensional electronic systems and fascinating objects to address manifold aspects of low-dimensional physics. However, such one-dimensional metallic chains are known to be inherently unstable at finite temperature. Here, we show that long-range order of atomic Au chains adsorbed on the Si(553) surface is not only stabilized by interaction with the substrate, but spontaneous self-healing of structural defects is enforced by the adsorption of atomic species such as Au or H (Fig.1 a,b).[1,2] This is true even for random adsorbate distribution. Combining atomistic models within density functional theory (DFT) with low energy electron diffraction (SPA-LEED) and high-resolution electron energy loss spectroscopy (EELS-LEED), we demonstrate that this counterintuitive behavior is mainly caused by adsorption-induced band filling of modified surface bands, i.e., by the strong electronic correlation throughout the whole terrace, which also results in a reduction of the plasmon dispersion (Fig.1 c). Although adsorption preferably occurs at the silicon step edge, it enhances the dimerization and the stiffness of the Au-dimers. [1,2] Thus, the intertwinement of quasi-1D properties with delocalized 2D effects enforces the atomic wire order. The present study demonstrates the intriguing interplay of local and nonlocal electronic properties in a quasi-1D system that leads to improved long-range structural ordering, strong electronic correlation, self-healing of defects, and dimensional crossover from 1D to 2D.

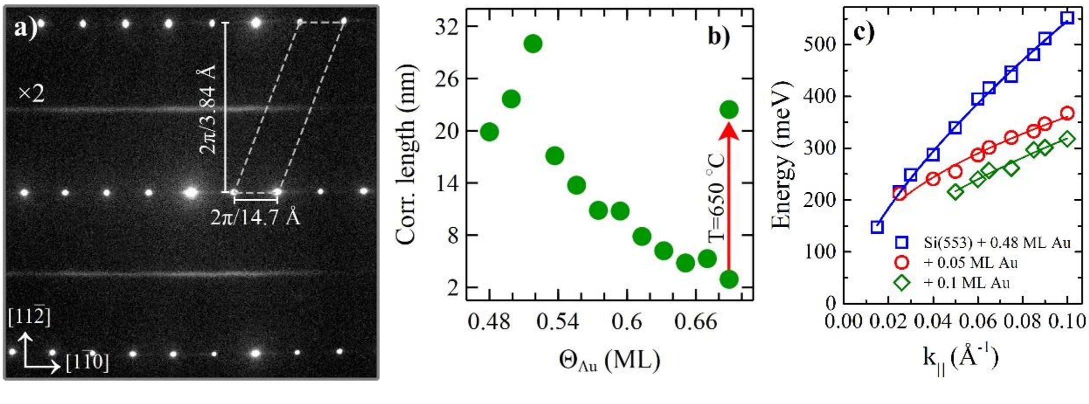


Fig.1: (a) SPA-LEED pattern for the Si(553) + 0.48 ML Au surface. (b) Correlation length along the Au chains deduced from 1D diffraction profiles as a function of surplus Au deposition at room temperature. (c) Plasmon dispersion for the clean and surplus Au deposited surfaces.

[1] Z. Mamiyev et al. Phys. Rev. B, 245414, 98 (2018).
[2] Z. Mamiyev et al. Phys. Rev. Lett, accepted (2021).

Universal approach towards bottom-up fabrication of 2D material nanoribbon based field-effect devices

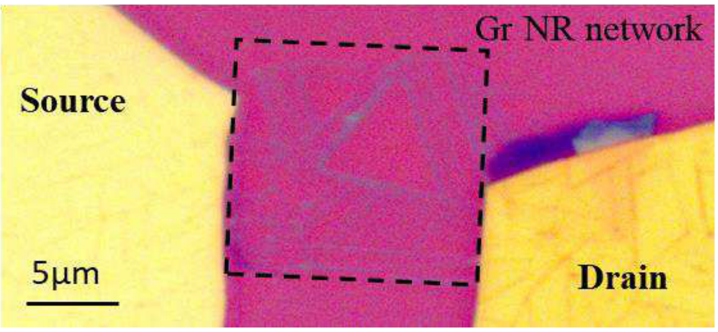
Muhammad A. Aslam [1,*], M. Kratzer [1], C. Teichert [1], Raul D. Rodriguez [2], and A.Matkovic [1]

muhammad.aslam@unileoben.ac.at

[1] *Institute of Physics, Montanuniversität Leoben, Leoben, Austria*
[2] *Tomsk Polytechnic University, Tomsk, Russia*

We demonstrate an approach to synthesize nanoribbon networks, which is suitable for many 2D materials. The approach is based on epitaxially grown organic nanostructures which self-assemble and self-align predominantly in either zig-zag or armchair orientation on 2D materials. [1,2] This study demonstrates their usage as a mask through which 2D materials are plasma etched to form single crystal nanoribbon networks. Raman spectroscopy and atomic force microscopy are employed to verify the quality of the ribbons. Furthermore, operational nanoribbon-network field-effect devices based on graphene and MoS_2 are demonstrated (example optical micrograph show).

Our method opens up a new avenue for straightforward production of 2D material nanoribbon networks on scales relevant to electronic applications. Their high edge-to-surface ratios will also be of technological relevance for the development of future light and chemical sensors.



[1] *Kratzer, Teichert, 2016. Nanotechnol.* ***27****, 292001.*

[2] *Matkovic et.al., 2019. Adv, Funct. Mater.* ***29****, 1903816*

Controlling Size and Nature of Nanoparticles Exsolved from Perovskite Oxides

Lorenz Lindenthal[1], Schrenk Florian[1], Hedda Drexler[1], Raffael Rameshan[1], Christoph Rameshan[1]

[1] *Technische Universität Wien, Institute of Materials Chemistry, Vienna 1060, Austria*

Perovskite oxides can incorporate easiliy reducible elements, either as a main component or as a dopant. These elements can be exsolved from the perovskite structure under reducing conditions, emerging as metal nanoparticles on the material surface [1]. Thus, they can enhance the properties of the perovskite, e.g. as an electrode material in solid oxide fuel cells or as a heterogeneous catalyst. To optimize the capabilities of the perovskite for applications, it is imperative to be able to control the size, distribution and composition of exsolved nanoparticles [2].

In order to understand the exsolution behavior, several perovskite materials have been studied under varying reducing conditions. Parameters that influence the resulting particles are for example the perovskite composition and morphology (e.g. powder or thin film), the reduction strength of the atmosphere, temperature, applied electrical polarization, and reduction time. Characterization was done utilizing various methods, namely (*in situ*) X-ray diffraction (XRD), *in situ* X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microcopy (TEM) combined with energy dispersive X-ray spectroscopy (EDX). The combination of these techniques enables a comprehensive understanding of how to tune exsolved particles. Figure 1 shows some exemplary data.

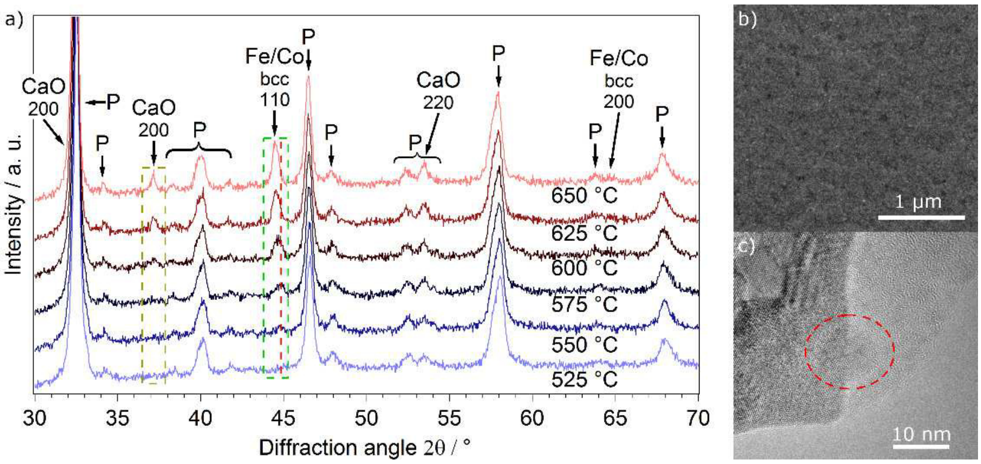


Figure 1: Investigation of $Nd_{0.6}Ca_{0.4}Fe_{0.9}Co_{0.1}O_{3-\delta}$. a) In situ XRD measurements during reduction with H_2/H_2O, showing an emerging metallic phase. b) SEM image after polarization assisted reduction in CO/CO_2, displaying small homogeneously distributed particles. c) TEM image of one of the particles of the sample in b).

[1] D. Neagu, V. Kyriakou, I.-L. Roiban, M. Aouine, C. Tang, A. Caravaca, K. Kousi, I. Schreur-Piet, I.S. Metcalfe, P. Vernoux, P., M.C.M. van de Sanden, M.N. Tsampas, ACS Nano, 12996-13005, 13 (2019).

[2] L. Lindenthal, R. Rameshan, H. Summerer, T. Ruh, J. Popovic, A. Nenning, S. Löffler, A.K. Opitz, P. Blaha, C. Rameshan, Catalysts, 268, 10 (2020).

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement n° 755744 / ERC - Starting Grant TUCAS)

Distribution of trace elements in plants – quantification strategies for 2D-µXRF and Laser ablation ICP-MS measurements

Anika Rogoll, Alexandra Becker, Bastian Wiggershaus, Korbinian Heimler, Carla Vogt

TU Bergakademie Freiberg, Institute of Analytical Chemistry, Leipziger Str. 29, 09599 Freiberg

Phytoremediation and phytomining techniques are considered to be environmental friendly plant-based „green“ approaches to cope with soil and environmental pollution. These techniques involve, among others, the extraction of potentially toxic or economically valuable elements from soils (phytoextraction). Most sites considered for these treatments are marginal, unfertile and heavy metal contaminated soils with suboptimal growth conditions, where water and nutrient deficiency as well as heavy metal stress must be considered as the key parameters fundamentally influencing the applicability and efficiency of plant-based remediation and mining techniques. To study plant availability of essential, toxic and commercially valuable trace elements in the rhizosphere selected plant species were treated with single or multiple doses of REEs and other economically valuable elements under controlled greenhouse conditions.

To estimate either positive or negative effects on toxicity or plant vitality as well as capacity to enrich certain elements from soil or nutrient fluids into the plant the trace element uptake into the plant tissue of corn and rapeseed was investigated. Thin sections of different parts of the plants with about 20 µm thickness were produced with a cryomictrotome and measurements of elemental distribution in the thin sections were performed using µXRF and LA-ICP-MS. For the quantification of selected elements reference materials on the basis of different polymers were synthesized with element concentrations in the lower ppm region. Elements, considered for this study, were Al, Ce, Cd, Cu, Gd, La, Mn, Nd, and Si.

The presentation will discuss effects of

(1) sample preparation for the different parts of the plants,
(2) preparation of reference materials and quality parameters of these materials, like homogeneity of element distribution, concentration range and stability, and
(3) challenges and figures of merit for the analytical methods applied as well as a comparison of both techniques for the analysis of plant tissue thin sections, when used for the same set of elements.

The main problems, which had to be overcome in the project, were

(a) the stability of the standards with respect to the conditions in the sample chambers of both analytical techniques,
(b) homogeneity of concentration in the standards on the low µm-scale, and
(c) detection limits in connection with measuring time or sample uptake.

Chemical imaging and analysis by Femtosecond LIBS with micrometer spatial resolution

Nikolaos Giannakaris[1], Stefan Trautner[1], Johannes D. Pedarnig[1]

[1]*Institute of Applied Physics, Johannes Kepler University, A-4040 Linz, Austria*
E-mail: nikolaos.giannakaris@jku.at

The aim of this work concentrates on the use of Femtosecond Laser-induced breakdown spectroscopy (LIBS) for chemical imaging with high spatial resolution, minimal ablated mass and single shot detection. Femtosecond lasers produce well defined craters due to the reduced heat affected zones and they are an excellent choice for high resolution LIBS [1]. A main challenge is the need to achieve efficient analysis with micrometer spatial resolution and small sample mass in the pg range. Measurements were conducted using a laser producing 400 fs pulses at a wavelength of 520 nm. The plasma radiation was detected in backwards direction. Our experiments on Cu thin films (520 nm) on glass substrate demonstrate accurate digital sample reconstruction with a lateral resolution down to 1.5 µm (Fig. 1). In an effort to maximally exploit the optical energy of each laser pulse for generating an intense plasma, hence enhancing the analytical capacity of the proposed method, we have investigated the amplifying role of orthogonal fs/fs double pulse (DP) LIBS. DP-LIBS includes the separation of the initial laser beam into two, with orthogonal geometry, in order to take into advantage the reheating of the plasma by the second pulse. DP-LIBS enhances the emission line intensities (factor 2) without having an influence on the spatial resolution.

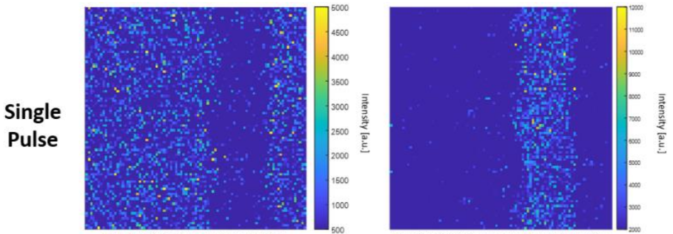


Fig. 1a: Digital image reconstruction using Cu I 510.5 nm line on SP mode

Fig. 1b: Digital image reconstruction using Na I 589 nm line on SP mode

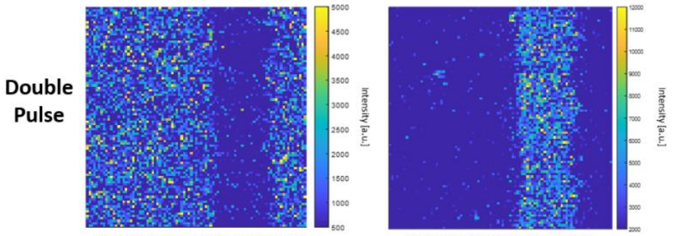


Fig. 2a: Digital image reconstruction using Cu I 510.5 nm line on DP mode

Fig. 2b : Digital image reconstruction using Na I 589 nm line on DP mode

Fig. 1: Chemical images of Cu stripes on glass obtained by fs-LIBS. Cu image at 510.5 nm (left) and Na image at 589 nm (right). Enhanced contrast by double-pulse excitation (bottom).

Acknowledgement: Financial support by the Austrian Research Promotion Agency FFG is gratefully acknowledged (K-project PSSP 871974).

[1] C. M. Ahamer, K. M. Riepl, J. D. Pedarnig, Spectrochim. Acta Part B 136 (2017) 56-65. Doi: 10.1016/j.sab.2017.08.005

Graphene on Copper Foil: Stacking Relations and Substrate Interaction

Philip Schädlich[1,2], Florian Speck[1,2], Chamseddine Bouhafs[3,4], Neeraj Mishra[3,4], Stiven Forti[3],
Camilla Coletti[3,4], Thomas Seyller[1,2]

[1] *Technische Universität Chemnitz, Institut für Physik, 09126 Chemnitz*
[2] *Center for Materials, Architectures and Integration of Nanomembranes (MAIN), 09126 Chemnitz*
[3] *Istituto Italiano di Tecnologia, Center for Nanotechnology Innovation @NEST, Pisa, Italy*
[4] *Istituto Italiano di Tecnologia, Graphene Labs, Genova, Italy*

Low-energy electron microscopy (LEEM) is used to investigate graphene grown by chemical vapor deposition (CVD) before and after the transfer on an epitaxially grown buffer layer on SiC(0001). Graphene-based device production requires graphene sheets of perfect crystallinity and low defect density on a large scale. Beyond mechanical exfoliation, where the average flake size is uncontrollable, there are two promising approaches for high-quality wafer-scale graphene growth: (i) the sublimation growth on silicon carbide by thermal decomposition of the substrate [1] and (ii) CVD on metal substrates [2]. While sublimation growth is possible on semi-insulating substrates, CVD grown graphene must be transferred from the metal onto a suitable substrate after the growth. LEEM and its related techniques give insight into the orientation and crystallinity of graphene layers and also reveal the interactions with the substrate of choice

By means of selected area LEED, we find a lattice match within $\pm 1°$ between the graphene and the Cu(111) surface, which shows a surface faceting depending on the graphene thickness on top. The analysis of electron diffraction data indicates the presence of (211) facets, which account for an inclination angle of 19.5° with respect to the (111) surface. From LEEM reflectivity spectra we find a general agreement with spectra obtained from epitaxial graphene on SiC(0001). The main difference is the larger width of the reflectivity minimum for the interface between the buffer layer and the transferred layers, which points towards the facetted structure of the graphene imprinted by the copper substrate. In dark field geometry using a first order diffraction spot of graphene, we observe domains of different Bernal stacking in bilayer areas. The boundaries of these domains are located at the steps of the facetted copper surface. Both features are preserved during the transfer onto a target substrate. It deserves to be mentioned, that a similar behavior might also be expected for other 2D materials.

[1] K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellog, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Röhrl, E. Rotenberg, A. K. Schmidt, D. Waldmann, H. B. Weber, Th. Seyller, Nature Mater. **8**, 203 (2009).

[2] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, Science **324**, 1312 (2009).

5.6 Session V — Thursday, October 7th

08:50 – 09:05	**Eduard Zenkevich** Nanoassemblies based on colloidal AIS/ZnS quantum dots and porphyrins:surface morphology, interface chemistry and exciton relaxation pathways
09:05 – 09:20	**Herbert Pfnür** Plasmon spectroscopy in quasi one-dimensional arrays of atomic wires
09:20 – 09:35	**Lukas Brunnbauer** Matrix-Independent Trace Metal Quantification in Polymers using LIBS
09:35 – 09:50	**Dina Friebel** Process-accompanying analysis of solid intermediate and end products for the extraction of high-purity tungsten by ETV-ICP OES
09:55 – 10:05	**Jakob Willner** Quantitative determination of sulfur uptake in selected polymers via LA-ICP-MS
10:05 – 10:20	**Grünberger Stefan** Comparing LIBS and Laser Ablation-Spark Discharge-OES: from imaging to analysis
10:20 – 10:30	**Company presentation 7**
10:30 – 10:40	**Company presentation 8**

Nanoassemblies based on colloidal AIS/ZnS quantum dots and porphyrins: surface morphology, interface chemistry and exciton relaxation pathways

Eduard Zenkevich,[1,2] Vladimir Scheinin,[3] Olexander Selyshchev,[4] Olga Kulikova,[3] Olexander Stroyuk,[5] Olexandra Raievska,[4] Volodimir Dzhagan,[6,7] Oscar Koifman,[3] Dietrich R.T. Zahn[4]

[1]*National Technical University of Belarus, 220013 Minsk, Belarus*
[2]*Fraunhofer Institute for Electronic Nano Systems, 09126 Chemnitz, Germany*
[3]*G.A. Krestov Institute of Solution Chemistry, RAS, 153045 Ivanovo, Russia*
[4]*Semiconductor Physics, University of Technology, Chemnitz, D-09107, Germany*
[5]*Helmholtz Institute Erlangen-Nürnberg for Renewable Energy, 91058 Erlangen, Germany*
[6]*V. Lashkaryov Institute of Semiconductors Physics, NAS of Ukraine, 03028 Kyiv, Ukraine*
[7]*Department of Physics, Taras Shevchenko National University of Kyiv, 01601 Kyiv, Ukraine*

At the moment, ternary I–III–VI (I = Cu, Ag; III = In, Ga, Al and VI = S, Se, Te, etc.) semiconductor quantum dots (QDs) received significant interest due to their compositional and structural versatility and strong photoluminescence, which may be tuned by QD composition, size, surface passivation, and ligand shell. Correspondingly, qualitative and quantitative analysis of surface and interface processes for these QDs and nanoassemblies including QDs and organic chromophores is a key challenge for those working on hybrid nanomaterials and their applications.

In the given contribution, we present a comparative description of surface properties, structural dynamics and pathways of excitation energy relaxation processes in QD-Dye nanoassemblies based on core/shell Ag-In-S/ZnS QDs stabilized by glutathione (GSH) and coupled with 5,10,15,20-(tetra-N-methyl-4-pyridyl)porphyn molecules via Coulomb attraction in water. Modern methods of nanoobjects visualization cannot display the fine structure of colloidal AIS/ZnS/GSH quantum dots surface *in situ*. In our study, this problem was solved using two approaches. On the basis of the available experimental data, the size-proportional 3D model of the QDs AIS/ZnS/GSH surface was constructed using the molecular mechanics method MM +. In addition, by means of synchronous UV-Vis/PL titration with pH control, a comparative study of the AIS/ZnS/GSH QD surface was carried out in water using functionalized optical porphyrin probes. Based on 3D model theoretical results and experimental data of steady-state absorption and PL experiments, time-resolved PL, and Raman spectroscopy, we propose a detailed description of interaction between porphyrin molecules and GSH-stabilized AIS/ZnS QDs including electrostatic attachment of the porphyrin molecule to the capping ligand shell, a fast metalation of porphyrin free base followed by a strong interaction with QD SH facet. Parameters of the energy transfer from QD to porphyrin, calculated using Förster model, are found to be in a reasonable agreement with the experimental data.

This work was funded by Volkswagen Foundation (Project “New Functionalities of Semiconductor Nanocrystalsby Controllable Coupling to Molecules”), BSPSR program “Convergence–2020 3.03”, RFBR grant № 18-53-00035 (Russia-Belarus), as well as by the European Union under Grant Agreement 732482 (Bio4Comp -Parallel Network-Based Biocomputation) and Visiting Scholar Program of TU Chemnitz, Germany(E.Z.).

Plasmon spectroscopy in quasi one-dimensional arrays of atomic wires

Herbert Pfnür[1], **Zamin Mamiyev**[1,2]
Institut für Festkörperphysik, Leibniz Universität Hannover, D-30167 Hannover, Germany
Institut für Physik, Technische Universität Chemnitz, D-09126 Chemnitz. Germany

Collective plasmonic excitations in quasi one-dimensional (1D) metallic wires are very attractive for directed energy transport on the nanoscale. They not only cover the range of energies between far and near infrared, their flat dispersion opens a perspective of localization down to a few nanometers because of their short wavelengths, and the quasi-linear dispersion in the long wavelength limit makes signal transmission easy. Ordered arrays of atomic wires, either as single or double chains, depending on step orientation, or filling complete terraces of nanometer width, exist on vicinal Si surfaces. They represent in fact the smallest possible quasi-1D objects that can be formed.

Here we report on a systematic study of the collective electronic excitations in arrays of Au chains and Ag wires on regularly stepped Si(553), (557) and Si(775) surfaces using electron loss spectroscopy with simultaneous high energy and momentum resolution (ELS-LEED) in combination with low energy electron diffraction (SPALEED).

Although purely 1D dispersion along the chain direction is found in all these systems, the actual charge distribution normal to the wires, in other words the crossover into the second dimension, is crucial for the quantitative interpretation of these quasi-1D phenomena and intimately related to the unoccupied bandstructure close to the Fermi level. As we show, it thus can be directly used as a spectroscopic tool.

Apart from spectroscopy that allows discrimination between various geometrical arrangements by comparison with density functional calculations, we present examples of plasmon manipulation by atomic doping, and plasmon confinement up to complete localization.

Matrix-Independent Trace Metal Quantification in Polymers using LIBS

Lukas Brunnbauer[1*], Jhanis Gonzalez[2,3], Hans Lohninger[1], Julia Bode[4], Carla Vogt[4], Michael Nelhiebel[5], Silvia Larisegger[5] and Andreas Limbeck[1*]

[1]TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-I^{2}AC, 1060 Vienna, Austria

[2]Applied Spectra, Inc., West Sacramento, CA, USA

[3]Lawrence Berkeley National Lab, Berkeley, CA, USA

[4]TU Bergakademie Freiberg, Institute of Analytical Chemistry, Leipziger Str. 29, 09599 Freiberg, Germany

[5]KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Technologiepark Villach Europastraße 8, 9524 Villach, Austria

The quantitative determination of the trace metal content in synthetic polymers is of great interest in many different fields. Conventionally, for this analysis the polymer has to be transformed into a solution with subsequent liquid ICP-MS/OES analysis. As dissolution of polymers is a challenging task often microwave-assisted digestion or combustion protocols have to be employed to ensure complete digestion. This approaches enables easy quantification but comes with many disadvantages such as time-consuming manual sample handling, need for harsh and hazardous chemicals, and loss of spatial information of the analyte within the sample.

Direct-solid sampling techniques such as Laser Induced Breakdown Spectroscopy (LIBS) allows to overcome all the aforementioned drawbacks. Nevertheless, for reliable quantification, matrix-matched standards are required, as the laser-matter interaction is highly dependent on the matrix of the sample under investigation. This is problematic for polymers, as this material comes in a wide range of different types and compositions as often additives are used to fine-tune the properties. Therefore, the application of matrix-matched standards is not feasible for polymer analysis.

In this work, we investigate the application of LIBS combined with multivariate data evaluation for the quantitative trace metal analysis in polymers without matrix-matched standards. Therefore, we use the unique capabilities of LIBS to provide not only adequate sensitivity for trace metal analysis but also enable the detection of polymer-specific emission signals which contain information about the samples' matrix. We prepared a library of standards of 8 different polymer types where each polymer type is considered a test polymer. Two multivariate data evaluation strategies were evaluated for the quantification without matrix-matched standards. The first approach is based on combining a classification model with conventional univariate calibration and the second approach is based on a Partial Least Squares (PLS) calibration model. To assess the performance of the two approaches we compared obtained errors to benchmark values from conventional matrix-matched and non-matrix-matched quantification.

Process-accompanying analysis of solid intermediate and end products for the extraction of high-purity tungsten by ETV-ICP OES

Dina Friebel[1], Thomas Vogt[1], Carla Vogt[1]

[1] TU Bergakademie Freiberg, Institute of Analytical Chemistry, Leipziger Str. 29, 09599 Freiberg

Many solids, such as samples from the production of high-purity tungsten, are difficult to dissolve. Digestion processes contain high risks of contamination and expensive high-purity reagents are needed. In the case of the tungsten matrix, many analytical spectroscopic methods like ICP OES can't be applied due to the enormous spectral line density of tungsten. Therefore, a highly efficient analytical method for direct qualitative and quantitative multi-element analysis of solids is required. As a suitable analytical technique for the analysis of poorly soluble matrices such as graphite, glass or ceramic, the electrothermal vaporization (ETV) as a sample introduction system for inductively coupled plasma optical emission spectrometry (ICP OES) was optimized for the analysis of tungsten-based materials.[1] All intermediate products in the production of high purity tungsten like ammonium paratungstate ($(NH_4)_{10}(H_2W_{12}O_{42}) \cdot 4\ H_2O$), yellow tungsten oxide (WO_3), blue tungsten oxide (WO_{2+x}), tungsten powder (W) and tungsten carbide (WC) were used as samples. In these compounds, especially contamination by the elements aluminum, boron, phosphorus, sulfur and silicon are of special interest, which affect the characteristics of the final products.[2] Furthermore, the analysis of oxygen in tungsten and tungsten carbide was investigated.

The optimization includes the selection of suitable plasma parameters and emission lines. Since, for example, almost all emission lines of sulfur are interfered by tungsten, a way had to be found to separate sulfur from the matrix. Various reaction gases and temperature programs were tested to investigate the release of the elements from the solid samples. With the assistance of a specific reaction gas and temperatures up to 2000 °C, the analytes can be vaporized while the tungsten matrix is retained in the graphite boats of the ETV unit. Due to inhomogeneities of some samples, comparatively high initial weights of 15 - 25 mg had to be selected.

Furthermore, a method for calibrating the system had to be found, since no suitable certified reference materials are available for the matrices under consideration. Therefore, the method had to be calibrated outside the matrix, whereby reference materials with different matrices and a liquid calibration were tested.[3] By optimizing the various parameters a simultaneous determination of all relevant elements from main constituents to trace elements can be achieved with one measurement.

References:

[1] M. Resano, F. Vanhaecke, M. T. C. de Loos-Vollebregt, J. Anal. At. Spectrom., 1450**,** 23 (2008).

[2] G. L. Krasko, Mater. Sci. Eng, 1071, A 234-236 (1997).

[3] A. Detcheva, P. Barth, J. Hassler, Anal. Bioanal. Chem. 1485, 394 (2009).

Quantitative determination of sulfur uptake in selected polymers via LA-ICP-MS

Jakob Willner[1], Lukas Brunnbauer[2], Michael Nelhiebel[1], Silvia Larisegger[1] and Andreas Limbeck[2]

[1]*KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Technologiepark Villach - Europastraße 8, 8524 Villach, Austria*

[2]*TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-IAC, 1060 Vienna, Austria*

Polymers cover a wide range of mechanical, thermal, physical and chemical properties. This makes them subject to a large number of applications, from more common uses such as packaging to highly specialized technological use (i.e. in the coating-, semiconductor-, medicinal-, automotive- or aviation industry). In these application fields, the properties of the polymers have to be tuned according to the specific requirements to ensure functionality. Further, they sometimes have to withstand harsh environmental conditions, such as high temperature and temperature cycles, exposure to radiation and corrosive gases. To limit the risk of failure of critical devices that contain functional polymer components, a detailed characterization and testing is necessary, requiring suitable analytical tools and methods.

Monitoring the degradation of polymers is accessible to FTIR spectroscopy, but this method has its limitations in performing depth resolved measurements as well as detecting inorganic contaminants. While electron probe methods (e.g. SEM-EDX, XPS) generally require conducting samples and high vacuum, they also lack sensitivity for measurement of trace constituents and the possibility to measure depth profiles in the low µm range. The application of liquid measurement using ICP-OES or ICP-MS after acid digestion brings the required high sensitivity and enable straightforward quantification using liquid standard solutions, but is labor intensive and provides only bulk information. An analytical technique, which overcomes these limitations and allows the depth-resolved elemental analysis of polymers with high sensitivity is LA-ICP-MS. Nevertheless, reliable quantification remains a major problem without the use of matrix-matched standards.

This work was focused on the determination of the sulfur uptake in different polymers after exposure to the corrosive gases hydrogen sulfide and sulfur dioxide. For this purpose, a newly adapted dried droplet calibration method for LA-ICP-MS investigations has been developed, enabling a depth resolved quantification of the sulfur uptake in various polymers for the first time. The developed method provides an excellent tool for future research in areas such as corrosion and reliability studies of polymers.

Comparing LIBS and Laser Ablation-Spark Discharge-OES: from imaging to analysis

Stefan Grünberger[1], Simon Eschlböck-Fuchs[2], Josef Hofstadler[2], Andreas Pissenberger[2], Hubert Duchaczek[2], Stefan Trautner[1], Johannes D Pedarnig[1]

[1] Institute of Applied Physics, Johannes Kepler University, A-4040 Linz, Austria
[2] voestalpine Stahl GmbH, A-4031 Linz, Austria

The chemical imaging and element analysis of various materials by two OES techniques, Laser-induced breakdown spectroscopy (LIBS) and Laser ablation-spark discharge-optical emission spectroscopy (LA-SD-OES), is compared. The nanosecond laser pulses used have mid (few mJ) to low (few µJ) energy. The method LA-SD-OES combines LIBS with electric spark discharge (spark-OES). Two types of discharge circuits are realized. In the first setup a high voltage (2.5 kV) discharge is triggered by a low energy laser pulse applied to the sample. The second setup consists of a modified commercial spark discharge generator routinely used in spark-OES in the steel industry. This device produces well defined electric discharges even without a trigger laser pulse. The optical emission exhibits a higher intensity ratio of singly ionized to neutral spectral lines in LA-SD-OES as compared to LIBS. Moreover, doubly ionized spectral lines not visible with LIBS under usual conditions are observed [1]. The appearance of such lines indicates that the mechanisms of plasma excitation are different in LA-SD-OES and LIBS. A higher sensitivity for minor elements in steel is obtained with LA-SD-OES when singly ionized lines are detected [2]. The poor localization in spark-OES is overcome and spectrochemical imaging with good spatial resolution can be performed with LA-SD-OES (Fig. 1).

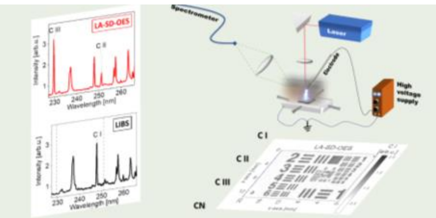


Fig. 1: LIBS and LA-SD-OES for chemical imaging and element analysis.

Acknowledgements
Financial support by the Austrian Research Promotion Agency FFG is gratefully acknowledged (K-project PSSP 871974).

References

[1] Stefan Grünberger, et al, Chemical imaging with Laser Ablation - Spark Discharge - Optical Emission Spectroscopy (LA-SD-OES) and Laser-Induced Breakdown Spectroscopy (LIBS), Optics and Laser Technology 123 (2020) 105944. https://doi.org/10.1016/j.optlastec.2019.105944

[2] Stefan Grünberger, et al, Analysis of minor elements in steel and chemical imaging of micro-patterned polymer by Laser ablation-spark discharge-optical emission spectroscopy (LA-SD-OES) and Laser-induced breakdown spectroscopy (LIBS), Spectrochimica Acta Part B 169 (2020) 105884. https://doi.org/10.1016/j.sab.2020.105884

5.7 Session VI — Thursday, October 7th

11:05 – 11:20	**Daniel Primetzhofer** Photochromic oxygen containing rare-earth hydride compounds: correlating composition, structure and optical performance
11:20 – 11:30	**Company presentation 9**
11:30 – 11:40	**Company presentation 10**
11:40 – 12:10	**Claus Danzer (invited)** The Way of Chemometrics - The Helpful Tool of Analytical Chemistry turns 50

Photochromic oxygen containing rare-earth hydride compounds: correlating composition, structure and optical performance

M. Moro[1], M. Hans[2], D. Moldarev[1,3], K. Kantre[1]. T. Tran[1], S.M. Aðalsteinsson[1], M. Wolff[1],
and D. Primetzhofer[1]

[1] *Dep. of Physics and Astronomy, Uppsala University, Box 526, Uppsala S-75120, Sweden*

[2] *Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, Aachen D-52074, Germany*

[3] *Dep. of Materials Science, MEPhI, Kashirskoe hwy 31, Moscow R-115409, Russia*

Oxygen-containing rare-earth hydrides show reversible photodarkening at ambient conditions, which makes this material class attractive for numerous technological applications [1]. For a detailed understanding of the properties of these material systems, comprehensive characterization of composition and structure of the material at the nanoscale is imperative. In this contribution, we will summarize our efforts in addressing these questions by presenting key results from recent studies.

Specifically, we deduced the phase-diagram of photochromic oxygen containing yttrium-hydride [2] illustrating the composition range for which optically active materials can be synthesized. This data was later confirmed and extended for other rare-earth based compounds with a similar behavior [3].

We have in-detail investigated the dependence of the photochromic behavior on the ambient and confirmed the absence of significant composition changes associated with the change in optical properties [4]. Detailed in-situ characterization during synthesis further solidified our understanding of the life-cycle of the thin film systems [5].

In an effort to understand the origin of the photochromic effect on the nanoscale we performed a combined study using atom-probe tomography, transmission electron microscopy and ion beam analysis which revealed a dual-phase nature of the system as well as a clear linkage of the photochromic effect to residual stress in the film systems [6].

Finally, we have tried to improve the long-term performance of our thin film systems by introducing capping layers [7]. Again, we correlated optical performance with composition, including the capping layers. Results indicate long-term stability and absence of exchange of material with the environment.

[1] T. Mongstad, et al., Sol. Energy Mater. Sol. Cells 95 (2011) 3596.
[2] D. Moldarev et al., Phys. Rev. Mater. 2 (2018) 1
[3] S.M. Aðalsteinsson et al., Nucl. Instr. Meth. Phys. Res. Sect. B 485 (2020) 36
[4] M.V. Moro et al., Sol. Energy Mater. Sol. Cells 201 (2019) 5
[5] K. Kantre et al., Scr. Mater. 186 (2020) 352
[6] M. Hans et al., Adv. Opt. Mater. (2020) 2000822
[7] M.V. Moro et al., submitted

The Way of Chemometrics

The Helpful Tool of Analytical Chemistry turns 50

Claus Danzer[1,2]

[1] *Friedrich Schiller University of Jena, D-07737 Jena*
[2] *Am Friedensberg 4, D-07745 Jena*

What does Chemometrics have to do with a conference on Solid State Analysis? Chemometrics developed into a science discipline in the early seventies. It was already represented at the 1st Conference on Solid State Analysis in 1975 by four contributions, dealing with typical chemometric topics: optimization, detection limit, computer simulation of spectra, and information theory.

Although Chemometrics has a fixed date of birth (Svante Wold created the name in 1971), important developments had preceded. Modern multivariate statistical methods had been developed since the 30s [1], and statistical evaluation was introduced into Analytical Chemistry in the 40s and 50s [2,3]. But in the 60s/70s three important developments took place:

(a) analytical methods had been improved and became able to produce large amounts of data,

(b) computers found the way into the analytical laboratories, and

(c) more and more complex interrelationships had to be investigated in basic research, industrial development, and environmental research.

Chemometrics, defined as "… chemical discipline that uses mathematical and statistical methods to design or select optimal procedures and experiments, and to provide maximum chemical information by analyzing chemical data" [4] not only offered solutions for such problems but could support the interactions between these developments. First spectacular results could clarify issues in criminal cases (identification of paper types) and food authenticity (origin of olive oil). But soon chemometric methods have been used in solid state analysis, such as testing homogeneity of solid samples, investigation of concentration gradients and profiles in solids, optimization of products and procedures, and so on. Today, several methods depend on chemometrics because of their immense amount of data (3D techniques, coupled methods).

Today chemometric tools are a natural part of modern analytical procedures and therefore of chemical education. The basic principles of chemometrics meanwhile can be found in other scientific disciplines (e.g. biometrics, technometrics) and in our daily life, too. Optimization, control and monitoring of washing machines, refrigerators, cars and other everyday devices are based on the same principles as that of analytical instruments, where methods of artificial intelligence are increasingly used. Consequently, chemometrics moves closer to Big Data Science, which is the more general field of data handling and evaluation covering almost all areas of science, technology, sociology, and politics.

[1] R.A. Fisher, *The Design of Experiments*, Oliver & Boyd, Edinburgh 1935
[2] H. Kaiser, Spectrochim. Acta **3** (1947) 40
[3] K. Doerffel, *Statistik in der analytischen Chemie*, Deutscher Verlag für Grundstoffindustrie, Leipzig 1960
[4] D.L. Massart et al, Chemometrics and intelligent laboratory systems, Vols. 1ff. Inside cover

5.8 Session VII — Thursday, October 7th

13:00 – 13:15	**Sven Kayser** Hybrid SIMS: New adaptive ion injection system (AIIS) for improved repeatability of quantitative Orbitrap SIMS measurements
13:15 – 13:30	**Korbinian Heimler** Figures of merit of a tabletop 3D-µXRF spectrometer and its application for nondestructive depth-resolved element analysis
13:30 – 13:45	**Parul Jain** High Resolution Reflection Microscopy via Absorbance Modulation
13:45 – 13:55	**Company presentation 11**
13:55 – 14:05	**Company presentation 12**
14:05 – 14:15	**Company presentation 13**

Hybrid SIMS: New adaptive ion injection system (AIIS) for improved repeatability of quantitative Orbitrap™ SIMS measurements

S. Kayser[1], A. Pirkl[1], H. Arlinghaus[1], A. Franquet[2], V. Spampinato[2]

(1) IONTOF GmbH, 48149 Muenster, Germany
(2) MCA, IMEC, Kapeldreef 75, 3001 Leuven, Belgium

To boost the performances of the next generation transistors, new materials and device architectures have been investigated in the semiconductor industries[1]. In this context, strained-Ge and SiGe channel FET's have received high interest due to their excellent hole mobility[2] and recently obtained results have encouraged the semiconductor device industry to incorporate them in its latest FinFET technology[3,4]. As a consequence, characterization techniques have to provide chemical information and high sensitivity with a spatial resolution compatible with the device structure of down to 10 nm.

During the last years we demonstrated that the improved mass resolution of the Hybrid SIMS[5] instrument, which integrated the Orbitrap™ mass analyzer into a SIMS instrument, has been extremely beneficial for advanced semiconductor structure analysis. Especially the application of the so-called Self-Focusing SIMS (SF-SIMS)[6,7] approach opened up new possibilities for the analysis of next generation devices.

Despite the very encouraging first results it also become clear that, depending on the individual analytical conditions, the Orbitrap™ mass analyzer can suffer from oversteering and saturation effects. These effects limited the repeatability, absolute quantification and matching to other analytical techniques. To overcome this limitation, we developed a unique adaptive injection system for the Orbitrap™ mass analyzer. The new system automatically adapts the number of injections (i.e., Orbitrap™ sprctra per frame) or number of pixels within the field of view to avoid oversteering and saturation effects in real time.

In this presentation we will explain the working principle, apply new adaptive ion injection system to different sample systems and report the advances for the measurement repeatability, the quantification and the matching to other analytical techniques.

[1] S. Datta, *Electrochem*. Soc. Interface **22** 41 (2013).
[2] J. Mitard et al., *Jap. J. Appl. Phys.* **50** 04DC17-1 (2011).
[3] M.J.H. van Dal et al., *IEEE International Electron Devices Meeting (IEDM)* 23.5.1- 23.5.4 (2012).
[4] R. Pillarisetty, *Nature* **479** 324 (2011).
[5] MK Passarelli, A Pirkl, et al., *Nature Methods*, **14**, 1175–1183 (2017)
[6] A. Franquet et al., *Applied Surface Science* **365**, 143-152 (2016).
[7] A. Franquet et al., *J. Vac. Sci. Technol.* B **34**(3), May/Jun (2016).

Figures of merit of a tabletop 3D-µXRF spectrometer and its application for nondestructive depth-resolved element analysis

Korbinian Heimler, Bastian Hansel, Carla Vogt

TU Bergakademie Freiberg, Institute of Analytical Chemistry, 09599 Freiberg, Germany

Tabletop 3D-µXRF unites have been introduced only recently and are the subject of studies by various research groups during the last years. The in-depth sensitivity of the spectrometer is based on a defined three-dimensional probing volume which is formed by the confocal arrangement of two polycapillary lenses in the excitation and the detection channel (Fig. 1). The spectrometer used in this study is a modified commercial tabletop µXRF spectrometer (M4 TORNADO) by *Bruker Nano GmbH*, the setup is based on research results obtained by the Kanngießer group at TU Berlin.[1] The spectrometer is equipped with a 30 W Rh micro focus tube, operating up to 50 kV and 600 µA. The commercial µXRF setup is equipped with a polycapillary lens with a spot size ≤ 20 µm (Mo Kα) for X-ray focusing and a 30 mm^2 silicon drift detector. Due to the modification a second polycapillary lens was installed perpendicular to the first one in front of a 60 mm^2 silicon drift detector.

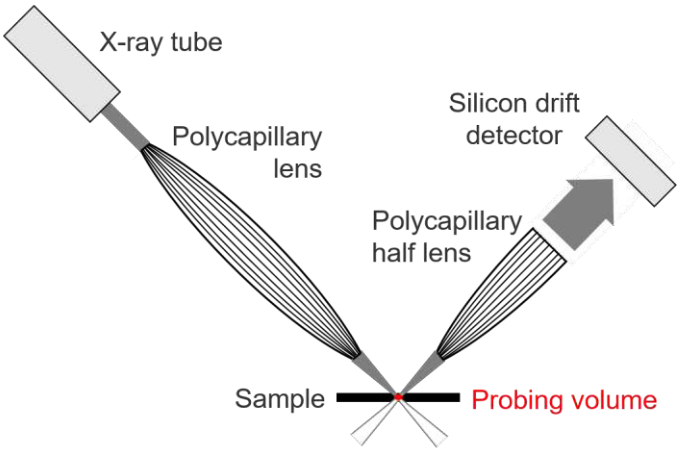


Figure 1. Schematic representation of the perpendicular arrangement of the polycapillary lenses and the thereby formed probing volume (red).

For the validation of the 3D-µXRF setup different parameters, like penetration depth, matrix effects, absorption effects and probing volume dimension, have been evaluated using inhouse stratified polymer standards with varying concentrations of selected elements. Afterwards the technique was applied to samples from different fields of application. To investigate antibacterial effects sponges and spongin scaffolds have been investigated, where the 3D-µXRF enabled to show the three-dimensional distribution of copper within a copper-containing wastewater treated sponge. Another important field of applications is the 3D analysis of minerals, especially with respect to the characterization of mineral inclusions. Due to the non-destructive character of the 3D-µXRF chemical phase composition analysis and corresponding phase identification is provided while maintaining the integrity of the isolated mineral inclusion. Other promising fields of application for 3D-µXRF are archaeometry at historical objects and 3D analysis of plant tissues.

References:

[1] I. Mantouvalou, T. Wolf, C. Seim, V. Stoytschew, W. Malzer, B. Kanngießer, Anal. Chem., 9774-9780, 86 (2014).

High Resolution Reflection Microscopy via Absorbance Modulation

Parul Jain[1], Viktor Udachin[2], Sven Nagorny[3], Claudia Geisler[1], Jörg Adams[4], Andreas Schmidt[3],
Christian Rembe[5], Alexander Egner[1]
[1] *Department of Optical Nanoscopy, Institut für Nanophotonik, Göttingen, Germany*
[2] *Clausthal Center of Materials Technology, TU Clausthal, Clausthal-Zellerfeld, Germany*
[3] *Institut für Organische Chemie, TU Clausthal,Clausthal-Zellerfeld, Germany*
[4] *Institut für Physikalische Chemie, TU Clausthal,Clausthal-Zellerfeld, Germany*
[5] *Institute of Electrical Information Technology, TU Clausthal, Clausthal-Zellerfeld, Germany*

Properties of composite materials are strongly influenced by their microstructural features. The size of these features can vary from a few nanometers to several micrometers. Optical microscopy, especially reflection microscopy, is one of the primary tools for the morphological characterization in material science. However, due to the wave nature of light, it cannot be focused to an arbitrarily small spot, thereby limiting the resolution of optical microscopes to the diffraction limit that is not sufficient for the analysis of these materials. Stimulated emission depletion (STED) microscopy, which is so far mostly used in life science imaging, surpasses the diffraction limit by exploiting the properties of fluorescent markers [1]. The concept of STED has been successfully applied in optical lithography and microscopy as a technique called absorbance-modulation [2]. In absorbance modulation, a layer of photochromic molecules, referred to as absorbance modulation layer (AML), is coated on the sample that can change their absorption properties when illuminated with light of different wavelengths. Thus, they can be reversibly switched between opaque and transparent configuration in a controlled manner and consequently, increase the resolution. This technique of absorbance modulation when applied for imaging is called absorbance modulation imaging (AMI). AMI in transmission microscopy has certainly demonstrated a high lateral resolution [3]. However, AMI in reflection microscopy has not yet been demonstrated, despite its potential to analyze a much wider range of materials including opaque, transparent, and even metallic samples.

Theoretical study on AMI in confocal reflection microscopy predicts that imaging beyond the diffraction limit is indeed possible [4]. Here we experimentally validate this prediction by demonstrating one-dimensional AMI. When a one-dimensional grating sample, coated with a thin layer of AML, is illuminated with a Gaussian-shaped focus superposed with a 1-D pattern (similar to transverse laser mode 01), a dynamic aperture is generated within the AML. The size of this effective aperture is below the diffraction limit which allows to achieve sub-wavelength resolution. Further resolution improvement is possible by optimizing the illumination scheme and tailoring the optical absorption response of the AML. The one-dimensional AMI that we demonstrate here can be easily extended to two dimensions which would facilitate high resolution optical imaging of microstructural features.

References:

[1] S. W. Hell, J. Wichmann, Opt. Letters, Vol. 19, No. 11 (1994).
[2] R. Menon, H. I. Smith, J. Opt. Soc. Am., A 23, 2290 (2006).
[3] H.Y. Tsai, S. W. Thomas, III, R. Menon, Opt. Express, Vol.18, No. 15 (2010).
[4] R. Kowarsch, C. Geisler, A. Egner, C. Rembe, Opt. Express, 26(5), p. 5327–5341 (2018).

5.9 Poster session II — Thursday, October 7th

P II.01	**Michel Werner** Influence of transfer and transformation processes on the service life of solid lubricated rolling bearings
P II.02	**Andrea Berlich** Penetration of ink components into paper - a Raman microscopic study
P II.03	**Michael Wahl** Combined XRD and Raman analysis for the study of cobalt-based alloys under high temperature friction load
P II.04	**Thomas Ruf** Assignment of dielectric contributions in multiferroic yttrium iron garnet - barium titanate heterostructures by Impedance Spectroscopy
P II.05	**Florian Pape** Investigations on the influence of metalworking fluids (MWFs) on friction and tribo-film formation
P II.06	**Apoorva Sharma** Control of magneto-optical properties of cobalt-layers by adsorption of α-helical polyalanine self-assembled monolayers
P II.07	**Reza Sharif** Investigation of metallurgical properties of electro-discharge textured steel working roll surfaces
P II.08	**Maria Toma** Characterization of ZnO, Ga-doped ZnO, and Nd+Ga doped ZnO thin films synthesized by RF magnetron sputtering technique
P II.09	**Mareike Loh** Analysis of corrosion layers on biodegradable magnesium alloys for medical applications
P II.10	**Yevhenii Havryliuk** The complex Raman characterization of Cu2ZnSnS4 nanocrystals - a perspective material for photovoltaic application
P II.11	**Fabian Teichert** Structural and electronic investigations of Bismuth multilayers
P II.12	**Mariella Denk** Surface resonant Raman scattering from Cu(110)
P II.13	**Milekhin Ilya** Tip-Enhanced Raman Scattering of CdSe-CdS Nanoplatelets on Plasmonic Substrates
P II.14	**Holger Schwarz** CoCrFeNi High-Entropy Alloy Thin Films Synthesized by Magnetron Sputter Deposition from Spark Plasma Sintered Targets
P II.15	**Niels Rösch** Electronic Structure of [(SnSe)1+δ]m(TiSe2)n investigated by Photoelectron Spectroscopy

P II.16	**Raana Hatami** Physical Characterization of Metal Nanoparticle/TiO 2 Composite Thin Films
P II.17	**Raana Hatami** Photocatalytic Antibacterial Activity Based on Nanocomposites of Ag Nanoparticles and TiO 2
P II.18	**Aravind Pushpahasan** AFM Characterization of TiO2 Thins Film Deposited using Reactive Magnetron Sputtering
P II.19	**Stefan Emrich** Surface analysis on solid lubricated ball bearings
P II.20	**Fabian Göhler** Investigating Interlayer Interactions by Controlling Nanoarchitecture in Layered Heterostructures
P II.21	**Mahfujur Rahaman** Plasmonic hot electron induced layer dependent Fröhlich interaction in InSe
P II.22	**Osadebamwen Sandra Omoragbon** Preparation of thin TiO2 films by DC magnetron sputtering for photocatalytic applications

Influence of transfer and transformation processes on the service life of solid lubricated rolling bearings

Werner M.[1], Emrich S.[2], Sauer B.[1], Kopnarski M.[2]

[1] Institute of Machine Elements, Gears and Transmissions, TU Kaiserslautern
[2] Institute for Surface and Thin Film Analysis IFOS, TU Kaiserslautern
Corresponding author: michel.werner@mv.uni-kl.de

Solid lubricated rolling bearings are used wherever external conditions do not permit conventional lubrication with grease or oil. In order to reduce friction in the bearings and thus increase the service life, various solids are used for lubrication. In this contribution, molybdenum disulfide (MoS_2) is used as a solid lubricant due to its lamellar structure, which allows the individual atomic layers to slide on each other, resulting in friction reduction of surfaces coated with MoS_2. Unlike other solid lubricants such as graphite, the lubrication properties of MoS2 improve in high vacuum, which is another selection criterion for this material [1]. In addition to the possibility of initial coating of the bearing components with solid lubricant, the cage can also be used as a lubricant depot [2]. In order to investigate the material flows between all components in frictional contact and their dependence on various operating parameters, the bearings are loaded under high vacuum, heated to 300°C. The bearing components are being examined afterwards. Figure 1 below shows the wear model used for this analysis, which was developed in [3], as well as the structure of the rolling bearing used.

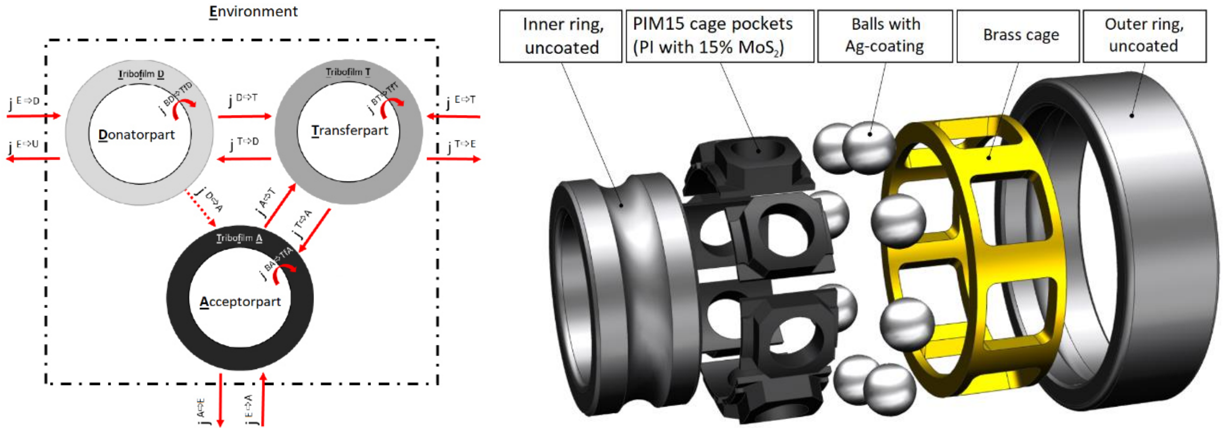


Figure 1: Left: Tribological model of the rolling bearing with material flows and transfer layers; Right: Structure of the bearing used.

The objective of the study is to validate the tribological model shown above and to determine the transfer factors that describe the material flows between the components of the bearing and can thus be used to estimate the service life of the bearing for known load cases. Here, in addition to frictional energy and mass change, the changes in the transfer layers are considered with regard to structure and material composition. In order to distinguish the influence of the operating conditions from that of the individual load cases, preliminary investigations were also carried out.

[1] Birkhofer, H. and Kümmerle, T., 2012, Feststoffgeschmierte Wälzlager. Einsatz, Grundlagen und Auslegung. Berlin Heidelberg: Springer Vieweg.

[2] Marquart, M.; Wahl, M.; Emrich, S.; Zhang, G.; Sauer, B.; Kopnarski, M.; Wetzel, B.: Enhancing the lifetime of MoS2-lubricated ball bearings, Wear, Volume 303, Issues 1–2, 15 June 2013, S.169-177, ISSN 0043-1648

[3] Pörsch, S.: Ansätze zur erweiterten Lebensdauerberechnung feststoffgeschmierter Wälzlager; Diss. Technische Universität Kaiserslautern (2019)

Penetration of ink components into paper – a Raman microscopic study

Alexandra Hodes[1], Simon Hamblyn[1], Ulrike Käppeler[1], Andrea Berlich[2], Matthias Schmidt[3], Lutz Engisch[1]

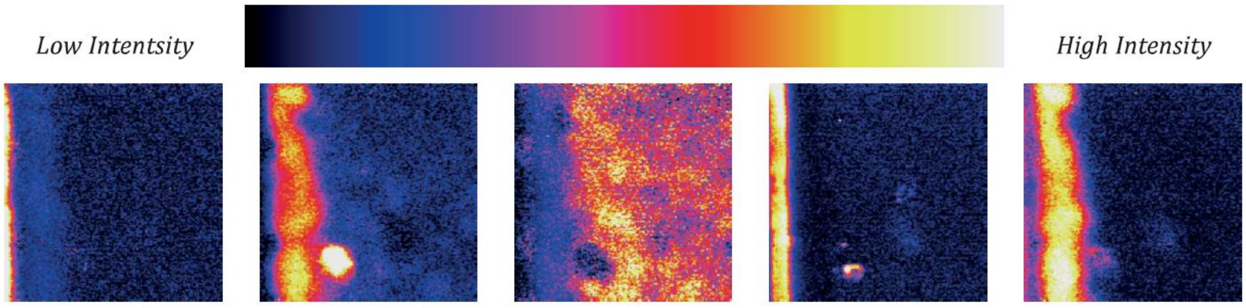
[1] Fakultät für Informatik und Medien, IP^3-Institute for Printing, Processing and Packaging

[2] Mathematisch-Naturwissenschaftliches Zentrum,
Hochschule für Technik, Wirtschaft und Kultur Leipzig, Karl-Liebknecht-Straße 132, 04277 Leipzig

[3]ProVIS – Zentrum zur Visualisierung biochemischer Prozesse auf zellulärer Ebene, Helmholtz-Zentrum für Umweltforschung GmbH – UFZ, Permoserstraße 15, 04318 Leipzig

Although printing methods have been known since about 500 years the underlying molecular processes are not completely understood yet. Caused by special applications such as printing of functional layers knowledge about migration processes of ink components and their distribution within the substrate is required. Furthermore, mineral oils that are used as solvents in printing inks are thought to be one possible source of contamination of food. Since such ink components like solvent or binder are colourless in contrast to the pigment and their chemical structure is similar to the paper it is challenging to determine their depth distribution. Vibrational spectroscopy with its structural sensitivity could be one tool to overcome these difficulties.

First studies have been done using FTIR microscopy. However, the resolution of the IR microscope as well as the low intensity of spectra did not allow depth profile analysis along cross sections of printing samples. The application of the ATR crystal failed because of the soft substrate. Raman microscopy, however, provided a resolution down to about 1 µm and could distinguish between the paper substrate, its $CaCO_3$ coating, the pigment and the mineral oil as ink components. The filtered images at distinct wavenumbers representative for each component (see picture) clearly demonstrate that the the mineral oil migrates into the paper if it is not coated but is trapped in the coating layer which prevents further migration [1].



PTFE-Film (716 cm^{-1} to 750 cm^{-1}) | Mineral Oil (93 cm^{-1} to 98 cm^{-1}) | Raw Paper (1101 cm^{-1} to 1130 cm^{-1}) | Pigment (1517 cm^{-1} to 1552 cm^{-1}) | Paper Coating (270 cm^{-1} to 310 cm^{-1})

Filtered Raman microscopic images of the distribution of ink components in a cross section of a coated and printed paper embedded into a PTFE foil (150x150 µm²)

[1] A. Hodes et al. J. Print Media Technol. Res. 31, 9(2020)

Combined XRD and Raman analysis for the study of cobalt-based alloys under high temperature friction load

Wahl M.[1], Brodyanski A.[1], Lösch J.[1], Kopnarski M.[1], Loos P. [2], Beau P. [2], Kolmer P.[2]

[1] Institut für Oberflächen- und Schichtanalytik IFOS GmbH,
Trippstadter Str. 120, 67663 Kaiserslautern
[2] Volkswagen Aktiengesellschaft, Group Innovation,
Brieffach 011/1777-4, 38436 Wolfsburg
Corresponding author: wahl@ifos.uni-kl.de

For high-temperature applications with metallic solids subjected to adhesive stress in the frictional contact (i.e. without lubricant), cobalt-based alloys known as “Tribaloy” are often used. In the temperature range around 800° C, these materials show a highly temperature-dependent tribological behavior. The aim of the analytical work, which will be reported on, was to contribute to the understanding of the temperature- and friction-driven processes involved.

For this purpose, the corrosion and / or oxidation products arising in the near surface area were analyzed by means of Raman microscopy and X-ray diffractometry. Our results show that, depending on the temperature and test time, oxides are formed on the surface of the Tribaloy sprayed coatings, which can be assigned to the following compound groups: (Co-) Molybdates, Co (II) oxide and Co (II, III) oxide. A non-oxidic Co3Mo phase is also partially formed. These components of alloy also arise when the surfaces are stressed in-situ by sliding friction. The formation of a well adhering top layer from these components, which occurs at a temperature level of 800° C, is obviously responsible for the favorable wear behavior observed in this Temperature range. Below this temperature level, only comparatively little molybdate and Co oxide are detected. At 100° C, the alloy components mentioned were only detectable under frictional loading and with significantly lower phase contents. In the high temperature range around 800° C, the frictional load evidently leads to the formation of cobalt oxides being increasingly present in the divalent form, while Raman spectra without friction load still show the Co (II, III) mixed valence as the predominant form. This indicates that the respective temperature level necessary for the oxidation or reduction of Co is lowered by friction-induced processes. On the basis of the analytical results found so far, measures are to be derived in the future that lead to a better or optimized pretreatment of the components for high-temperature applications.

Assignment of dielectric contributions in multiferroic yttrium iron garnet - barium titanate heterostructures by Impedance Spectroscopy

Thomas Ruf[1], Holger Hochmuth[2], Stefan Merker[3], Roberto Köferstein[4], Stefan G. Ebbinghaus[4], Michael Lorenz[2], Reinhard Denecke[1]

[1] *Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstraße 2, D-04103, Leipzig*

[2] *Felix-Bloch-Institut für Festkörperphysik, Universität Leipzig, Linnéstraße 5, D-04103, Leipzig*

[3] *Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103, Leipzig*

[4] *Institut für Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120, Halle*

Measurements of the interaction between different compounds in a solid-state heterostructure are a demanding task. The technological relevance of such studies is the introduction of new functionalities by the heterostructure. A possible scenario is the combination of ferroic compounds to couple their ferroic orders, such as ferrimagnetism and ferroelectricity, resulting in an electric-field control of magnetism or magnetic-field control of ferroelectricity.[1]

In this work, heterostructures of yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG, ferrimagnetic) and barium titanate $BaTiO_3$ (BTO, ferroelectric) are synthesized by Pulsed Laser Deposition as 2-2 (i.e. layered) multiferroic composites. Although the nominal structural compatibility between the two compounds seems to be low concerning the structure type and related symmetry, thin BTO films (200-500 nm) with preferential (110) orientation on single crystalline YIG(100) substrates can be achieved with decent crystallinity as shown by X-ray Diffraction. X-ray Photoelectron Spectroscopy of these BTO films show Ba-rich surface compositions compared to a standard sample of BTO polycrystalline powder, possibly implying Ba^{2+}-segregation due to the low structural compatibility.

Impedance Spectroscopy or Dielectric Spectroscopy using different electrode geometries allows to distinguish different resistive, capacitive and inductive components and to assign them to regions of homogeneous dielectric behaviour. The assignment is possible as the dielectric contributions of these regions are characterized by different relaxation frequencies and their physical parameters show distinct temperature dependencies.[2] In this way, information about interfaces can be obtained. As an example, dielectric contributions attributed to YIG interfaces exhibit a change in the slope of Arrhenius plots of electrical resistivity at the Curie temperature of YIG (~280 °C). Additionally, a "bulk" component reflects the dielectric anomaly of BTO at its structural phase transition (~ 120 °C) by distinct changes of capacitance in this temperature region. The latter component also shows a very slight kink in the capacitance-vs-T curve at the YIG phase transition temperature, but the interpretation as evidence of coupling is speculative. Further Impedance Spectroscopy measurements, also under application of a magnetic field, may clarify this point.

[1] J.-M. Hu, L.-Q. Chen, C.-W. Nan, Adv. Mater., 15-39, 28 (2016)

[2] J.T.S. Irvine, D.C. Sinclair, A.R. West, Adv. Mater., 132-138, 2 (1990)

Investigations on the influence of metalworking fluids (MWFs) on friction and tribo-film formation

Florian Pape[1], Haichao Liu[1], Dennis Mallach[2], Dieter Lipinsky[2], Heinrich F. Arlinghaus[2], Gerhard Poll[1]

[1] *Leibniz University Hanover, Institute of Machine Design and Tribology, Hanover, Germany*

[2] *Westfälische Wilhelms-Universität Münster, Physikalisches Institut, Münster, Germany*

Metalworking fluids (MWFs) are of great importance in machining. They dissipate heat generated during machining and reduce the friction between interfaces of chip-tool sliding contact and tool-workpiece contact. Additives are added for these purposes in MWFs, in addition to the base oil and the water phases. Typically, defoamers, biocides, emulsifiers, corrosion protection additives, high-pressure additives are used. These additives form protective layers on the component surfaces, which would help to improve the surface quality and to save energy costs in the machining processes. To gain knowledge on the rheometric and tribological properties of the cutting fluid is of main importance to optimize metal cutting processes. The resulting surface and protective film on chips is analyzed with the help of ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry). Figure 1 shows the formation of a sulphur-containing film on a chip surface generated with MWF (Fig. 1a) compared to the signals on a dry generated chip surface (Fig. 1b). The current work investigates the influence of MWFs on friction and tribo-film formation using a milli tribometer. With the tribological investigations, the friction between a ball and a metal plate is investigated under oscillating sliding motion using a pin-on-plate setup. A heatable tank (20°C-100°C) is used, which is filled with MWFs. The friction is recorded as a function of temperature, ball materials (100Cr6, ceramics) and loads. It is shown that the temperature has a significant influence on the frictional properties of the surfaces with MWFs.

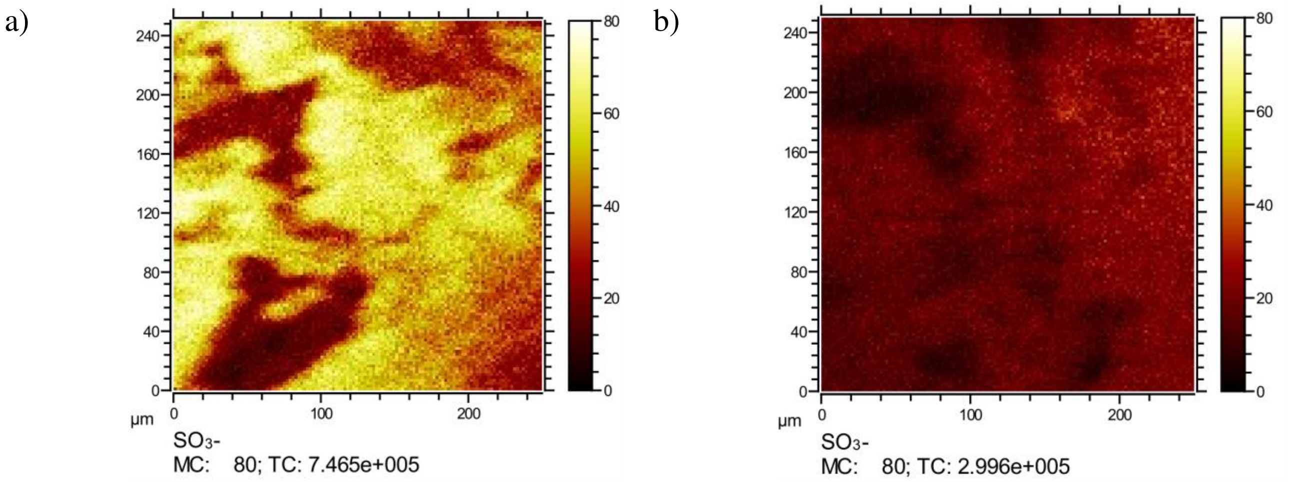


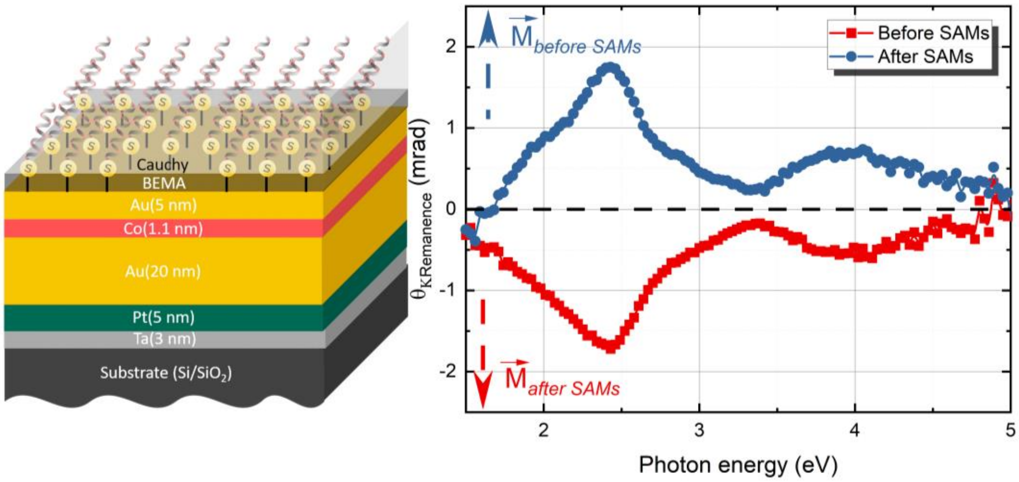
Fig. 1: ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) image, a) sulphur-containing film on a chip surface generated with MWF, b) signals on a dry generated chip surface.

Control of magneto-optical properties of cobalt-layers by adsorption of α-helical polyalanine self-assembled monolayers

A. Sharma[1], P. Matthes[2], I. Soldatov[3], S. S. P. K. Arekapudi[1], B. Böhm[1], M. Lindner[1], O. Selyshchev[1], N. T. N. Ha[1], M. Mehring[4], C. Tegenkamp[1], S. E Schulz[2], D. R. T. Zahn[1], Y. Paltiel[5], O. Hellwig[1] and G. Salvan[1]

[1] Institute of Physics, Chemnitz University of Technology, 09126 Chemnitz, Germany
[2] Fraunhofer Institute for Electronic Nanosystems, 09126 Chemnitz, Germany
[3] Leibniz Institute for Solid State and Materials Research (IFW) Dresden, 01069 Dresden, Germany
[4] Institute of Chemistry, Chemnitz University of Technology, 09126 Chemnitz, Germany
[5] Department of Applied Physics, Hebrew University of Jerusalem, Jerusalem, Israel

Recently, it was demonstrated that helical polyalanine molecules possess spin-polarising properties, allowing only electrons with a well-defined spin direction to pass along the chain, depending on the handedness of the molecule as well as on the direction of the electric field acting on the electron within the chiral molecule.[1] Various studies confirmed the spin-dependent properties using different experimental approaches. This phenomenon is called chirality-induced-spin-selectivity (CISS) and has the potential to open a new perspective for organic spintronic devices.[2] In addition to the CISS effect, it was recently reported that the adsorption of the pure enantiomers of α-helical polyalanine (AHPA-L or AHPA-D) on a gold-covered ferromagnetic thin film could switch the out-of-plane magnetisation of the ferromagnetic thin film in a direction dictated by the chiral nature of the enantiomer.[3] This effect was named as magnetism induced by the proximity of adsorbed chiral molecules (MIPAC). The same molecules were used to demonstrate the local magnetisation in gold-capped cobalt thin films by using the exchange interaction between the polyalanine molecules adsorbed on an atomic force microscopy (AFM) tip apex and the sample.[4] On the other hand, it was reported that the enantiomers of chiral molecules selectively chemisorb to an Au-capped ferromagnetic thin film substrate depending on the magnetisation, an effect which was further exploited to separate the enantiomers from their racemic mixture.[5] Thus, it is of utmost importance to understand the self-assembling of chemisorbed helical molecules at the macro-scale (mm-range) and its influence on the magnetic properties of the substrate. In this work, we used spectroscopic ellipsometry in combination with magneto-optical Kerr effect spectroscopy and wide-field magneto-optical Kerr effect microscopy to provide the first magneto-optical experimental characterisation of α-helix polyalanine-L (AHPA-L) SAMs on ferromagnetic thin films capped with a noble metal. The result obtained from this study were recently published in ref.[6].



1 P. C. Mondal, *et al.*, *Acc. Chem. Res.*, 2016, **49**, 2560–2568.
2 R. Naaman, *et al.*, *Nat. Rev. Chem.*, 2019, **3**, 250–260.
3 O. Ben Dor, *et al.*, *Nat. Commun.*, 2017, **8**, 14567.
4 A. Ziv, *et al.*, *Adv. Mater.*, 2019, **31**, 1904206.
5 K. Banerjee-Ghosh, *et al.*, *Science*, 2018, **360**, 1331–1334.
6 A. Sharma, *et al.*, *J. Mater. Chem. C*, 2020, **8**, 11822–11829.

Investigation of metallurgical properties of electro-discharge textured steel working roll surfaces

Reza Sharif[1, 3], Manuel Winter[1], Peter Oberhumer[2], Benjamin Kieberger[1], Josef Faderl[1],
Heiko Groiss[2], and Johannes D. Pedarnig[3]

[1]*Voestalpine Stahl GmbH, voestalpine Straße 3, 4020 Linz, Austria*

[2]*Christian Doppler Laboratory for Nanoscale Phase Transformations, Center of Surface and Nanoanalytics, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria*

[3]*Institute of Applied Physics, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria*

In the automotive industrial market, the surface properties of galvanized steel used for the outer body part are very important in terms of micro-geometry (roughness, peaks count, and waviness) as there is a direct correlation between the tribological properties, end-user paint appearance, and the surface features. For this reason, we need a specific surface pattern or texture on the steel work roll surfaces, which creates the needed surface topography during the skin pass process. Such processes are used as a finishing step for hot and cold-rolled steel strips for outer auto bodies or other steel products [1, 2, and 3]. Electro-discharge texturing (EDT) of the working roll for skin pass process is the most commonly used technique in the steel industry. EDT is an adaptation of the well-known electrical discharge machining (EDM) in which the removal of material is carried out by electrical discharges while there is a small gap between the work roll and tool electrodes immersed in a dielectric liquid [4].

In this work, the effect of different electrical and mechanical EDT parameters on the surface integrity of the textured working roll is presented. Experiments were conducted on an industrial steel working roll with the defined process parameters established formerly for the skin pass process. The investigations were carried out by different microscopic and spectroscopic methods, and our results show that the changing parameters of the EDT process have a significant impact on the textured working roll's physical and chemical surface properties.

[1] K. Kitagawa, K. Michishita, Y. Koga, M. Kawano, Nippon Kokan Tech. Rep, 40-46, 33(1981)

[2] O. Pawelski, W. Rasp, W. Zwick, H-J. Nettelbeck, K. Steinhoff, J. Mater. Process. Technol, 215-222, 45(1994)

[3] E. Evin, M. Tomas, J. Kmec, Materials, 1223, 13(2020)

[4] N. Mohri, T. Tani, Second International Conference on Multi-Material Micro Manufacture, Elsevier, 23-26, 4(2006)

Characterization of ZnO, Ga-doped ZnO, and Nd+Ga doped ZnO thin films synthesized by RF magnetron sputtering technique

M. Toma[1,*], R-A.Domokos[1], D. Marconi[1,2], C. Lung[1], and A. Pop[1]

[1]Babes-Bolyai University, Physics Faculty, M. Kogalniceanu No.1, 400084, Cluj-Napoca, Romania

[2]Department of Molecular and Biomolecular Physics, National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania

[*] *e-mail:* mary02.toma@gmail.com

Over the last decade, zinc oxide (ZnO) thin films have drawn considerable interest due to being an excellent n-type semiconductor with a wide and direct band gap (3.37 eV), high electron mobility and large exciton binding energy. However, pure ZnO thin films show weak optical features that usually occur from point defects (such as oxygen vacancies or interstitial Zn). As a result, adding dopants in the ZnO host material plays an important role in improving the structural, optical and electrical properties **[1]**. In this direction, gallium oxide (Ga_2O_3) and neodymium oxide (Nd_2O_3) were incorporated into the thin film structure and prepared by RF magnetron sputtering technique. To investigate the changes upon crystallographic structure of the thin films, X-ray diffraction (XRD) analysis was performed. Raman spectra highlight that doping with Ga (GZO) and co-doping with Ga+Nd (Nd-GZO) introduce $2B_{1(low)}$ band and leads to the increase of intensity for LO's band, suggesting the increase of oxygen vacancies. Atomic force microscopy (AFM) images revealed variations in the surface morphology with uniformly distributed spherical grain structures and optical transmittance measurements showed a transparency in the visible range around 85%. Temperature dependent resistivity curves $\rho(T)$ were measured for the GZO and Nd-GZO films showing a semiconducting behavior transition **[2]** between 150 K and 180 K.

Keywords: doped zinc oxide, RF magnetron sputtering, XRD, AFM, Raman, Transmittance

References:

[1] M. Toma, D. Marconi, Mariana Pop, C. Lung, and A. Pop, Analytical Letters, p. 2227-2238, vol. 52, no. 14, (2019).

[2] M. Nistor, E. Millon, C. Cachoncinlle, W. Seiler, N. Jedrecy, C. Hebert, and J. Perrière, Journal of Physics D: Applied Physics, p. 195103, vol. 48, no. 19, (2015).

Analysis of corrosion layers on biodegradable magnesium alloys for medical applications

Mareike Loh[1], Anika Rogoll[1], Korbinian Heimler[1], Petra Maier[2], Carla Vogt[1]

[1] Technical University Bergakademie Freiberg, Institute for Analytical Chemistry
[2] University Stralsund, Department of Mechanical Engineering

Implants are introduced into the body by surgery to replace certain functions of the organism. Temporary implants (e.g. screws, plates, nails) often have to be removed after healing or in case of inflammatory reactions [1], [2]. In recent years, efforts have been made in medical technology to develop biocompatible, degradable implants that decompose in the organism after they have fulfilled their function [2]. Magnesium is suitable as a biodegradable implant because it is degraded by corrosion in body fluids, has similar material properties to human bone and stimulates the growth of new bone tissue [3], [4].

The mechanical properties, microstructure, and corrosion behavior of the magnesium alloy *Resoloy*® (10 ω% Dy, 1 ω% Nd, 1 ω% Zn, and 0.2 ω% Zr) have already been characterized by MAIER *et al.* [5]. Therefore, the focus of this investigation was on the characterization of the corrosion layer in Ringer's and Hanks' Balanced Salt Solutions (HBSS). The composition of the corrosion products provides information for the biological compatibility and the resistance of the samples in body fluids. Solid-state spectroscopic methods (SEM-EDX, FT-IR, RAMAN spectroscopy and XRD), ICP-MS and ICP-OES were used to analyze the corrosion products formed. The site-dependent elemental distribution in the corrosion layer was based on mappings and linescans using µXRF, SEM-EDX and LA-ICP-MS.

The *in vitro* corrosion experiments showed that both the corrosion progress and the composition of the products depend on the composition of the physiological medium. The corrosion products in Ringer's solution consist mainly of magnesium hydroxide, calcium carbonate and oxidic compounds of the alloying elements. In contrast, the corrosion layer of the samples corroded in HBSS has a depth-dependent composition, where the outer layer consists mainly of calcium phosphate. This is followed by an inner corrosion zone in which the alloying elements (except Mg) presumably accumulate in the form of oxides and hydroxides compared to bulk material.

A comparison to the degradation of alloys with similar composition but reduced concentrations of individual alloying components was performed to understand the degradation process and to further develop alloys with optimum degradation behavior for medical applications.

[1] S. Hein und P. Imgrund, Innovative Technik – Neue Anwendungen, 53, 1-2 (2012).
[2] S. V. Dorozhkin und M. Epple, Angew. Chem., 114, 3260-3277 (2002).
[3] Autorenkollektiv, Magnesium Taschenbuch, Düsseldorf: Aluminium-Verlag, (2000).
[4] K. Y. Chiu, M. Wong, F. T. Cheng und H. Man, Surf. Coat. Technol., 202, 590-598 (2007).
[5] P. Maier, A. Steinacker, B. Clausius und N. Hort, JOM, 72, 1870-1879 (2020).

The complex Raman characterization of Cu_2ZnSnS_4 nanocrystals – a perspective material for photovoltaic application

Yevhenii Havryliuk[1,2], Volodymyr Dzhagan[2], Nazar Mazur[2] Oleksandra Raievska[1], Oleksandr Selyshchev[1], Dietrich R.T. Zahn[1]

[1] *Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany*
[2] *V.E. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, Kyiv, Ukraine*

In recent decades, an increasing demand for energy, especially autonomous sources, has intensified the research on renewable sources, in particular photovoltaics (PV). An exponential growth of the predominantly silicon-based PV market in the last years has also stimulated search for affordable, non-toxic materials with high absorption coefficient in the entire solar range, which could help to reduce the costs and increase the efficiency of novel solar cells of third-generation PV. In this context, Cu_2ZnSnS_4 (CZTS) and related compounds form a family of new promising photovoltaic materials [1]. One of the advantages of these materials is that they can be obtained in the form of nanocrystals (NCs) by “green” low-temperature colloidal synthesis in aqueous media.

However, because of the complexity of these multinary compounds, they may contain numerous structural defects as well as binary and ternary secondary phases. Due to the similarity of their crystal lattice with that of CZTS, detecting these secondary phases in NCs using X-ray diffraction or electron microscopy is difficile. Vibrational Raman spectroscopy has been shown to be an efficient tool in CZTS NCs characterization, capable of distinguishing not only all secondary phases [2], but even so-called “ordered” and “disorder” kesterite structures of CZTS itself [3].

In order to determine all of the possible secondary phases that could appear in our CZTS NCs, all binary and ternary combinations (CuS, ZnS, SnS, Cu-Sn-S, Zn-Sn-S, and Cu-Zn-S) were obtained under the same synthesis conditions as the parental compound. This gives us a better understanding of the formation of secondary phases as well as “reference” spectra for the identification of secondary phases in CZTS NCs obtained by “green” colloidal synthesis.

The conditions of NC film formation can be determinant for its functional properties, but this is often overlooked in the literature. We established that the prolonged exposure of CZTS NCs to ambient moisture in air results in a partial hydrolysis/oxidation of CZTS with the formation of $Cu_{2-x}S$ as a secondary phase and a transformation of the remaining CZTS phase into a disordered kesterite one. Consequently, we determined the optimal depositing conditions for CZTS NC films without formation of secondary phases.

Another issue important for applications is the improvement of the quality of CZTS NC films. Here, we demonstrate the efficiency of the flash lamp annealing in improving the crystallinity of the CZTS phase, with a simultaneous reduction of the content of secondary phases.

[1] O. Stroyuk, A. Raevskaya, N. Gaponik, Chemical Society Reviews, 5354-5422, 47 (2018).
[2] O. Selyshchev, Ye. Havryliuk, M. Valakh, V. Yukhymchuk, O. Raievska, O. Stroyuk, V. Dzhagan, D.R.T. Zahn, ACS Applied Nano Materials, 5706–5717, 3 (2020).
[3] R. Caballero, E. Garcia-Llamas, J.M. Merino, M. León, I. Babichuk, V. Dzhagan, V. Strelchuk, M. Valakh, Acta materialia, 412-417, 65 (2014).

Structural and electronic investigations of Bismuth multilayers

Fabian Teichert[1], Chitran Ghosal[1], Angela Thränhardt[1], Christoph Tegenkamp[1]

[1] *Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany*

Bismuth shows a variety of interesting properties as bulk material but also as thin film, e.g. it is a topological isolator, shows strong spin-orbit coupling effects, has a semimetal-semiconductor transition concerning film thickness and harmonic-oscillator-like quantum well states [1,2].

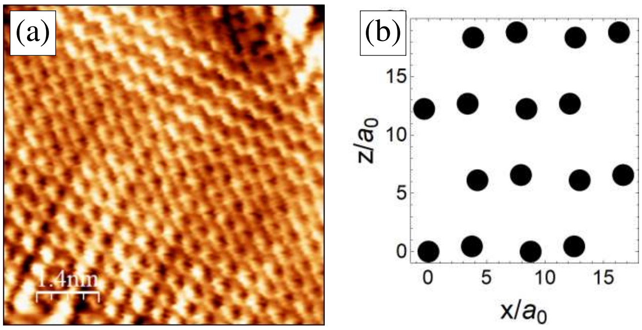


Fig. 1: Four monolayer Bi(110) slab. (a) STM image of the topmost layer. (b) DFT-calculated structure (vertical cut).

We have grown Bi multilayers epitaxially on graphene substrate. (110) slabs have been figured out and are treated with scanning tunneling microscopy (STM) measurements for various slab thicknesses, see Fig. 1(a). We found an even/odd scheme concerning the number of monolayers as well as concerning the number of bilayers indicating a structural relaxation like the black phosphorus allotrope. Density functional theory (DFT) calculations have been done for Bi(110) multilayers to get insights into the concrete structure, see Fig. 1(b). We found also an even/odd scheme in DFT in accord with STM. Further calculation with graphene and highly oriented pyrolytic graphite (HOPG) substrate will be performed soon to figure out if dead layers, e.g. structurally separated and electronically decoupled layers, are present at the substrate interface. Concerning the electronic properties, we measured the differential conductance and calculated the density of states to figure out if the structural even/odd scheme also effects electronics in a similar way.

At conference we present our latest results concerning the Bi(110) multilayer structure and its electronic properties, comparing STM experiments and DFT calculations.

[1] P. Kröger, D. Abdelbarey, M. Siemens, D. Lükermann, S. Sologub, H. Pfnür, C. Tegenkamp, Phys. Rev. B 97, 045403 (2018).

[2] F. Teichert, E. Kuhn, A. Thränhardt, Optical and Quantum Electronics, accepted (2021), arXiv: 1910.12522 [quant-ph].

Surface resonant Raman scattering from Cu(110)

M. Denk,[1] E. Speiser,[1] J. Plaickner,[1] S. Chandola,[1] P. Zeppenfeld,[2] and N. Esser[3, 1]

[1] Leibniz Institute for Analytical Sciences – ISAS e.V., Department Berlin, Schwarzschildstr. 8, 12489 Berlin, Germany

[2] Institute of Experimental Physics, Johannes Kepler University, Altenberger Str. 69, 4040 Linz, Austria

[3] Institute for Solid State Physics, EW 6-1, Technical University Berlin, Hardenbergstraße 36, 10623 Berlin, Germany

We report the first evidence of Raman scattering from surface phonons of a pristine metal surface. Our study reveals a Raman-active surface vibrational resonance on Cu(110) with a surprisingly large scattering efficiency. With the incident photon energy close to the energy of the Cu(110) surface state electronic transition, the Raman scattering from the surface optical resonance can be significantly enhanced, while any contribution from bulk phonons is absent.

Tip-Enhanced Raman Scattering of CdSe-CdS Nanoplatelets on Plasmonic Substrates

Ilya A. Milekhin[1], Mahfujur Rahaman[1], Tatyana A. Duda[2,3], Ekaterina E. Rodyakina[2,3],

Kirill V. Anikin[2,3], Roman B. Vasiliev[4], Volodymyr M. Dzhagan[5], Alexander G. Milekhin[2,3],

Alexander V. Latyshev[2,3], and Dietrich R. T. Zahn[1]

[1] *Semiconductor Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany*

[2] *A.V. Rzhanov Institute of Semiconductor Physics RAS, Lavrentiev Ave. 13, 630090 Novosibirsk, Russia*

[3] *Novosibirsk State University, Pirogov 1, 630090 Novosibirsk, Russia*

[4] *Department of Material Science, Moscow State University, Moscow, Russia*

[5] *V.E. Lashkaryov Institute of Semiconductor Physics, UA-03028 Kiev, Ukraine*

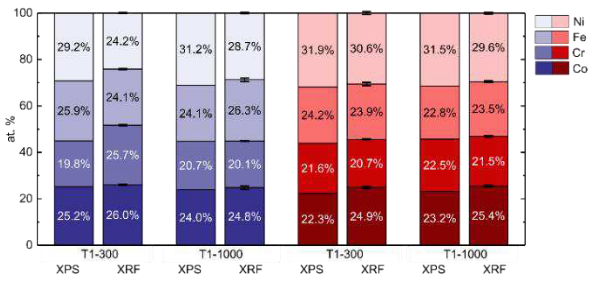
We present the results on a gap-plasmon tip-enhanced Raman scattering (TERS) study of CdSe-CdS nanoplatelets deposited on periodic arrays of Au nanodisks, which serve as plasmonic substrates. The fabrication of Au nanodisks with a diameter of 110 nm and a height of 50 nm on silicon substrates covered with 77 nm SiO_2 was performed by electron beam lithography. CdSe-CdS core-shell nanoplatelets with a characteristic size of 100 nm x 30 nm x 3 nm were deposited onto the plasmonic substrate using the Langmuir–Blodgett technique. We observe a remarkable Raman enhancement of the phonon modes of the CdSe core and the CdS shell from nanoplatelets located in the plasmonic gap between Au nanodisks and the Au tip of the atomic force microscope used in the TERS experiment. Gap-mode TERS imaging is performed at 638 nm and 785 nm excitation and allowed us to visualize near the field distribution of the gap-plasmon and to enhance the phonon response of the CdSe-CdS nanoplatelets. A spatial resolution of 2 nm is achieved with a relative TERS contrast of about 30 (between the Au disks and the substrate). Due to the very good spatial resolution, we are able to observe the response from the edges of a single platelet on top of an Au disk. The high sensitivity and spatial resolution achieved are promising for the investigation of many other 2D materials.

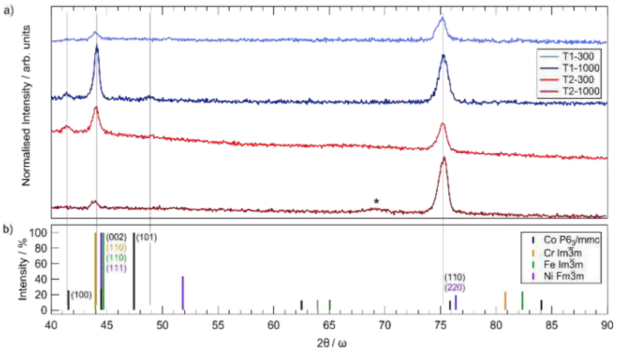
CoCrFeNi High-Entropy Alloy Thin Films Synthesized by Magnetron Sputter Deposition from Spark Plasma Sintered Targets

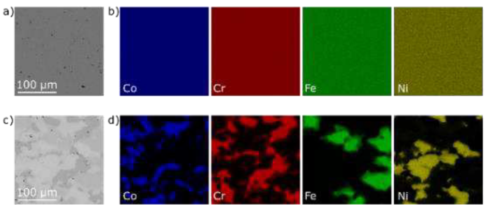
Holger Schwarz[1], Thomas Uhlig[2], Niels Rösch[1], Thomas Lindner[2], Fabian Ganss[1], Olav Hellwig[1,3], Thomas Lampke[2], Guntram Wagner[2] and Thomas Seyller[1,3]

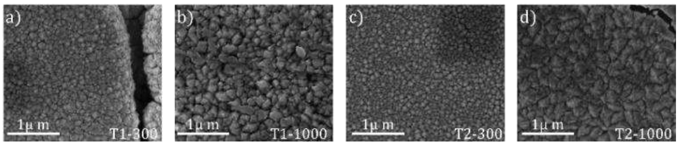
[1]*Institute of Physics, Faculty of Natural Sciences, TU Chemnitz, 09126 Chemnitz, Germany*
[2]*Institute of Materials Science and Engineering, Faculty of Mechanical Engineering, TU Chemnitz, 09126 Chemnitz, Germany*
[3]*Center for Materials, Architectures and Integration of Nanomembranes (MAIN), 09126 Chemnitz, Germany*

Multicomponent alloys of at least four elements with near equimolar percentage were first reported and investigated by Cantor *et al.* in 2004 [1] and are nowadays often referred to as High-Entropy Alloys (HEAs) [2, 3]. This group of materials has raised high attention in the field of material research due to its almost infinite possibilities of element combination and resulting physical properties. To prepare large area thin film coatings from a bulk material, magnetron sputtering has been proven to be an efficient method. In this work, two magnetron sputter targets of CoCrFeNi HEA have been prepared by spark plasma sintering. One of the targets has been fabricated from a homogeneous HEA alloy powder produced via gas atomization, for the second target a mixture of pure element powders, both in equal atomic ratio, was used. Economic benefits can be achieved by mixing pure powders in the intended ratio in comparison to the gas atomization of the specific alloy composition. In this work thin films deposited via magnetron sputtering from both targets on Si(100) and stainless steel type EN 1.4404 substrates are analyzed. The surface elemental composition is investigated by X-ray photoelectron spectroscopy whereas the bulk stoichiometry is measured by X-ray fluorescence spectroscopy. Phase information and surface microstructure are investigated using X-ray diffraction and scanning electron microscopy, respectively. It is demonstrated that the stoichiometry, phase composition and microscopic structure of the as-deposited HEA thin films are almost identical if the same deposition parameters are used.









[1] B. Cantor, I. Chang, P. Knight, A.Vincent, Mat. Sci. Eng. A, 213-218, 375-377 (2004)
[2] D.B. Miracle, O. Senkov, Acta. Mater., 488-511, 122 (2017)
[3] D.B. Miracle, JOM, 2130-2136, 69 (2017)

Electronic Structure of $[(SnSe)_{1+\delta}]_m(TiSe_2)_n$ investigated by Photoelectron Spectroscopy

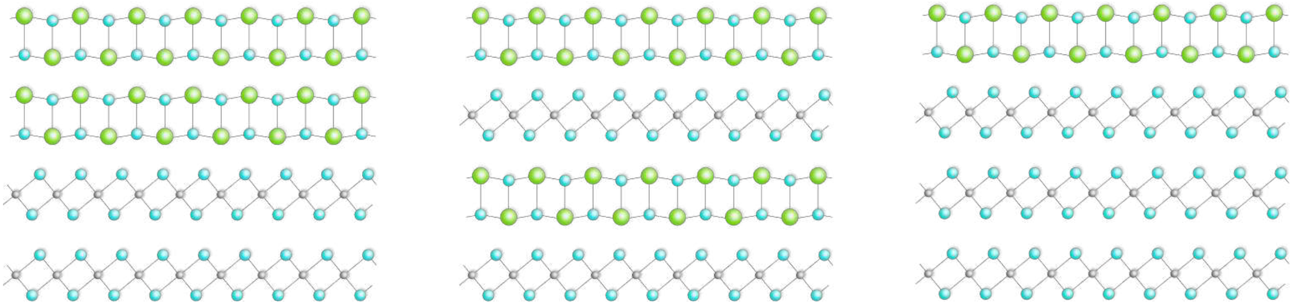
Niels Rösch[1], Fabian Göhler[1], Danielle M. Hamann[2], David C. Johnson[2], Thomas Seyller[1]

[1] *Technische Universität Chemnitz, Institut für Physik, 09126 Chemnitz*
[2] *University of Oregon, Department of Chemistry, Eugene OR 97401*

A new method to grow layered heterostructures is the Modulated Elemental Reactants (MER) synthesis. In MER, a precursor is prepared via sequential physical vapour deposition. Structure and composition of the precursor can be manipulated deliberately to resemble the targeted heterostructure. The precursor is subsequently crystallized by annealing at low temperatures in inert atmosphere. Low temperatures enable the growth of thermodynamically metastable compounds, but at the cost of rotational, turbostratic disorder between layers. With this technique, it is possible to construct a series of layered heterostructures by systematically changing the stacking sequence of individual layers.

In this work, the electronic structure of a series of $[(SnSe)_{1+\delta}]_m(TiSe_2)_n$ heterostructures was explored by using X-ray photoelectron spectroscopy [1]. It can be shown that a transfer of electrons occurs from the SnSe layers into the $TiSe_2$ layers. Understanding the charge transfer in heterostructures is of great interest for potential applications, as a targeted doping may be possible via controlled layering of the heterostructure.

[1] Göhler, F., Hamann, D. M., Rösch, N., et al., *J. Mater. Res.* 34 (12): (2019)



$[(SnSe)_{1+\delta}]_2(TiSe_2)_2$ $[(SnSe)_{1+\delta}](TiSe_2)$ $[(SnSe)_{1+\delta}](TiSe_2)_3$

Figure 1: Schematic depiction of three examples of different stacking order for the compounds made of SnSe and $TiSe_2$. The samples are approximately 50 nm thick.

Physical Characterization of Metal Nanoparticle/TiO_2 Composite Thin Films

Raana Hatami Naderloo[1], Oleksandr Selyshchev[1], Stefania D. Iancu[2], Teresa I. Madeira[1],
Dietrich R.T. Zahn[1]

[1] *Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany*
[2] *Biomolecular Physics, Babes-Bolyai University, Cluj-Napoca, Romania*

TiO_2 is well known photocatalysts for organic pollutants degradation, water splitting reaction, CO_2 reduction, *etc.* [1]. However, due to the wide bandgap of its main crystal modifications, anatase (3.2 eV) and rutile (3.0 eV), the sensitivity of TiO_2 to visible light is low. This issue can be overcome by using sensitizers, *i.e.* materials that absorb visible light, transfer charges/energy to TiO_2, and in this way activate it. Sensitizers can be organic dyes, semiconductors with bandgaps in the visible range, or nanoparticles.

Here, the efficiency of plasmonic Au and Ag nanoparticles (NPs) in TiO_2 photocatalyst films was probed. TiO_2 films prepared by a sol-gel process were crystallised by annealing in the presence of Au and Ag NPs thus forming the Ag/TiO_2 and Au/TiO_2 composite photocatalysts.

Complementary analytical techniques, including Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-ray Diffraction (XRD), Raman Spectroscopy, and Spectroscopic Ellipsometry (SE), were used to characterize the structural and optical properties of the resulting Ag/TiO_2 and Au/TiO_2 composites.

The results show that the Au and Ag NPs in the TiO_2 matrix not only provide appropriate absorption regarding to visible light but also prevent charge recombination processes.

[1] G.S. Mital, T. Manoj, Chin Sci Bull, 1639−1657, 56 (2011).

Photocatalytic Antibacterial Activity Based on Nanocomposites of Ag Nanoparticles and TiO_2

Raana Hatami Naderloo[1], Oleksandr Selyshchev[1], Stefania D. Iancu[2], Teresa I. Madeira[1],
Dietrich R.T. Zahn[1], Alireza Allafchian[3], Fathallah Karimzadeh[4]

[1] Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany
[2] Biomolecular Physics, Babes-Bolyai University, Cluj-Napoca, Romania
[3]Nanotechnology and Advanced Materials, Isfahan University of Technology, Isfahan, Iran
[4] Material Engineering, Isfahan University of Technology, Isfahan, Iran

Silver at nanoscale is well known as an antibacterial material. Ag nanoparticles (NPs) are considered toxic to pathogens and they show distinct electrical, magnetic, catalytic, and special optical properties compared to the bulk metal [1]. The combination of Ag NPs and TiO_2 with a core-shell structure have increased antibacterial properties. The active species in TiO_2 such as very active hydroxyl radicals oxidize the cells of microorganisms under visible light irradiation leading to their death [2]. The usage of materials such as silver leads to a change in the photocatalytic properties, and as a result shifts the optical absorption from the ultraviolet to the visible range. On the other hand, the increased light absorption also results in increased photocatalytic removal of bacteria and viruses [3].

Previous work on complex Fe_3O_4/TEOS-APTES/Ag and Fe_3O_4/TEOS-APTES/Ag@TiO_2 nanocomposites revealed that Fe_3O_4/TEOS-APTES/Ag@TiO_2 nanocomposites show a much better antibacterial activity in comparison with Fe_3O_4/TEOS-APTES/Ag and Ag NPs only thus pointing out the vital role of TiO_2 in the nanocomposites.

Consequently we decided to simplify the system to Ag NP/TiO_2 nanocomposite films and characterize the efficiency of plasmonic Ag NPs in TiO_2 photocatalyst films for bacterial removal. TiO_2 films prepared by a sol-gel process were crystallised by annealing in the presence of Ag NPs thus forming the Ag/TiO_2 composite photocatalysts.

Complementary analytical techniques, including Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-ray Diffraction (XRD), Raman Spectroscopy, and Spectroscopic Ellipsometry (SE), were used to characterize the structural and optical properties of the resulting Ag/TiO_2 and Au/TiO_2 composites.

The results show that the Ag NPs in the TiO_2 matrix provide enhance absorption in the visible range and thus promise improved antibacterial activity.

[1] R. Hatami, A.R. Allafchian, F. Karimzadeh, Micro. Nano. Lett, 196-201, 14 (2019).

[2] O. Carp, C.L. Huisman, A. Reller, Prog. Solid State Chem, 33–177, 32 (2004).

[3] O. Akhavan, E. Ghaderi, Surf. Coatings. Technol, 3676–3683, 204 (2010).

AFM Characterization of TiO_2 Thins Film Deposited using Reactive Magnetron Sputtering

Aravind Vadakkekoithuruthil Pushpahasan, Mahfujur Rahaman,
O. Sandra Omoragbon, Teresa I. Madeira, Dietrich R. T. Zahn

Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany

This work targets the topographic characterization of TiO_2 thin film samples prepared by reactive magnetron sputtering with varying parameters like oxygen concentration, deposition power, and substrate temperature.

Surface characterization was performed using Atomic Force Microscopy (AFM) in intermittent mode and Current Sensing AFM (CS-AFM). The non-destructive intermittent mode is used to map the surface of the samples and provides the surface morphology. CS-AFM is a modified version of contact mode AFM that simultaneously measures the topography of a material and the electric current flow at the contact point of the tip with the surface of the sample.

As the samples under consideration are prepared for photocatalytic applications, information on the thickness, crystallinity, and roughness of the deposited TiO_2 layers is vital to understand which factor, or combination of factors, contributes efficiently to the photocatalytic process that takes place on the surface of the thin films. In particular, the surface roughness increases the surface exposed to light and environmental conditions, and therefore plays an essential role in the photocatalytic process. Here we attempt to correlate the topographic and electrical properties with the photocatalytic performance of the TiO_2 thin films. By considering the general trend that samples having the same crystal structure the photocatalytic response should be higher for those with more effective surface areas, a strong relationship could be found between the surface roughness, particle size, crystal structure, nanoscale electrical properties, and photocatalytic response. We discuss how it is possible to alter the functional properties by varying the deposition parameters.

Surface analysis on solid lubricated ball bearings

Emrich S.[1], Werner M.[2], Pörsch S.[2], Sauer B.[2], Kopnarski M.[1]

[1] *Institute for Surface and Thin Film Analysis IFOS, TU Kaiserslautern*
[2] *Institute of Machine Elements, Gears, and Transmissions, TU Kaiserslautern*
Corresponding author: emrich@ifos.uni-kl.de

Due to their high performance ability and reliability rolling bearings belong among the most used machine elements. Generally such a ball bearing is made up of an outer and an inner ring, separated by rolling bodies. In addition most ball bearings also consist of a cage to keep the rolling bodies at a certain angular distance. Finally all kinds of rolling bearings require some kind of lubrication, such as oil or grease. Beside the object to reduce the friction of those various contacts inside the bearing, e.g. rolling body to inner and outer raceway, the lubrication can also be used to cool the system. The application of a bearing system in vacuum environment requires special solutions. There are also other conditions, which might enforce special ways for the setup of a bearing system. Examples are temperatures above 250 °C, radioactive contamination or law enforcements, e.g. due to hygienic reasons. The named surroundings primarily result in an incompatibility with the use of standard lubrications, such as oil or grease. One option to use ball bearings in this context is the utilization of solid lubrication [1] [2] [3]. Adding the lubricant exclusively as a coating on the raceways is necessary to get the system running but only provides a short lifetime of such a rolling bearing. Adding lubricant additionally to the cage leads to an enhancement of lifetime [4] [5] [6].

Results of surface analysis (SEM, EDX, AES, FIB, TEM) investigating substrates, coatings and the transfer of additional lubrication from the cage to the primary contact between rolling body and raceway are presented. Based on this results, the presentation will show options to enhance lifetime of solid lubricated ball bearings by redesigning the cage. Additionally, the release process of solid lubricant from the cage, the transportation to and deposition on the raceways and the tribological properties are tested on a pin-on-ring-tribometer (four-bearing-vacuum-test-bench) in ambient and vacuum conditions at different loads [7]. Results show, that different transfer films are formed depending on the environmental conditions, affecting the tribological behaviour of the system.

[1] Wang, H., Xu, B. and Liu, J., 2012, "Micro and Nano Sulfide Solid Lubrication." Berlin Heidelberg: Springer.

[2] Birkhofer, H. and Kümmerle, T., 2012, "Feststoffgeschmierte Wälzlager. Einsatz, Grundlagen und Auslegung." Berlin Heidelberg: Springer Vieweg.

[3] Gardos, M. N., 1980, "Theory and Practice of Self-Lubricated, Oscillatory Bearings for High-Vacuum Applications." *Lubr. Eng.* **11**, pp. 641–656.

[4] Meeks, C.R., 1981, "Theory and Practice of Self-Lubricated, Oscillatory Bearings for High-Vacuum Applications." *Lubr. Eng.* **10**, pp. 592–602.

[5] Rüblinger, W., 1984, "Optimierung feststoffgeschmierter, hochbelasteter Kugellager bei Temperaturen bis 300°C." Dissertation." Darmstadt.

[6] Marquart, M.; Wahl, M.; Emrich, S.; Zhang, G.; Sauer, B.; Kopnarski, M.; Wetzel, B.: Enhancing the lifetime of MoS2-lubricated ball bearings, Wear, Volume 303, Issues 1–2, 15 June 2013, S.169-177, ISSN 0043-1648

[7] Pörsch, S.: Ansätze zur erweiterten Lebensdauerberechnung feststoffgeschmierter Wälzlager; Diss. Technische Universität Kaiserslautern (2019)

Investigating Interlayer Interactions by Controlling Nanoarchitecture in Layered Heterostructures

Fabian Göhler[1,2], Marisa Choffel[3], Constance Schmidt[1,2], Fabian Ganss[1,2], Olav Hellwig[1,2],
Dietrich R. T. Zahn[1,2], David C. Johnson[3], Thomas Seyller[1,2]

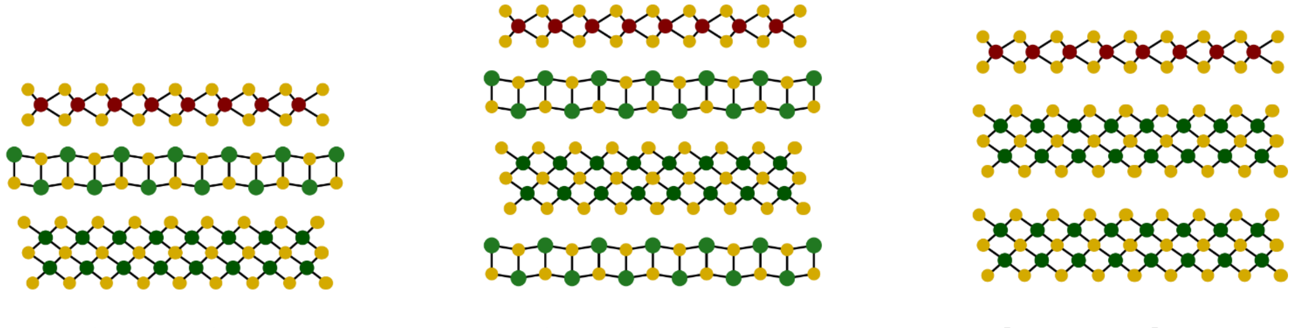
[1] *Technische Universität Chemnitz, Institut für Physik, 09126 Chemnitz*
[2] *Center for Materials, Architectures, and Integration of Nanomembranes (MAIN), 09126 Chemnitz*
[3] *University of Oregon, Department of Chemistry, Eugene OR 97401*

The Modulated Elemental Reactants (MER) method offers a new avenue to synthesize a virtually unlimited number of previously unknown heterostructures. In this two-step synthesis, amorphous precursors are first deposited via sequential physical vapor deposition. By calibrating the thicknesses and layering sequence of the constituents to mimic the targeted structure, it is possible to crystallize the precursors into a layered thin film via annealing in inert atmosphere. Due to the structuring of the precursors on an atomic level, the necessary energy input as well as layer intermixing during crystallization is reduced, enabling the synthesis of metastable structures with arbitrary complexity [1].

By controlling the nanoarchitecture of the thin films, we synthesized a series of heterostructures consisting of different stacking arrangements of BiSe, Bi_2Se_3, and $MoSe_2$ layers in the repeat unit (Figure 1). Using a combination of X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy, we were able to unravel the interlayer interactions that stabilize metastable constituent layers such as rock-salt structured BiSe, or the metallic 1T-phase of $MoSe_2$.

Recently, we were able to push the MER synthesis towards the two-dimensional limit by preparing a one monolayer thick, nanocrystalline layer of $MoSe_2$ on a substrate of epitaxial graphene on SiC [2]. Building on these results, we are now exploring the effects that the incorporation of bismuth selenide layers into the heterostructure have on the electronic and structural properties of the $MoSe_2$.

[1] R. Westover, R. A. Atkins, M. Falmbigl, *et al.*, *J. Solid State Chem.*, 173, 236 (2016).
[2] F. Göhler, E. C. Hadland, C. Schmidt, *et al.*, *Phys. Stat. Sol. B*, 1800283, 256 (2018).



$(Bi_2Se_3)_{1.25}(BiSe)_{0.96}MoSe_2$ $(BiSe)_{0.97}(Bi_2Se_3)_{1.26}(BiSe)_{0.97}MoSe_2$ $[(Bi_2Se_3)_{1.27}]_2MoSe_2$

Figure 1: Scheme of the repeat unit of three examples of different heterostructures made up from a combination of individual BiSe, Bi_2Se_3, and $MoSe_2$ layers. Samples were grown as thin films with a total thickness of 30-50 nm.

Plasmonic hot electron induced layer dependent Fröhlich interaction in InSe

Mahfujur Rahaman, Muhammad A. Aslam, Lu He, Teresa I. Madeira, and Dietrich R. T. Zahn

Semiconductor Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany

Abstract

Fröhlich interaction is of central importance in compound semiconductors as it plays a fundamental role in several material properties such as surface related scattering, vibrational properties of low-dimensional materials, coupling to polarons, exciton relaxation, exciton linewidth[1-3]. In the reduced dimensionality of 2D semiconductors Fröhlich interaction can become even more significant. InSe, a III-VI layered material outperforms other 2D semiconductors with its superior electron mobility (~10^3 $cm^2V^{-1}s^{-1}$) in ultra-thin films (6 layers) measured at RT[4] and thus also offers great promise of outperforming existing Si devices in scaling limitation[5]. However, Fröhlich interaction is one of the main limiting factors of charge transport/carrier mobility in polar semiconductors. In order to explore InSe for nanoelectronic devices, it is therefore, important to understand how dimensionality influences the strength and nature of Fröhlich coupling in InSe. Here, we investigated the layer dependent Fröhlich interaction in InSe from bulk to monolayer induced by plasmonic hot electron doping. We combined InSe with three different metal (Ag, Au, Al) nanostructures and excite the heterostructures near the localized surface plasmon resonance (LSPR). Plasmonic nanostructures, when excited near LSPR produce highly energetic electrons (hot electrons), which are then captured by a semiconductor such as InSe at the interface. These electrons then couple to the polar optical phonons via Fröhlich interaction in InSe. We observed a strong enhancement of polar optical phonons (which are more active in the infrared absorption) in the Raman spectra at near LSPR excitation. When monitoring these polar phonons as a function of the layer InSe number, we observed that the Raman intensities initially increases gradually with decreasing layer number and then drops drastically from 7L to 6L, *i.e.* at the thickness, where the transition from quasi-direct to indirect bandgap occurs at room temperature. Additionally, a gradual decrease of intensity of the polar modes with decreasing layer thickness below this transition point was observed, which is due to the increasing indirect bandgap nature of InSe. This suggests reduced Fröhlich coupling at ultra-thin thicknesses. A finite element method simulation was used to understand the coupling between the plasmonic nanostructures and InSe and we found a very good agreement between the calculations and experimental Raman conditions. Our results shed light on fundamental understanding of Fröhlich interaction in InSe, which is crucial for electronic and optoelectronic applications of this promising 2D material.

[1] N. Kuroda, and Y. Nishina, Sol. Stat. Commun., 439, 28, 1978.

[2] A. Chernikov, V. Bornwasser, M. Koch, S. Chatterjee, C. Bottge, T. Feldtmann, M. Kira, S. Koch, T. Wassner, S. Lautenschl¨ager, B. K. Meyer, and M. Eickhoff, Phys. Rev. B, 035201, 85, 2012.

[3] W. Li, S. Poncé, and F. Giustino, Nano Lett., 1774, 19, 2019.

[4] D. Bandurin, A. Tyurnina, G. Yu, A. Mishchenko, V. Zolyomi, S. Morozov, R. Kumar, R. Gorbachev, Z. Kudrynski, S. Pezzini, Nat. Nanotechnol., 223, 12, 2017.

[5] F. Wei, Z. Wei, G. Feng, and H. PingAn, Sci. China Tech. Sci., 1121, 60, 2017.

Preparation of thin TiO_2 films by DC magnetron sputtering for photocatalytic applications

O. Sandra Omoragbon[1], Lu He[1], Dominik Weber[2], Toni Junghans[2], Teresa I. Madeira[1], Dietrich R. T. Zahn[1]

[1]*Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany*
[2] *Nanotechnology Group, University of Applied Science Zwickau, Zwickau, Germany*

In order to satisfy the increasing energy demand of the world, massive amounts of fossil fuels are burned, leading to an ever-increasing carbon dioxide (CO_2) emission, which is the known main cause of global warming. Photocatalytic reduction of volatile organic compounds (VOC) into solar fuels and chemicals is a promising technology to curb the global warming and partially fulfil the energy requirements. Therefore, considerable efforts are made in the design and development of visible-responsive photocatalysts. TiO_2 thin films very promising in this field [1].

Here we report some preliminary studies of TiO_2 thin films deposited on intrinsic, n-type, and p-type silicon substrates by DC pulsed magnetron reactive sputtering using a titanium metal target and Ar and O_2 as working gases. During the deposition, the working pressure was kept constant. Likewise, the Ar gas flow rate was kept constant at 30 sccm and the O_2 gas flow rate was varied (1, 3, 9, 12, 20 sccm), as well as the temperature of the substrate.

X-ray diffraction (XRD) and Raman Spectroscopy were used to characterize the film structure; the photocatalytic activity characterization (pollutant reduction in air) was performed using a measuring chamber, developed and calibrated at the Nanotechnology Group at the University of Applied Sciences Zwickau, in which acetone is decomposed according to the following chemical reaction:

$$CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O \text{ [2,3]}$$

The acetone concentration is monitored by a photoionization detector (*VOC-TRAQ® II Flow Cell*; AMETEK MOCON - Baseline); the CO_2 formation is monitored by a sensor (*BasicEVO*; smartGAS Mikrosensorik GmbH) based on a non-dispersive dual-wavelength infrared measurement integrated into the system. For the activation of the TiO_2 layer, two different LED lamps are available, which are operated with a power of 30 W and a forward current of 1 A.

The main goal of all combined procedures is to determine the parameters that enable the best results in terms of photocatalytic performance.

[1] N. Shehzad, M. Tahir, K. Johari, T. Murugesan, A critical review on TiO_2 based photocatalytic CO_2, J. CO_2 Util., 98-122, 26 (2018).
[2] Q. Xiang, *et al.; Pivotal role of fluorine in enhanced photocatalytic activity of anatase TiO_2 nanosheets with dominant (0 0 1) facets for the photocatalytic degradation of acetone in air;* Applied Catalysis B, Environmental, 557-564, 96 (2010)
[3] D. Kozlov, *et al.; Effect of the acidity of TiO_2 surface on its photocatalytic activity in acetone gas-phase oxidation;* Catalysis Letter, 86, (2003)

5.10 Session VIII — Friday, October 8th

08:50 – 09:20	**Renato Zenobi (invited)** Tip-enhanced Raman Spectroscopy for Nanoscale Chemical Analysis of Sensitive 2D Materials
09:20 – 09:35	**Yang Pan** Raman signature of moiré phonons in twisted bilayer WSe2
09:35 – 09:50	**Norbert Esser** Surface Structure Analysis by Vibrational Raman Spectroscopy
09:50 – 10:05	**Pauline Dill** Multilayers on reinforcement fiber fabrics with Atomic layer deposition
10:05 – 10:20	**David Poppitz** TEM Investigation of Hierarchical Large-Pore Mesoporous Silicas for Enzyme Immobilization
10:20 – 10:30	**Company presentation 14**
10:30 – 10:40	**Company presentation 15**

Tip-enhanced Raman Spectroscopy for Nanoscale Chemical Analysis of Sensitive 2D Materials

Renato Zenobi

ETH Zürich, Department of Chemistry and Applied Biosciences, CH-8093 Zürich, Switzerland
e-mail: zenobi@org.chem.ethz.ch

Tip-enhanced Raman Spectroscopy (TERS) is a nanoscale chemical analysis and imaging method with a spatial resolution of ≈10 nm [1]. TERS relies on the enhancement of the local electromagnetic field by a plasmonic metal nanostructure that is scanned over the sample by means of a scanning probe microscope, using either AFM or STM feedback. Analogous to SERS, the local electromagnetic field of Raman scattered light is enhanced by many orders of magnitude in TERS, large enough to render monomolecular films and 2D materials spectroscopically visible that would otherwise be optically too thin to be analyzed with conventional vibrational spectroscopy. However, the study of sensitive samples (e.g., biological membranes) and organic materials with TERS has been quite problematic so far, partially due to sample degradation.

The working principle, experimental realization, and capabilities of TERS will first be presented [1]. Several practical issues will be discussed, including interpretation (and misinterpretation) of TERS spectra, tip lifetimes and tip protection [2], tip contamination issues, and the danger of sample decomposition due to the very high local field under the TERS tip. Recent data from our lab shows that this is due not only to thermal effects, but also due to plasmon-driven, photocatalytic reactions [3]. I will also present strategies to mitigate sample decomposition, for imaging studies of fragile samples over extended periods of time, and strategies to improve the reproducibility of TERS, especially for investigation of biological samples.

In the second part of this presentation, applications of TERS to the spatially resolved chemical analysis and imaging of molecular nanomaterials will be discussed. I will choose examples from TERS studies two-dimensional polymers (2DPs) [4], self-assembled monolayers and model membranes, biological nanostructures such as amyloid forming proteins [5], and catalysts [6].

[1] J. Stadler, T. Schmid, and R. Zenobi, *Nanoscale* **4** (2012) 1856-1870.

[2] L. Opilik, Ü. Dogan, C.-Y. Li, B. Stephanidis, J.-F. Li, and R. Zenobi, *J. Phys. Chem. C* **120** (2016) 20828-20832.

[3] J. Szczerbiński, L. Gyr, J. Kaeslin, and R. Zenobi, *Nano Lett.* **18** (2018) 6740-6749.

[4] F. Shao, W. Dai, Y. Zhang, W. Zhang, A.D. Schlüter, and R. Zenobi, *ACS Nano* **12** (2018) 5021–5029.

[5] E. Lipiec, D. Perez-Guaita, J. Kaderli, B. Wood, and R. Zenobi, *Angew. Chem. Int. Ed.* **57** (2018) 8519-8524; E. Lipiec, J. Kaderli, J. Kobierski, K. Skirlińska-Nosek, R. Riek, K. Sofińska, M. Szymoński, and R. Zenobi, *Angew. Chem. Int. Ed.*, published online, Sep. 23, 2020, DOI: 10.1002/anie.202010331

[6] H. Yin, L.-Q. Zheng, W. Fang, Y.-H. Lai, N. Porenta. G. Goubert, H. Zhang, H.-S- Su, B. Ren, J.O. Richardson, J.-F. Li, and R. Zenobi, *Nature Catal.* **3** (2020) 834-842.

Raman signature of moiré phonons in twisted bilayer WSe_2

Yang Pan, Mahfujur Rahaman, Dietrich R. T. Zahn

Semiconductor Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany

Moiré superlattices in twisted van der Waals heterostructures have attracted great research attention recently because of their potential application in optoelectronic devices[1], photonic crystal for nano-light[2], and as superconductive materials[3]. The moiré superlattice prepared by artificial stacking of 2D materials can lead to a correlation between the moiré period and the emerging electrical and optical properties[4]. The periodic potential induced by Moiré patterns modifies the lattice dynamics of monolayer constituents to generate additional phonons or modify existing phonons, which are referred to as Moiré phonons[5]. Here, the Raman signature of moiré phonons in artificially stacked twisted bilayer WSe_2 is investigated. Twisted WSe_2 / WSe_2 bilayers are prepared by breaking a single flake of monolayer WSe_2 into two parts and stacking one on top of the other with a desired twisting angle with a precision of 1°. Raman measurements are carried out at room temperature using Xplora Plus Raman spectrometer and an electron multiplying charged couple detector. A 532 nm laser is used to excite the samples and the Raman signals were dispersed by a 2400 l/mm grating onto the detector with a spectral resolution of 1 cm^{-1}. The Raman spectra of WSe_2 bilayer with different twisting angle are shown in Fig 1. The peak marked with dash red line at 309 cm^{-1} is assigned to the B_{2g} mode, which is an out-of-plane vibrational mode and can be markedly influenced by interlayer coupling. A clear periodic modulation can be found in the peak intensity, position, and width with different twisting angles identifying the B_{2g} mode as a moiré-type phonon. A polarization dependent Raman is performed to detect the atomic reconstruction. The study aims to find moiré phonons and to provide characteristic fingerprints.

[1] J. Yin, H. Wang, H. Peng, Z. Tan, L. Liao, L. Lin, X. Sun, A. L. Koh, Y. Chen, H. Peng, Z. Liu, Nat. Commun. 1-8, 7 (2016).

[2] S. S. Sunku, G. X. Ni, B. Y. Jiang, H. Yoo, A. Sternbach, A. S. McLeod, T. Stauber, L. Xiong, T. Taniguchi, K. Watanabe, P. Kim, M. M. Fogler, D. N. Basov, Science. 1153-1156, 362 (2018).

[3] M. Yankowitz, S. Chen, H. Polshyn, Y. Zhang, K. Watanabe, T. Taniguchi, D. Graf, A. F. Young, C. R. Dean, Science. 1059-1064, 363 (2019).

[4] S. Brem, K. Q. Lin, R. Gillen, J. M. Bauer, J. Maultzschm J. M. Lupton, E. Malic, Nanoscale, 11088–11094, 12 (2020).

[5] M. Lin, Q. Tan, J. Wu, X. Chen, J. Wang,Y. Pan, X. Zhang, X. Cong, J. Zhang, W. Ji, P. Hu ,K. Liu, P. Tan, ACS nano. 8770-8780, 12 (2018).

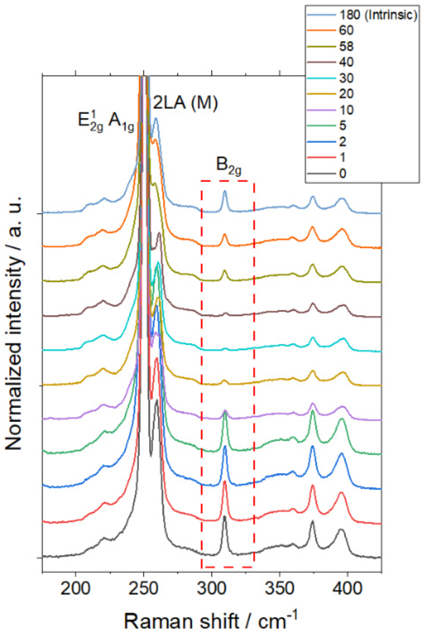


Fig 1. Raman spectra of twisted bilayer WSe_2 with different angle.

Surface Structure Analysis by Vibrational Raman Spectroscopy

N. Esser[1,2], E. Speiser[1], J. Plaickner[1], S. Chandola[1,3], M. Denk[1,4], P. Zeppenfeld[4], W.G. Schmidt[3], S. Sanna[5]

[1] Leibniz-Institut für Analytische Wissenschaften -ISAS- e.V., 12489 Berlin, Germany
[2] Technische Universität Berlin, Institut für Festkörperphysik, 10623 Berlin, Germany
[3] Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33095 Paderborn, Germany
[4] Institut für Experimentalphysik, Johannes Kepler Universität, 4040 Linz, Austria
[5] Institut für Theoretische Physik and Center for Materials Research (LaMa), Justus-Liebig-Universität Gießen, 35392 Gießen, Germany

Raman spectroscopy of vibrational excitations is a standard analytical method to study the structure of inorganic and organic materials. Despite the low cross section of inelastic light scattering, Raman spectroscopy nowadays has become a standard tool for the analysis of nanoscopic structures on surfaces by utilizing the plasmonic field enhancement (SERS, TERS). But even without any field enhancement, i.e. in "non-plasmonic" systems, Raman spectroscopy may be sensitive enough to record surface vibrational modes, i.e. vibrational modes confined to the uppermost 1-3 atomic layers of a solid. This is strongly favoured by resonance enhancement involving surface electronic transitions.

Recent examples of our research concern Au nanowires on structurally complex, stepped Si(553) surfaces, intercalation of Tb below the uppermost surface layers of Si(111), and the formation of 1D-Cu-O-rows on Cu(110). We record specific Raman spectra related directly to the surface atomic structures. In comparison with calculations of surface structure, vibrational modes and Raman spectra we are able to assign Raman lines to individual surface phonon modes and clarify atomic structures which have been under controversial debate in spite of a multitude of "classical" surface analysis investigations.

A microscopic picture of the scattering process is also achieved from the comparison of experiment and theory. We show that this is a general surface effect which is not limited to certain classes of materials or surface structures.

Refs.:

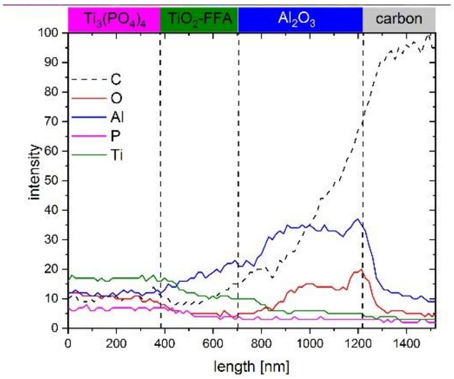
E. Speiser, N. Esser, B. Halbig, J. Geurts, W.G. Schmidt, S. Sanna, Surf. Sci. Rep. **75** (2020) 100480.

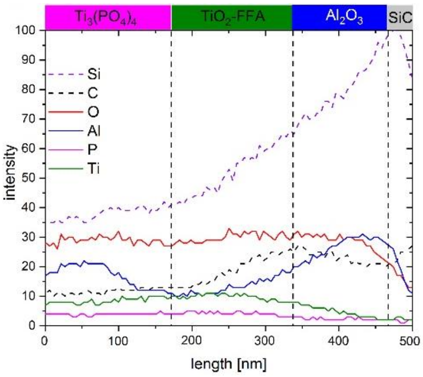
Multilayers on reinforcement fiber fabrics with ALD

[1]Pauline Dill**,** Florian Pachel, Christian Militzer, Walter Krenkel, Georg Puchas, Alexander Held, Christoph Tegenkamp, Werner A. Goedel

Physical Chemistry, Chemnitz University of Technology, Straße der Nationen 62, 09111 Chemnitz, Germany, E-Mail: pauline.dill@chemie.tu-chemnitz.de.

Carbon fiber fabrics, with a size of 30 cm ×8 cm and SiC fiber fabrics (size 8 cm×40 cm) were coated with combinations of three different Atomic layer deposition layers (ALD). We used inorganic ALD coating (Al_2O_3[1], $Ti_3(PO_4)_4$[2]) as well as an organic-inorganic TiO_2/furfuryl alcohol coating.[3] The thickness of each ALD layer is almost independent of the place in the reactor while coating. The thickness and appearance do not depend on the type of fiber substrate. The layer thickness and the homogeneity of each layer and the combination of the three layers were investigated with scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The elemental analysis of the coating in the different layers was investigated with energy-dispersive X-ray spectroscopy (EDXS). It is possible to distinguish the layers based on the intensity and the appearance of each element at the line scan. Also, SEM shows the morphology of the layers.





[1] A. K. Roy, W. Baumann, S. Schulze, M. Hietschold, T. Mäder, D. J. Nestler, B. Wielage, W. A. Goedel, *J. Am. Ceram. Soc.* **2011**, *94*, 2014, DOI: 10.1111/j.1551-2916.2010.04340.x.

[2] C. Militzer, J. Buchsbaum, V. Dzhagan, D. R. T. Zahn, H. Wulff, C. A. Helm, W. A. Goedel, *Adv. Mater. Interfaces* **2018**, *5*, 1800423, DOI: 10.1002/admi.201800423.

[3] C. Militzer, S. Knohl, V. Dzhagan, D. R. T. Zahn, W. A. Goedel, *J. Vac. Sci. Technol. Vac. Surf. Films* **2017**, *35*, 01B107, DOI: 10.1116/1.4965699.

TEM Investigation of Hierarchical Large-Pore Mesoporous Silicas for Enzyme Immobilization

D. Poppitz[a], *G. Mhanna*[a], *R. Gläser*[a]

[a]*Institute of Chemical Technology, Universität Leipzig, Linnéstr. 3,*
04103 Leipzig, Germany

Introduction

The immobilization of various enzymes is a way to establish new opportunities for multi-step enzyme-catalyzed reactions. Therefore, support materials containing two co-existing and interconnected mesopore systems with different pore widths, known as hierarchical pore systems, are presented in this study. Large-pore mesoporous silica materials (LPMS) with adjustable pore width and high specific surface area are applied as parent material and a second mesopore system with a different pore width is introduced by pseudomorphic transformation [1,2]. A key issue of this study is the investigation of the formation and interconnectivity of the two mesopore systems by means of transmission electron microscopy (TEM) and electron tomography. Furthermore, LPMS materials are attractive candidates for the immobilization of enzymes due to their eminent biocompatibility, chemical inertness and modifiable surface [1].

Results and Discussion

LPMS parent materials were prepared by combining both methods of Feng et al. [3] and Chen et al. [4] and small mesopores are introduced by post-synthetic pseudomorphic transformation [5]. This procedure allows adjusting the degree of transformation by the ratio of the structure-directing agents to the mixture and varying proportions of the two mesopore systems are achieved. The resulting materials were characterized by nitrogen sorption at 77K, X-ray powder diffraction, scanning electron microscopy, pulsed field gradient (PFG) NMR spectroscopy and transmission electron microscopy. The interconnectivity and degree of the transformation were additionally characterized by electron tomography experiments.

References

[1] T. Martin, A. Galarneau, F. Di Renzo, F. Fajula, D. Plee, Angew. Chem. Int. Ed. 41 (2002) 2590-2592.

[2] W.-D. Einicke, D. Enke, M. Dvoyashkin, R. Valiullin, R. Gläser, Materials 6 (2013) 3688-3709.

[3] P. Feng, X. Bu, D.J. Pine, Langmuir 16 (2000) 5304–5310.

[4] D. Chen, Z. Li, Y. Wan, X. Tu, Y. Shi, Z. Chen, W. Shen, C. Yu, B. Tu, D. Zhao, J. Mater. Chem. 16 (2006) 1511-1519.

[5] W.-D. Einicke, H. Uhlig, D. Enke, R. Gläser, C. Reichenbach, S.G. Ebbinghaus, Colloids and Surfaces A: Physicochemical and Engineering Aspects 437 (2013) 108-112.

5.11 Session IX — Friday, October 8th

11:00 – 11:15	**Kateryna Artyushkova** Application of a Laboratory-Based Scanning XPS/HAXPES Instrument for the Characterization of Buried Interfaces
11:15 – 11:30	**Daniel Leidlmair** Elemental and chemical depth profiling of organic coatings on steel with XPS
11:30 – 11:45	**Maximilian Winzely** AFM Investigation of APAC (Antiplatelet and Anticoagulant, A Heparin Proteoglycan mimetic)
11:45 – 12:00	**Christian Müller** Structural Investigations in Resistive Switching Architectures based on Prussian Blue Analogs
12:00 – 12:15	**Alexandra Girod** Surface analytical characterisation of low-friction thin films in an application-oriented tribological system
12:15 – 12:30	**Aleksandar Matkovic** Electrode engineering for two-dimensional semiconductors
12:30 – 13:00	**Dietrich RT Zahn (invited)** Exploiting Enhancement Effects in Raman Spectroscopy

Application of a Laboratory-Based Scanning XPS/HAXPES Instrument for the Characterization of Buried Interfaces

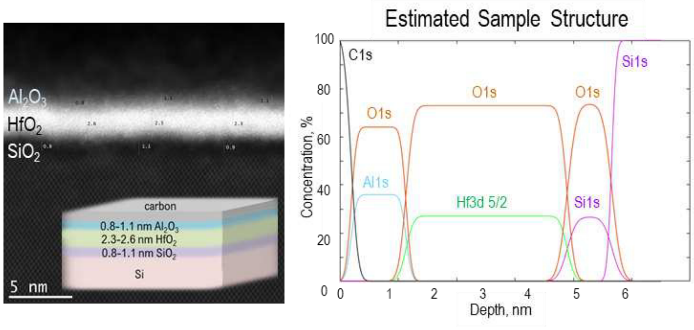
Kateryna Artyushkova[1], Jennifer E.Mann, John G. Newman[1], Risayo Inoue[2], Katsumi Watanabe[2], Hiromichi Yamazui[2], Anja Vanleenhove[3], Thierry Conard[3]

[1]Physical Electronics, 18725 Lake Dr E, Chanhassen, MN 55317, USA

[2]ULVAC-PHI, Inc, 2500 Hagisono, Chigasaki, Kanagawa, 253-8522, Japan

[3]IMEC , Kapeldreef 75, Leuven, 3001 Belgium

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analysis technique with many well established industrial and research applications. The surface sensitivity (top 5-10 nm) of XPS and its ability to provide short-range chemical bonding information make the technique extremely popular in materials characterization and failure analysis laboratories. While its surface sensitivity is an important attribute, in some cases, the depth of analysis of XPS is not sufficient to analyze buried interfaces without first sputter etching the sample surface. However, sputter etching can often lead to alterations of the true surface chemistry. An alternative to sputter etching the sample is Hard X-ray Photoelectron Spectroscopy (HAXPES), available at some synchrotron facilities. By increasing the photon energy of the X-ray source, the mean free path of photoelectrons is increased, resulting in an increased information depth obtained from the sample. Depending on the energy used, these hard X-rays can provide depths of analysis three or more times than that of soft x-rays used on conventional XPS systems. In this presentation, we will present applications of a laboratory-based instrument, the PHI *Quantes*, for analysis of buried interfaces. The *Quantes* is equipped with two scanning microprobe monochromated X-ray sources, Al Kα (1486.6 eV) and Cr Kα (5414.7 eV), thus enabling both traditional XPS and HAXPES experiments in the same instrument. Combining both soft and hard X-ray analyses, we can gain an even better understanding of composition with depth and information at buried interfaces. We will demonstrate advances in quantification of HAXPES data and show thickness calculations for multilayered structures using *Strata*PHI software.



Thickness, nm	
Al_2O_3	0.93±0.20
HfO_2	2.80±0.20
SiO_2	0.76±0.26

Sample structure calculated using *Strata*PHI from angle-dependent HAXPES data for three-layered structure. The thickness calculated is within expected by TEM analysis.

Elemental and chemical depth profiling of organic coatings on steel with XPS

D.Leidlmair[1,2], T. Greunz[2], J. Duchoslav[1,2], B. Strauß[3] and D. Stifter[2]

[1] CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH,
Viktor Kaplan Straße 2, 2700 Wiener Neustadt, Austria; E-Mail: daniel.leidlmair@cest.at
[2] ZONA Zentrum für Oberflächen- und Nanotechnologie, JKU Linz,
Altenberger Straße 69, 4020 Linz, Austria;
[3] voestalpine Stahl GmbH, voestalpine-Straße 3, 4031 Linz, Austria;

Organic coatings applied on steel substrates are representing a valuable enhancement in several ways, typically linked to decorative and corrosion inhibitive purposes. Despite being extensively used, especially in the construction and automotive industry, organic coating systems employed on steel are by far not fully understood in terms of their final structure and chemistry.

Particularly for the elemental and chemical investigation of such organic systems X-ray photoelectron spectroscopy (XPS) stands out due to its high surface sensitivity (< 10 nm). In order to examine the interior composition XPS is usually combined with common destructive depth profiling techniques, e.g. sputtering with Ar^+-ions, that can be applied to a vast number of materials. For organic polymers, however, it has been demonstrated that ion bombardment leads to a prompt heavy degradation of the chemical matrix [1]. Alternatively, the XPS analysis on conventional cross-sections is not a choice either as the smallest available spot size for high-resolution scanning in XPS exceeds the coating thickness by several times.

In our work elemental and chemical depth profiling is therefore achieved by combining XPS with ultra-low-angle microtomy (ULAM). Compositional analysis of the interior coating matrix and the detection of chemical gradients inside the organic polymer layer is achieved by XPS line scans performed on an extended taper in the millimeter range. In contrast to former studies of polyester-melamine based coatings [2,3], the gained expertise is extended to a 50 µm-thick high-build polyester-polyurethane coating system. Further complementary characterization by energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy and attenuated total reflection infrared (ATR-IR) spectroscopy added to the comprehensive description of the observed organic coating. The linearity and surface topography of shallow-angle microtomy cuts created at different preparation conditions was additionally evaluated by coherence scanning interferometry at macroscopic scale as well as by atomic force microscopy (AFM) and scanning electron spectroscopy (SEM) at microscopic scale.

[1] R. Steinberger, J. Sicking, J. Weise, J. Duchoslav, T. Greunz, D.C. Meyer, D. Stifter, Applied Surface Science, 15-22, 403 (2017)
[2] T. Greunz, Anal. Bioanal. Chem., 405, 7153 (2013).
[3] T. Greunz, C. Lowe, E. Bradt, S. Hild, B. Strauß, D. Stifter, Prog. Organ. Coat., 115, 130 (2018).

AFM Investigation of APAC (Antiplatelet and Anticoagulant, A Heparin Proteoglycan mimetic)

Maximilian Winzely[1], Annukka Jouppila[2,3], Laurin Lux[1], Georg Ramer[1], Riitta Lassila[2,3],
Gernot Friedbacher[1]

[1] Institute of Chemical Technologies and Analytics, Vienna University of Technology,
Getreidemarkt 9/164, A-1060 Wien, Austria
[2] Faculty of Medicine, University of Helsinki, Haartmaninkatu 4, F-00014 Helsinki, Finland
[3] Aplagon Ltd., Tukholmankatu 8 B, F-00290 Helsinki, Finland

Antiplatelet and anticoagulant drugs can be classified as antithrombotic agents with the main purpose to reduce the formation of blood clots. Antiplatelet drugs are hindering the formation of platelet aggregates, whereas anticoagulant drugs are preventing thrombin generation and fibrin polymerization. For a successful treatment of many known complex cardiovascular diseases the need of more than one antithrombotic agent is inevitable. However, by increasing the number of drugs with different mechanism of action there is also an enhanced risk of bleeding [1].

Dual anticoagulant and antiplatelet (APAC), a new semisynthetic antithrombotic drug, has shown to provide both anticoagulant and antiplatelet features, thereby offering a new exciting approach for the treatment of cardiovascular diseases [2].

For a better understanding of the biological functions of APAC, comprehensive knowledge about its structure is essential. APAC is tailored and manufactured of a human serum albumin-core, to which several heparin chains are conjugated [2]. In this study, atomic force microscopy was used to characterize APAC according to its structure and the molecular interactionswith von Willebrand factor (VWF), since intravascularly administered APAC co-localizes with VWF at injured vessel walls [2]. Furthermore, the successful adsorption of APAC to a flat gold surface was confirmed by photothermal induced resonance.

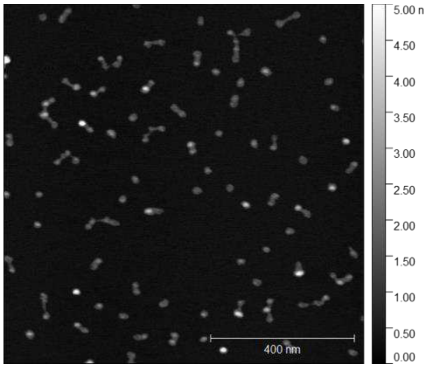


Figure 1: *TM-AFM images of APAC drop-casted on mica from a buffer solution containing 20 mM MgCl₂.*

In order to obtain good TM-AFM images of APAC, different drop-cast methods were investigated, in which using a PBS-buffer solution containing 20 mM $MgCl_2$ gave the best results for a uniform and less agglomerated adsorption onto the mica surface (Fig. 1). By calculating the volume of over 300 individual APAC molecules, it was possible to achieve a size distribution which suggests that besides monomers also various oligomers exist.

Moreover, we have also successfully recorded AFM-IR spectra on individual APAC molecules.

[1] J. Chen, C. C. Verni, A. Jouppila, R. Lassila, S. L. Diamond, Thrombosis Research, 169, 143-151, (2018)

[2] K. A. Barreiro, R. Tulamo, A. Jouppila, A. Albäck, R. Lassila, European Journal of Vascular and Endovascular Surgery, 58(6), 903-911, (2019)

Structural Investigations in Resistive Switching Architectures based on Prussian Blue Analogs

Christian K. Müller

University of Applied Sciences Zwickau, Faculty of Physical Engineering/Computer Sciences, 08056 Zwickau, Germany

The physical and chemical properties of Prussian blue (PB) and Prussian blue analogs (PBA) have increasingly attracted the attention of the scientific-technological community due to its promising applications in electrochemical sensing, electrochromic devices, batteries, supercapacitors, and magnetic/ photomagnetic systems [1-4]. Recently, we have reported about resistive switching in electrodeposited PB films [5] enabling additional applications in electronics. However, electrical property characterization of PB and PBA films, in combination with control of morphology and structure are rarely investigated.

In this work, the relationship between resistive switching behavior and structural properties of electrodeposited PB and PBA films with controlled morphology will be discussed (see Figure 1). The structural characterizations were performed with electron microscopy in combination with Raman spectroscopy and x-ray techniques.

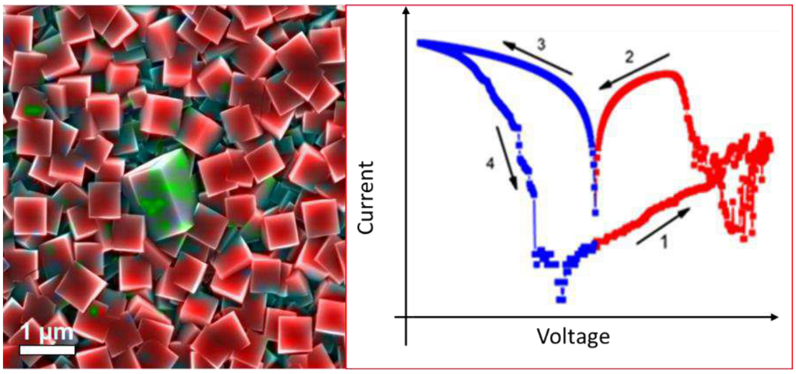


Figure 1. Bipolar switching in PB-films with cube morphology.

References:

[1] V. Katic et al., ACS Appl. Mater. Interfaces, 35068, 11 (2019).
[2] V. B. Ishfani et al., Electrochim. Acta, 282, 304 (2019).
[3] E. S. Goda et al., J. Energy Chem., 206, 50 (2020).
[4] Fornasieri, G. et al., Eur. J. Inorg. Chem., 259, (2018).
[5] L. B. Avila et al., Materials, 5618, 12 (2020).

Surface analytical characterisation of low-friction thin films in an application-oriented tribological system

A. Girod, M. Kopnarski [1]

[1] *Institute for Surface and Thin Film Analysis (IFOS GmbH), University of Kaiserslautern,*
Trippstadter Str. 120, 67663 Kaiserslautern, Germany
email: girod@ifos.uni-kl.de

With the aim of optimising the efficiency of combustion engines, a major focus of tribological research in recent decades has been on reducing the coefficient of friction in the tribological system 'piston ring vs. cylinder liner'. In particular, in order to reduce the running-in period, new Mo-based piston ring coatings were tested realistically on the rotational tribometer [1] and coefficients of friction in the range of CoF < 0.01 were measured. Friction with such low CoF is called superlubricity in tribology and is investigated both theoretically and experimentally in laboratory tests. [2] For the explanation of the effect on an atomic or molecular level, extremely thin tribofilms often play a decisive role, which can also be generated dynamically under the tribological load in the respective tribosystem.

The aim of our research is to find characteristic properties of the tribofilms in the above-mentioned tribosystem close to the application, which lead to such low CoF up to the range of superlubricity. For this purpose, methods of modern surface and thin film analysis are used, which on the one hand allow the necessary information about structure and chemical composition of the layers to be recorded with the highest resolution. On the other hand, considering the heterogeneous and complex chemical-structural composition of the surfaces in real technical applications, it is difficult to find the representative properties that are responsible for the occurrence of the superlubricity effect using methods of nano- and micro-range analysis. Using the example of the tribological structures created on the piston rings and the cylinder liners in the rotational tribometer, the contribution shows how an appropriate characterisation can succeed with the combination of different analytical methods (TEM, AES, XPS, EDX and SNMS). Furthermore, it is shown that a suitable preparation of the surfaces prior to the surface analytical measurement is indispensable in order to obtain statistically reliable and significant characteristic values. The possibilities and limitations of the methodology will be discussed, especially with regard to the high experimental effort.

[1] J.Biberg, H.-J. Füßer: Tribo. Int., 111-124, 113 (2017).

[2] A. Erdemir, J.-M. Martin: Superlubricity. 1. ed. Amsterdam: Elsevier (2007).

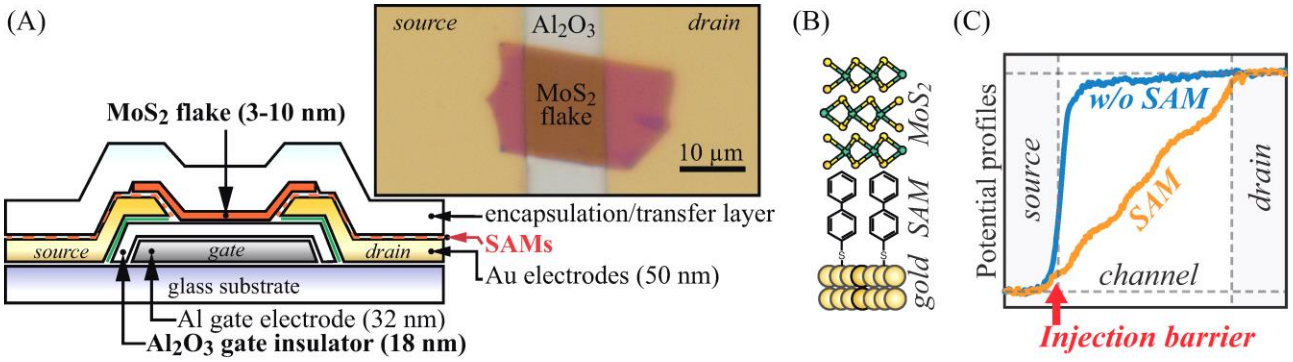
Electrode engineering for two-dimensional semiconductors

Aleksandar Matković[1,*], Andreas Petritz[2], Gerburg Schider[2], Markus Krammer[3], Markus Kratzer[1],
Esther Karner-Petritz[2], Alexander Fian[2], Herbert Gold[2], Michael Gärtner[4], Andreas Terfort[4],
Christian Teichert[1], Egbert Zojer[3], Karin Zojer[3], Barbara Stadlober[2]

aleksandar.matkovic@unileoben.ac.at

[1] *Institute of Physics, Montanuniversität Leoben, Leoben, Austria.*
[2] *Joanneum Research MATERIALS, Institute for Surface Technologies & Photonics, Weiz, Austria.*
[3] *Institute of Solid State Physics, Graz University of Technology, Graz, Austria.*
[4] *Institut für Anorganische und Analytische Chemie, Goethe-University Frankfurt, Frankfurt am Main, Germany.*

Bottom-contact architectures with common electrode materials like gold are crucial for the integration of two-dimensional semiconductors into existing device concepts. The high contact resistance to gold – especially for bottom contacts – is, however, a general problem in two-dimensional semiconductor thin film transistors (TFTs). This study investigates pyrimidine-containing self-assembled monolayers (SAMs) on gold electrodes for tuning the electrode work functions in order to minimize that contact resistance [1]. Its frequently ignored asymmetric and bias-dependent nature is recorded by Kelvin probe force microscopy (KPFM) through a direct mapping of the potential drop across the channel during device operation. A reduction of the contact resistances exceeding two orders of magnitude has been achieved via a suitable self-assembled monolayer, which vastly improves the overall device performance.



(**A**) Schematic cross-section of the TFTs, indicating characteristic layer thicknesses. Inset of (A) optical micrograph of a device. (**B**) Schematic cross-section of the electrode interface. (**C**) Potential profiles of two MoS_2-TFTs during operation, measured by in-operando KPFM.

[1] A. Matkovic, et.al., Adv. Electron. Mater, 2000110, **6** (2020).

Exploiting Enhancement Effects in Raman Spectroscopy

Dietrich RT Zahn[1]

[1] *Semiconductor Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany*

The ever decreasing dimensions of components in (opto-)electronic devices towards the nanometer scale clearly reveals the need for optical spectroscopies to be sensitive to ultra-small amounts of matter as well as break the diffraction limit of light in order to achieve ultra-high lateral resolution. Raman spectroscopy is a widely used optical spectroscopy as it provides a vast amount of information including *e.g.* composition, strain, crystal structure, and crystallinity. However, the Raman cross section is very small and therefore enhancement mechanisms have to be employed to achieve sufficient Raman signals and lateral resolution for low-dimensional structures.

In this lecture I will first review techniques to enhance the Raman signals of very small amounts of material. One important ingredient of enhancing Raman signals is employing resonance excitation, *i.e.* choosing the exciting laser photon energy so that it coincides with a maximum in optical absorption. Often resonance enhancement alone is not sufficient when the amount of matter is very small, for instance for detecting the Raman spectrum of a few or even a single nanostructure. Then further enhancement strategies need to be engaged such as interference-enhanced Raman spectroscopy (IERS) and in particular surface-enhanced Raman spectroscopy (SERS). In the case of SERS manifold realisations using ordered nanostructured surfaces with various metals have been applied. The metallic nanostructures can be prepared by expensive techniques such as electron beam lithography or less expensive ones such as nanosphere lithography or films on nanospheres. The Raman signals can be even further enhanced by combining metal nanostructures with photonic crystals.

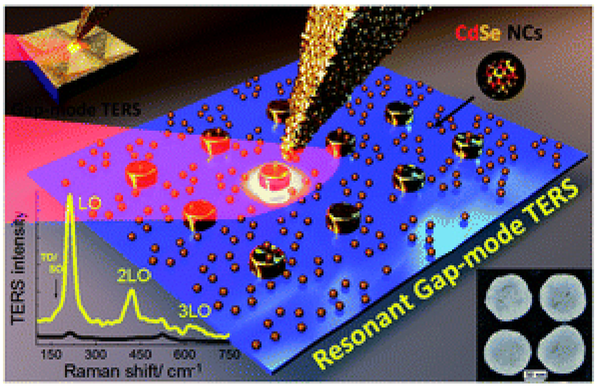


***Figure 1**: Sketch of a TERS experiment on CdSe nanocrystals deposited on a Si substrate with an ordered array of Au nanocylinders [1].*

The last part of the lecture will be devoted to achieving lateral resolution on the nanoscale using tip-enhanced Raman spectroscopy (TERS). The technique requires the combination of a Raman spectrometer and an atomic force microscope using a conductive tip for the plasmonic enhancement so that the lateral resolution is determined by the tip radius. Giant enhancement is observed when detecting the Raman spectra of materials in the plasmonic gap between the metallic tip and metallic nanostructures. Finally the detection of the Raman spectrum of a single semiconductor quantum dot is demonstrated.

[1] I. A. Milekhin, M. Rahaman, K. V. Anikin, E. E. Rodyakina, T. A. Duda, B. M. Saidzhonov, R. B. Vasiliev, V. M. Dzhagan, A. G. Milekhin, A. V. Latyshev, D. R. T. Zahn, *Resonant Tip-Enhanced Raman Scattering by CdSe Nanocrystals on Plasmonic Substrates*, Nanoscale Adv. 5441, 2 (2020).

Program Overview

Wednesday, October 6th	
08:00-08:45 Uhr	Registration
	Opening remarks
08:50-10:30 Uhr	**Session I**
10:30-10:55 Uhr	Coffee break
10:55-12:10 Uhr	**Session II**
	Lunch break (Mensa TU Bergakademie Freiberg)
13:00-14:35 Uhr	**Session III** (Advances in Electron Microscopy I)
14:35-15:05 Uhr	Coffee break
15:05-17:05 Uhr	**Session IV** (Advances in Electron Microscopy II)
17:10-19:10 Uhr	**Poster session I**
Thursday, October 7th	
08:00-08:50 Uhr	Registration
08:50-10:40 Uhr	**Session V**
10:40-11:05 Uhr	Coffee break
11:05-12:10 Uhr	**Session VI**
	Lunch break (Mensa TU Bergakademie Freiberg)
13:00-14:15 Uhr	**Session VII**
14:15-16:15 Uhr	**Poster session II** & coffee break
17:00-18:30 Uhr	Social program / AOFKA committee meeting
19:00-22:00 Uhr	Banquet (Poster Award / Logo contest)
Friday, October 8th	
08:00-08:50 Uhr	Regsitration
08:50-10:40 Uhr	**Session VIII**
10:40-11:00 Uhr	Coffee break
11:00-13:00 Uhr	**Session IX**
	Closing remarks

TECHNISCHE UNIVERSITÄT
CHEMNITZ

Faculty of Natural Sciences — Institute of Physics
www.tu-chemnitz.de/physik

AOFKA21
www.aofka21.de