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Dean's Office

The Dean's office coordinates the activities of the department in collaboration with various commissions.

Staff Members

Dean: Prof. Dr. Wolfram Jaegermann
Vice dean: Prof. Dr. Christoph Schüth
Dean of studies Materials Science: Prof. Dr. Lambert Alff
Dean of studies Applied Geosciences: Prof. Dr. Andreas Hoppe
Scientific coordinator, department and Materials Science: PD Dr. Boris Kastening
Scientific coordinator, Applied Geosciences: Dr. Karl Ernst Roehl
Secretary of department and exams: Renate Ziegler-Krutiz
Secretary of personnel and finances: Christine Hempel
Competence center for materials
characterization: Dr. Joachim Brötz
IT group: Andreas Hönl
Building services: Heinz Mohren

Publications of Permanent Members of the Dean's Office


Dear colleagues and friends,

In the year 2010, the Institute of Materials Science of the faculty of Materials and Geo Sciences at TU Darmstadt continued to develop positively in terms of students, funding and personnel. The number of students at the end of 2010 rose to 397 (224 Bachelor, 161 Diploma, 12 other), up 17% from 2009. The number of freshman Bachelor students in fall 2010 was 100, up 33% from the year before. For the development of student numbers through recent years, see Fig. 1. Additionally 127 Ph.D. students carried out their research at the end of 2010. The total amount of third-party funds spent in 2010 reached 11.3 million €, an increase of almost 20% compared to 2009. Our workforce consisted of about 250 staff members at the end of 2010.

While our Bachelor of Science course is now well consolidated in its third year on the strength of lectures, exercises and lab courses, this year further elaboration of the Master of Science constituted one of the main tasks as far as lecturing is concerned. The Bachelor course itself was successfully accredited up to year 2014.

In the field of research it is worth mentioning that we were successful with the application to continue our Sonderforschungsbereich (Collaborative Research Center) 595 for a further 4 years. The Deutsche Forschungsgemeinschaft (German Research Foundation) has been funding this coordinated program entitled “Electrical Fatigue in Functional Materials” with Prof. Dr. Jürgen Rödel as the spokesperson since January 2003 with the focus on production, characterization, modeling and properties of ferroelectrics, ionic conductors and semiconducting polymers.

A variety of research initiatives were launched in 2010 including an application in the framework of the so called LOEWE Center of Excellence funded by the state of Hessian well as a pre-proposal for establishing a Center of Excellence funded by the German federal and state governments in the field of advanced ceramics. These research programs are highly competitive and the results of the assessments will not be announced until 2012.

In the following, I wish to highlight the most important events at our Materials Science Institute:

**Honors:**

On March 02 we were proud to celebrate the award of the prestigious Adolf-Messer-Grant to Junior Professor PD Dr. Christina Roth, head of our group “Renewable Energy”. The Adolf-Messer-Award is granted every year to young excellent scientists who have already achieved significant and widely acknowledged research results and is endowed with 50,000 € of research money.

Prof. Dr. Horst Hahn, our adjunct Professor at KIT and head of the group of “Nanomaterials”, was elected as member of the German National Academy of Sciences Leopoldina as well as of the European Academy of Sciences.
Faculty Members:
In line with our ambitious efforts to expand and to complement materials science at TU Darmstadt, we had the opportunity to search for two new faculty members. In one case, the search committee was successful and we could welcome Prof. Dr. Robert Stark as a new faculty member on April 01. Prof. Stark is head of the group “Physics of Surfaces” and is a member of the Cluster of Excellence “Smart Interfaces”. The second vacancy could not yet be filled and we are still in the process of hiring a suitable colleague but are optimistic to conclude the search soon in 2011.

Prof. Dr. W. Ensinger, head of the “Materials Analysis” group, was elected as a new member on the advisory board of the Vereinigung von Freunden der Technischen Universität Darmstadt e.V. Prof. Ensinger succeeded Prof. Dr. H. von Seggern, who was in charge as board member for many years.

Our long-standing consultant faculty member, Prof. Dr. R. Neumann, retired in November and was thus relieved of his duties on the faculty board. Prof. Neumann was department head of the GSI Helmholtzzentrum für Schwerionenforschung in Darmstadt and always supported strong research and personal links to the Materials Science Institute.

![Number of students (without Ph. D. students) in Materials Science at Technische Universität Darmstadt over the last 10 years](image)

**Fig. 1:** Number of students (without Ph. D. students) in Materials Science at Technische Universität Darmstadt over the last 10 years

More Events:
In April, Prof. Dr. W. Jaegermann handed over the role of faculty dean to Prof. Dr. R. Riedel, who was elected by the faculty for two years. In June and August Dr. A. Gurlo and Dr. T. Granzow successfully passed their final habilitation examinations.
Our annual summer party was arranged shortly before the summer break as one of the most important social events of the Materials Science Institute. As a tradition, along with the summer party, we grant an award to the three best students having accomplished their Diploma in the period between the past winter semester and the present summer semester. In 2010, the following students were awarded the so called MaWi-Prize:

1. Anne Fuchs
2. Oliver Gerbig
3. Lorenz Kehrer, Jennifer Schuster, Michael Sinn (aequo loco)

Another relevant event in 2010 was the retirement of Jochen Korzer, who managed our machine shop over 18 years always in an authoritative and reliable way. Therefore, the Materials Science Institute will have to undertake a great effort to replace him adequately as soon as possible.

Finally, the year culminated with our legendary Christmas party attended by nearly every research group of the Materials Science Institute. All the students were also invited to join the festivities. As usual, the party was organized by the students and the research groups and lasted until the early morning hours. And for some people even longer....

On the following pages, you will find details of the research activities conducted by the individual groups in 2010. These results clearly reflect the dedication and concerted effort of all members of the Institute of Materials Science, comprising our excellent machine shop staff headed by J. Korzer, technical and administrative staff in the research groups, students working on their diploma theses, Ph.D. students, and last, but definitely not least, our postdocs in the respective research groups. While expressing our gratitude to all of them for their valuable contributions, we look forward to sustaining a motivational and highly productive work environment in a constantly evolving institute facing new and exciting challenges.
Physical Metallurgy

Research and teaching of the Physical Metallurgy group in general focus on a deeper understanding of the relationships between processing, microstructure and properties of metallic materials. The major goal of this research is on the one hand to quantitatively describe existing materials with respect to their processing and performance in order to fully exploit their application potential. On the other hand, we search for and subsequently develop novel alloy systems with improved properties by utilizing the basic principles of physical metallurgy. If potential alloy systems may be identified, it is of not only prime importance to extensively characterize these materials with respect to the foreseen application but also to give appropriate feedback to the material developers for further optimization.

Our current research deals with Al, Mg and Ti based light alloys, steels, nickel-base superalloys and refractory alloys. Mechanical properties such as creep, fatigue and wear are mainly studied including their interaction with corrosion and oxidation phenomena. Recent progress includes functionally graded materials as well as improvements in the wear resistance of metallic alloys by mechanical surface treatments. The major research topics on which our group presently concentrates are first, ultra-fine grained (UFG) materials which created special interest in recent years, as they favorably combine very high strength with good ductility. In several research projects the evolution and the mechanical properties of these microstructures are investigated and new forming processes for the continuous production of UFG-bulk materials are developed in collaboration with the department of mechanical engineering. Second, development of structural metallic materials which could withstand applications in air at temperatures beyond 1200°C would be attractive not only from scientific but also industrial standpoints. A successful alloy development would eventually allow for a substitution of single-crystalline nickel-base superalloys in gas turbine applications.

Teaching covers basic courses on phase transformation in metals and alloys (including phase diagrams), mechanical properties of (structural) engineering materials and fundamentals of deformation and fracture. Special courses are given on solidification and heat treatment mechanisms, quantitative image analysis for the characterization of microstructures and high temperature alloys. Extensive laboratory exercises on all levels are offered to facilitate and intensify the technical understanding in these topics and to improve the practical skills for investigating metallic materials.

The Physical Metallurgy group has numerous collaborations with other groups within the department and with others of Darmstadt Technical University, in particular with Mechanical Engineering through the DFG CRC 666. On the national level, cooperation in academia is characterized by the close relation to the other members of the WAW (Wissenschaftlicher Arbeitskreis der Universitätsprofessoren der Werkstofftechnik e.V.). Internationally, we have a continuing cooperation with groups from Australia, Czech Republic, France, UK, Ukraine, Canada and USA which also includes exchange of students and scientists. Strong relations with industry (Daimler-Benz, Ecoroll, Heraeus, Opel, Pfalz-Flugzeugwerke, Plansee, VW) give multiple opportunities for scientific interaction and personal exchange. Department members participate in and organize national and international conferences, seminars and workshops thereby gathering information which supports to keep teaching and research on an actual level.
### Staff Members

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| **Research Associates** | Prof Dr.-Ing. Clemens Müller  
                               Dipl.-Ing. Enrico Bruder  
                               Dipl.-Ing. Katharina von Klinski-Wetzel |
| **Technical Personnel** | Ulrike Kunz  
                                 Claudia Wasmund  
                                 Petra Neuhäusel  
                                 Michael Rohloff |
| **Secretaries**      | Christine Hempel                                 |
| **PhD Students**     | Dipl.-Ing. Enrico Bruder  
                               Dipl.-Ing. Daniel Janda  
                               Dipl.-Ing. Daniel Schliephake  
                               Dipl.-Ing. Florian Gang  
                               Dipl.-Ing. Vanessa Kaune  
                               Dipl.-Ing. Jennifer Schuster  
                               Dipl.-Ing. Jan Scheil  
                               Dipl.-Phys. Peter Pörsch |
| **Diploma Students** | Benedikt Peter  
                               Katrin Barth  
                               Jörn Niehuesbernd  
                               Rudolf Seiler  
                               Christoph Seemüller  
                               Lukas Schlicker  
                               Franziska Resch  
                               Christoph Baumann |
| **Research Fellow**  | Dr. Shanmugasundaram Tharangaju                  |
| **Guest Scientists** | Dr. Alexander Dudka                              |

### Research Projects

- “Beyond Nickelbase Superalloys” (DFG research unit FOR 727, 2007-2013).
- “Effect of Load Frequency on the Fatigue Life of Aluminum Wrought Alloys in the VHCF-Regime”, joint project with SzM-Darmstadt within the DFG Priority Programm 1466, DFG, since 04/2010.
- “FeAl-based Alloys - Materials, Casting Process and Exhaust Gas Turbocharger”, joint project with one academic and 4 industrial partners, BMWi, since 08/2010.
- “Hybrid Silicide-Based Lightweight Components for Turbine and Energy Applications (HYSOP)”, collaborative project with 7 European partners, EU, since 10/2010.
- “Improved Wear Resistance of Forming Tools by Mechanical Surface Treatments” joint project with PTU-Darmstadt, AIF, since 09/2006.


**Publications**


HALL-PETCH RELATIONSHIP IN A NANOSTRUCTURED AL-CU ALLOY

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1Department of Materials Science, TU Darmstadt, D-64287 Darmstadt, Germany
2Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai, 600036 India

ABSTRACT: Mechanical properties of bulk nanocrystalline Al-4Cu alloys with grain sizes from 47 to 105 nm, synthesized by mechanically alloying followed by vacuum hot pressing at different temperatures, were analyzed through Hall-Petch relation. Hall-Petch analysis revealed a high frictional stress (170 MPa) and a high positive slope (0.13 MPa√m) as compared to pure Al (15-30 MPa and 0.06-0.09 MPa√m). From a detailed evaluation of different strengthening mechanisms it is inferred that the Al2Cu precipitates and oxide particles are the likely reason for such high values of frictional stress and slope.

INTRODUCTION: The main interest towards bulk nanomaterials is due to their very high strength which is usually linked to their fine grain size causing grain boundary strengthening [1]. For polycrystalline materials, the grain size strengthening is described by the Hall-Petch (HP) relationship [2,3], which suggests that the yield strength increases with a decreasing grain size according to the equation

\[ \sigma = \sigma_0 + kd^{1/2} \] (1)

where ‘\(\sigma\)’ is the yield strength (YS), ‘d’ is the average grain size. Typically ‘\(\sigma_0\)’ is rationalized as either a frictional stress resisting the motion of gliding dislocations or as an internal back stress and ‘k’ is the HP slope which is considered to be a measure of the resistance of the grain boundary to slip transfer. Generally, HP constants ‘\(\sigma_0\)’ and ‘k’ should depend on solid solution and particle strengthening [4].

Mechanical alloying (MA) technique has been used to produce nanocrystalline (NC) or ultra fine grained microstructures in Al-Cu alloys [5]. Many bulk NC materials produced by MA/mechanical milling (MM) routes show very high strength and follow the HP relation but with both, a higher HP slope and frictional stress [6,7]. Since NC materials synthesized by ball milling often have impurities and large number of defects (dislocations), other strengthening mechanisms such as solid solution hardening, dislocation (forest) hardening and dispersion (Orowan) hardening could also contribute to the overall yield or flow strength of the materials at room temperature [8]. In view of this, considering only the experimentally measured YS values for evaluating the strength-grain size correlations may not be the appropriate method to determine HP constants for the original mechanism of grain boundary dislocation pile-up [2,3]. A compilation of ‘\(\sigma_0\)’ and ‘k’ values [6,7,9,10] reveals a large scatter for both parameters ranging from \(\sigma_0 = 17\) to 375 MPa and \(k = 0.06\) to 0.28 MPa√m, respectively. In the present study, we want to shed light onto this confusing situation by evaluating the strengthening contributions from different sources with a view to isolate the contribution from grain size and to extract the “true” HP relation. This approach is exemplified with an Al-4Cu alloy.

EXPERIMENTAL: NC Al-4Cu alloy powders were prepared by mechanical alloying of high purity (99.9%) elemental Al and Cu powders. A detailed microstructural characterization on bulk Al-4Cu compacts was performed using transmission electron microscopy (TEM). Vacuum hot pressing (VHP) was used to consolidate the mechanically alloyed NC powders. The mechanically alloyed (30h) powders were consolidated at a pressure of 300 MPa for 2h
at different temperatures (250, 350 and 450°C). In order to measure the YS of the bulk compacts, the VHP samples were machined to produce compression test specimen (3 mm diameter and 6 mm height with compression axis parallel to the hot pressing direction). For a comparison, Al-4Cu wrought alloy in solutionized (535°C- 1h) and quenched (SQ) condition was also tested.

RESULTS AND DISCUSSION: Fig. 1 shows the TEM micrographs of Al-4Cu alloy after VHP at 450°C for 2h. The average grain size measured from TEM micrographs was 47 ± 6, 70 ± 8 and 105 ± 11 nm, for the alloy consolidated at 250, 350 and 450°C, respectively. The high thermal stability against grain growth observed in this alloy is attributed to the presence of dispersoids (marked with circles in Fig. 1(a)). These dispersoids could be either oxides or carbides of aluminum originating from the interaction with the process control agent (stearic acid) during processing [11] and they are likely to hinder grain boundary movement through Zener pinning. The average particles size of these dispersoids, measured from TEM micrographs, was 8.1 ± 2.3, 9.7 ± 2.1 and 10.3 ± 2.6 nm, for the alloy consolidated at 250, 350 and 450°C, respectively. The volume fraction of the dispersoid particles, estimated from TEM micrographs, for all the consolidated samples was same (~ 0.003). In addition to the dispersoids and due to the Cu content of the alloy, the stable Al$_2$Cu precipitate particles were identified (marked with arrows in Fig. 1a) with an average size of about ~ 110 nm for all the consolidated samples compacted at these temperatures. The residual solute content of Cu in the matrix measured from TEM - energy dispersive spectroscopy is about 1.2±0.3 wt. %.

The compression test results of the Al-4Cu alloy samples prepared from VHP compacts are shown in Fig. 2(a). Coarse grained pure Al exhibits comparatively low YS (~100 MPa) and shows substantial work hardening up to a compressive strain of 0.2. The NC Al-4Cu alloy compacted at 250°C exhibits very high YS (~750 MPa), limited strain hardening and the compressive deformability is ~2%. With increasing compaction temperature, the strength decreased and plastic strain to fracture increased (Fig. 2(a)). The plot of YS of NC Al and

![Fig. 1](image.png)
Al-4Cu alloys versus the inverse squareroot of grain size \( (d^{-0.5}) \) (Fig. 2(b)) shows that the strength is significantly higher for NC Al-Cu alloys for a given grain size. Hall-Petch analysis of the data of NC Al-4Cu alloy reveals high values for the constants \( k \) and \( \sigma_0 \) which are 0.13 MPa/\( \sqrt{\text{m}} \) and 170 MPa, respectively. In addition to the grain size strengthening (GS), other mechanisms such as solid solution strengthening (SS), dispersion strengthening (DS) and precipitation strengthening (PS) are likely to be contributing to the overall strength due to the microstructure described above. The overall YS can be expressed as

\[
\sigma_{\text{YS}} = \sigma'_0 + \sigma_{\text{ss}} + \sigma_{\text{gs}} + \sigma_{\text{Or}}
\]

(2)

where \( \sigma'_0 \) is the yield stress of pure Al (35 MPa [12]), \( \sigma_{\text{ss}} \) is the solution strengthening, \( \sigma_{\text{gs}} \) is the grain size strengthening, \( \sigma_{\text{Or}} \) is the Orowan strengthening, which consists of both DS and PS. The solid solution strengthening (SS) from Cu in Al is 7 MPa per weight percent [12]. So, the YS increase due to SS in the bulk Al-4Cu alloy is about 8 MPa (as 1.2% Cu is in solution after VHP) and in the SQ Al-4Cu it is about 28 MPa (4% Cu in the solution). The YS and average grain size of SQ Al-4Cu are 70 MPa and 65\( \mu \text{m} \), respectively. The average size of the precipitates measured from TEM micrographs is about 110 nm and the volume fraction of the particles calculated from phase diagram is about 0.024. The associated Orowan strengthening contribution can be estimated by [13, 14]

\[
\sigma_{\text{Or}} = M G b \sqrt{\frac{f}{r}} = M G b \frac{1}{L}
\]

(3)

where \( G \) is the shear modulus (27 GPa for Al), \( b \) is the burgers vector (Al: 0.286 nm), \( M \) is the Taylor factor (~3 for randomly oriented fcc polycrystals), \( L \) is the average particle spacing \( (L = r/\sqrt{f}) \), and \( r \) is the average radius of the particle. For the sake of simplicity we assume spherical shape of the precipitates and also neglect the correction of \( L \) for the more appropriate interparticle spacing \( L-2r \) here [14], since \( L >> 2r \). The Orowan strengthening due to Al-Cu precipitates (estimated using eqn. 3) was 63 MPa. However, since the size of these precipitates was found to lie in the same range as the grain size of the NC material, it is debatable how much they will contribute to the Orowan strengthening in the NC material. The (Orowan) strengthening contribution from dispersoid particles was also evaluated using eqn. (3) from the average radius and volume fraction of the dispersoids particles measured.
from TEM micrographs. The strength contribution from dispersoids are ~310, 259 and 255 MPa for the alloy consolidated at 250, 350 and 450°C, respectively. The “true” contribution to strength from grain size can be determined from

$$\sigma_{gs} = \sigma_{YS} - (\sigma'_0 + \sigma_{ss} + \sigma_{Or})$$

(4)

which is plotted in Fig. 2(b) as an upper (no Orowan strengthening due to precipitates) and lower bound (“full” Orowan strengthening by precipitates, 63 MPa as per equation (3)). From Fig. 2b it can be seen that the data fits quite well those from the NC pure Al and SQ Al-4Cu alloy, which are both truly single phase materials, irrespective of whether Al$_2$Cu precipitation strengthening was taken into account or not. This supports our approach that, if particles are present in the microstructure, appropriate quantities for particle strengthening have to be considered for a serious assessment of HP strengthening. In contrast, the strength of the SQ Al-4Cu alloy comes from only two effects, namely from solid solution and from grain size. If the strengthening effect from solid solution (28 MPa) is subtracted from the total YS (70 MPa) the grain size effect remains (42 MPa). This (latter) quantity (condition 'D' in Fig. 2(b)) then also fits quite well with the data points for pure nanostructured Al (condition 'B' and 'C' in Fig. 2(b)). Consequently, the HP analysis of all these data points yields values for $k$ and $\sigma_0$ of 0.08 MPa$^{\frac{1}{2}}$m and 29 MPa, respectively, which are also in good agreement with values reported for pure Al [9,15] being in the range of 0.06 to 0.09 MPa$^{\frac{1}{2}}$m and 15-30 MPa, respectively. This is shown clearly in Fig. 2(b) by shaded area, where the true Hall-Petch effect of the pure Al fails.

From the above analysis it is reasoned that the originally observed higher $\sigma_0$, and $k$ values in bulk NC Al-4Cu alloy overestimates the grain size strengthening contribution. Rather, it is due to the superposition of other strengthening contributions from solute atoms, but more importantly from dispersion and precipitation strengthening. Very likely, the HP constants reported in literature for other Al alloys [6, 7, 10] are influenced in a similar way. This assumption manifests itself in the fact that dispersion strengthened Al [10], cryomilled Al [6] and cryomilled AA5083 [7], exhibit substantially higher $\sigma_0$ values than pure NC Al. However, except for AA5083 their HP slope is virtually identical to the one of NC Al.

References:

Ceramics Group

The emphasis in the ceramics group is on the correlation between microstructure and mechanical as well as functional properties. A number of processing methods are available in order to accomplish different microstructure classes, to determine their specific properties in an experiment and to rationalize these with straightforward modelling efforts. Thus, a materials optimization is afforded which allows effective interplay between processing, testing and modelling. In particular, new lead free piezoceramics, lead-free high-temperature dielectrics and lead-containing high-temperature piezoceramics can be obtained and extensively characterized electrically and mechanically.

The scientific effort can be grouped as follows:

I. Processing and sintering of oxides
   (Dr. Olivier Guillon - Emmy Noether independent junior research group)

Following topics are investigated:
• Continuum mechanical description of sintering in the case of ceramic films and laminates (modelling of shrinkage, stress state, curvature during co-sintering…)
• Measurement of densification behaviour and viscous parameters by means of sinter-forging
• Macroscopic and microscopic characterization of sintering anisotropy under mechanical loading and geometrical constraint provided by a substrate
• Drying of thin films from suspensions and conditions for cracking
• Sintering mechanisms of electrical Field Assisted Sintering Technique and processing of dense nanocrystalline materials
• Effect of particle size on the phase transformation behaviour of oxides using chip calorimetry and TEM.

Materials considered are mainly Al$_2$O$_3$, ZrO$_2$, ZnO as well as materials for LTCC (Low Temperature Cofired Ceramics) and SOFC (Solid Oxide Fuel Cell) applications.

II. Mechanical properties of ceramics and composites
   Dr. Ludwig Weiler

Work on mechanical properties is geared towards an improved understanding of fracture strength, fracture toughness, R-curve behaviour and subcritical crack growth. Together with several European research groups we prepare and characterize metal-ceramic composites and metal-ceramic functionally graded materials.

Materials under consideration are Al$_2$O$_3$/Cu and Al$_2$O$_3$/Al.

III. Electrical properties of ferroelectrics
   Dr. Torsten Granzow

Materials with a crystalline structure lacking a center of inversion display a multitude of peculiar physical effects and are therefore prime candidates both for fundamental scientific research as well as practical technical applications. The focus of the work in this group therefore lies on the reaction of non-centrosymmetric materials to different external stimuli like electric fields, mechanical loads or high temperatures. Ferroelectric behavior and domain switching are of particular interest. Typical objects of the studies are polycrystalline...
materials based on perovskite structures, which form the most extended and diverse group of polar materials. These materials are always ferroelastic as well as ferroelectric in the non-cubic phase. The general aim is to develop an understanding of the basic physical principles that allows improvement of the properties of the material or to optimize the use of existing properties in a given application.

One topic of investigation is the effect of combined electrical and mechanical loading on domain structures. In this context, the method of stress-supported poling was developed: a high degree of polarization can be reached with comparably small electric fields if a mechanical load is applied perpendicular to the poling direction. The mechanical and electrical behavior of donor- and acceptor-doped materials is investigated. The data will be used to develop a mathematical model that allows a prediction of the development of polarization and strain during an arbitrary electrical, mechanical and thermal procedure from as few parameters as possible.

Apart from the research on ferroelectric properties, transitions between different polar phases or polar and non-polar phases are also of interest. One observes a stabilization or destabilization of long-range ferroelectric order by controlled introduction of charged defects, e.g. by a reduction treatment. The work is closely connected to that of the group developing new lead-free piezoelectric materials, as their superior properties are tied to the existence of a high-temperature phase that is probably relaxor-like in nature.

The work in this group is embedded in the Collaborative Research Center 595 on electrical fatigue in ferroelectric materials. The aim is to identify the causes for degradation of a material during use of a device and eliminate them as far as possible. Another topic within this project is the connection between domain structure, reversible and irreversible domain wall motion, large-signal parameters such as polarization and strain, and small-signal parameters like the components of the dielectric and piezoelectric tensors.

IV. Development of new piezoceramics
Dr. Wook Jo

In response to the recent demands for environmentally friendly piezoelectric materials for electrical and electronic applications, the principal focus of this group is the development of non-toxic piezoceramics with electromechanical performance comparable to their lead-containing counterparts. Among all the potentially promising candidates special attention has been given to bismuth-based materials whose properties can be effectively tailored using the so-called morphotropic phase boundary (MPB) concept. Extensive compositional research has been performed on various bismuth-based solid solution systems that contain a MPB between separating different crystal symmetries of the members. To better understand the mechanisms governing the enhancement of electromechanical properties of materials and to make our search for alternative materials more effective fundamental scientific research on model systems have been performed in parallel to the compositional investigations. We employ various characterization techniques such as macroscopic dielectric, ferroelectric and ferroelastic property measurements as well as crystallographic structural analyses based on synchrotron and neutron diffractions, Raman, nuclear magnetic resonance, electron paramagnetic resonance spectroscopic techniques, and transmission electron microscopy. We are also simultaneously establishing thermodynamic and phenomenological models which are verified by the first principles calculations. Currently, we have extensive and active international collaborations with eminent ferroelectric groups throughout the world.
V. **Mechanical properties of ferroelectrics**  
*Dr. Kyle Webber*

The focus of this research group is on the mechanical behavior of ferroelectric materials, specifically the impact of ferroelasticity on fracture and high temperature constitutive behavior. To this end, the fracture behavior of novel high toughness piezoceramics is being investigated as part of an EU Project for the potential inclusion in actuator applications in extreme environments, such as wind turbines and active damping of motor vibrations. Work has focused on determining the change in R-curve behavior from an addition of second phase of tetragonal stabilized zirconia as well as the transition from inter- to transgranular fracture. Additional investigations on the high temperature constitutive behavior of ferroelectric materials are also underway. A novel experimental arrangement has been constructed capable of measuring the strain and polarization of samples in response to uniaxial compressive stress at temperatures up to approximately 400 °C. This has been used to investigate hard and soft PZT up to the Curie temperature as well as current lead-free compositions with more complex phase structures. Phase field modeling is used to better understand the switching and fatigue behavior of the materials considered.

### Staff Members

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<th>Role</th>
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Prof. Edwin Garcia (Purdue University)
Prof. Xiaoli Tan (Iowa State University)
Dr. Ali Hussain (Faculty of Mat. Sci, Topi, Pakistan)
Prof. Ratnamala Chatterjee (Physics Department, I.I.T. Delhi)

Research Projects

- Processing of textured ceramic actuators with high strain (SFB 595, 2003–2014)
- Mesoscopic and macroscopic fatigue in doped ferroelectric ceramics (SFB, 2003–2014)
- Melting of ceramic nanoparticles: Application to transient liquid phase sintering (DFG 2006–2010)
- Synthesis and characterization of nanostructured materials by FAST sintering (DFG 2006-2010)
- Thin film cracking (DFG 2006–2010)
- Thin film sintering: liquid phase vs. solid state sintering (DFG 2008-2010)
- Printed Electronics: Thin film ZnO (Merck 2006-2010)
- Effect of load and temperature on domain switching (DFG 2008-2010)
- Development of new lead–free piezoceramics (ADRIA, state funding, 2008-2013)
- Development of new high-temperature piezoceramics (ADRIA, state funding, 2008-2013)
- Toughening of ferroelectrics (EU 2009-2012)
- Stress and strain fields in ferroelectrics (Graduate school “computational engineering 2009-2012)
- High-temperature piezoceramic BF-PT (DFG 2006-2010)
- Metal-ceramic composites (EU 2010-2012)
- High-temperature dielectrics (DFG 2010-2013)

Publications


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K. T. P. Seifert, W. Jo, J. Rödel; *Temperature-Insensitive Large Strain of (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$- (Bi$_{0.5}$K$_{0.5}$)TiO$_3$-(K$_{0.5}$Na$_{0.5}$)NbO$_3$ Lead-Free Piezoceramics*, JOURNAL OF THE AMERICAN CERAMIC SOCIETY, 93 (2010) 1392-1396.

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S. Schaab, T. Granzow; Temperature dependent switching mechanism of (Pb₀.₉₂La₀.₀₈)(Zr₀.₆₅Ti₀.₃₅)O₃ investigated by small and large signal measurements, APPLIED PHYSICS LETTERS, 97 (2010) 132902.


K. Sang, L. Weiler, E. Aulbach; Wetting and pressureless infiltration in the CuTi/Al₂O₃ system under poor vacuum, CERAMICS INTERNATIONAL, 36 (2010) 719-726.


Electronic Material Properties

The department Electronic Materials introduces the aspect of electronic functional materials and their properties into the Institute of Materials Science. The associated research concentrates on the characterization of various classes of materials suited for implementation in information storage and organic electronics. Three major research topics are presently addressed:

- Electronic and optoelectronic properties of organic semiconductors.
- Charge transport and polarization in organic and inorganic dielectrics.
- Photo- and photostimulated luminescence in inorganic phosphors.

For novel areas of application a worldwide interest exists in the use of organic semiconductors in electronic and optoelectronic components, such as transistors and light-emitting diodes. So far, multicolour and full colour organic displays have been implemented in commercially available cameras, car-radios, PDAs, mp3-players and even television sets. Organic devices reaching further into the future will be simple logic circuits, constituting the core of communication electronics such as chip cards for radio-frequency identification (RFID) tags and maybe one day flexible electronic newspapers where the information is continuously renewed via mobile networks. In view of the inevitable technological development, the activities of the group are concerned with the characterization of organic material properties regarding the performance of organic electronic and optoelectronic devices. The major aspect deals with the charge carrier injection and transport taking place in organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs). In particular the performance of unipolar and ambipolar light-emitting OFETs and the stability of OFETs and OLEDs are subjects of recent investigations. To conduct these demanding tasks, various experimental techniques for device fabrication and characterization are installed. Beside basic electric measurement setups, a laser spectroscopy setup used for time-of-flight as well as for life-time measurements and a Kelvin-probe atomic force microscope to visualize the potential distribution of organic devices with nanometer resolution are available.

In the field of polymer electrets current research comprises the characterization of surface charge distribution, charge stability, and charge transport properties of fluoropolymers, as well as their applications in acoustical transducers. Present investigations of charge transport and polarization in organic dielectrics are directed towards the basic understanding of polarization buildup and stabilization in PVDF and in novel microporous dielectrics. Latter are scientifically interesting as model ferroelectric polymers. Moreover, the fatigue behaviour of electrically stressed inorganic PZT ceramics is investigated. The focus lies on preventing the operational fatigue of ferroelectric devices due to cyclic and static electrical stress. The available equipment includes poling devices, such as corona and high voltage setups, and a thermally stimulated current setup to investigate the energetic trap structure in dielectrics as well as the thermal charging and discharging under high electric fields. In addition, the laser induced pressure pulse (LIPP) method allows to investigate the spatial distribution of stored charges in organic as well as in inorganic ferroelectrics.

The field of photoluminescent and photostimulated luminescent (PSL) materials (phosphors) is concerned with the synthesis and characterization of suited inorganic compounds used as wavelength converters in fluorescent lamps and in scintillating and
information storing crystals. Present work is focused on x-ray detection materials, providing improved resolution and high PSL-efficiency needed in medical imaging. In particular the storage phosphors CsBr:Eu2+ and BaFBr:Eu2+ are under investigation. Research is concentrated on the influence of humidity on the sensitivity of CsBr:Eu2+. Before and after the treatment the materials are studied by means of spectroscopic methods as well as scanning electron microscopy. The exchange of water during the thermal treatment is measured in situ by thermal analysis methods. New synthesis methods for BaFBr:Eu2+ used in commercial image plates are of interest and new synthesis routes will be tested for other storage phosphors and scintillators. On the one hand the mechanism of PSL-sensitization, which is found to be mainly due to the incorporation of oxygen and water, is investigated. On the other hand the implementation of BaFBr:Eu2+ powders into organic binders in order to form image plates is in the focus of the work.

In the field of scintillators undoped and doped CsI is investigated concerning the afterglow. This afterglow is unfavourable in medical applications like CT where a series of images is made in a very short time. The task is to find the physical reason for this afterglow and a way to suppress it.

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- Dipl.-Phys. Jörg Schütrumpf
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- Prof. Dr. Lucas F. Santos
- Prof. Dr. Sergei Fedosov
- Prof. Dr. Shengyi Yang

Research Projects

Fatigue of organic semiconductor components (SFB (DFG), 2003-2014)
Phenomenological modelling of bipolar carrier transport in organic semiconducting devices under special consideration of injection, transport and recombination phenomena (SFB (DFG), 2003-2014)

Polarization and charge in electrically fatigued ferroelectrics (SFB (DFG), 2006-2014)

Kelvin probe investigation of organic field-effect transistors (MaDriX, BMBF-PolyIC, 2007-2010)

Ambipolar light-emitting transistors (TICMO Graduiertenkolleg 1037, 2007-2010)

Development and optimization of tuneable optical filters and VCSEL based on piezoelectric and electret actuators (TICMO Graduiertenkolleg 1037, 2007-2013)

Development of organic piezo sensors (LOEWE AdRIA 26200026, 2008-2011)


Charge carrier injection and transport in doped organic light-emitting diodes (TOPAS, BMBF-OSRAM OS, 2009-2011)

Investigation of the functional principal and optimization of an organic field-effect transistor (DFG, 2009-2010)

Influence of oxygen and water on the optical properties of the X-ray storage phosphor CsBr:Eu2+ (DFG, 2009-2011)

Development of fibre-based organic semiconductor devices for textile applications (LUMOLED, BMBF/VDI/ VDE/ IT, 2010-2012)

**Publications**


Ambipolar field-effect transistors with voltage-dependent emission colour

Eva J. Feldmeier, Christian Melzer, and Heinz von Seggern

The organic light-emitting field-effect transistor (OLET) provides novel aspects for modern organic optoelectronic applications. In particular the full control over the position of the recombination region within the transistor channel [1, 2] appears to be one of the most exploitable properties of OLETs. This property was used to realize OLETs with voltage-dependent emission colours. Two approaches were developed. The first approach contains the combination of an efficient OLET with an independent colour conversion layer on top of the transistor. The colour conversion is achieved by mixing of the transmitted light from the transistor channel and the reemitted light succeeding photo excitation in the conversion layer to longer wavelengths due to a material specific Stokes shift. As the semiconductor and the conversion layer do not need to match electronically an optimized ambipolar transistor setup [1] in terms of carrier transport and quantum efficiency can be chosen. We used a bottom-contact top-gate transistor with F8BT (poly(9,9-di-n-octyl-fluorene-alt-benzothiadiazole)) as the bipolar semiconductor material and PMMA (poly(methylmethacrylate)) as the dielectric gate insulator. To achieve a colour shift of the emitted light, rubrene is evaporated on the semitransparent top-gate contact of the F8BT transistor partially covering the channel. As the absorption spectrum of rubrene matches the emission spectrum of F8BT a colour change can be expected once the rubrene layer is excited via the F8BT emission.

Figure 1:
a) Transistor setup and micrographs of the transistor channel at different gate voltages at a drain voltage of 100 V. The position of the emission region appears as bright but narrow vertical strip in the transistor channel highlighted by the arrows.
b) Electroluminescence spectra of a F8BT / rubrene transistor at VGate = 40 V and 80 V at VDrain = 100 V.
c) Micrograph of the channel taken at long exposure time at increased VGate in 5 V steps from 10 V to 90 V.
The emission colour change from green to yellow in conjunction with the position of the recombination zone is summarized in Figure 1a, where the position of the emission region appears as bright but narrow vertical strip in the transistor channel highlighted by the arrows. The electroluminescence spectra taken at gate voltages of 40 V and 80 V in Figure 1b show the shift of the maxima of 30 nm. The colour change from green to yellow is also obvious in the electroluminescence map in Figure 1c taken at long exposure time for stepwise increased gate voltage at a constant source drain voltage of 100 V.

The second approach contains an OLET with colour tuneable light emission whereby the emission colour can be defined by the vertical position of the recombination zone and thus by the applied voltages. The device is realized by a parallel layer stack of two ambipolar organic semiconductors with different optical and suited electrical properties. Once the transistor is switched from the unipolar to the ambipolar regime a shift in the emission maximum of 50 nm is achieved as the spectra in Figure 2 display. The position of the recombination zone is vertically moved through the layer stack and depending on the material, the emitted light is either red or green. Micrographs of the recombination zone and transistor schemes are also shown in Figure 2.

![Electroluminescence spectra, photographs of the recombination zone and transistor schemes at different gate voltages and V_Drain = 100 V.](image)

**Figure 2:** Transistor with a semiconductor stack consisting of different materials and calcium/gold contacts. Electroluminescence spectra, photographs of the recombination zone and transistor schemes at different gate voltages and V_Drain = 100 V.

**References:**


The understanding of polarisation switching dynamics of ferroelectrics is of great importance for practical applications and is being steadily advanced for ferroelectric ceramics and polymers for more than half a century. The temporal behaviour of polarisation reversal in ferroelectric polymers like polyvinylidene fluoride (PVDF) cannot be satisfactorily explained by simple models such as the classical Kolmogorov–Avrami–Ishibashi nucleation and growth theory [1-3] or by models considering stretched exponential laws. In the present results the Inhomogeneous Field Mechanism (IFM) model recently proposed for PZT ceramics [4] has been applied to polymer ferroelectrics for the first time.

We think the IFM model is suitable for PVDF, because it is semi-crystalline and has different permittivities $\varepsilon$ for the amorphous ($\varepsilon_a = 3$) and the crystalline ($\varepsilon_c \sim 20$) phase. This concise difference in $\varepsilon$ makes PVDF an appropriate material for the IFM model. Considering that the displacement in a material is proportional to $\varepsilon^*E$, PVDF shows a distribution in the electric field $E$ over the material volume.

The IFM model is based on the assumption that the switching volume is divided into many regions with independent dynamics, only determined by the local electric field $E$. The local field values are randomly distributed over the ensemble of regions due to intrinsic inhomogeneities of the material. Therefore, an inhomogeneous switching behaviour is induced by the varying local fields of each region. The electric field distribution can be directly extracted from the experimental data. As can be seen from Fig 1a, one starts with the polarisation $\Delta P$ over the mean value of the electric field $E_m$ for different switching times. Normalising the logarithmic derivative $\Delta P/dE_m$ and plot it over the parameter $E_m/[E_m^* \times K(t)]$ shows a similar behaviour for all different switching times (Fig 1b). This indicates that a switching data set for various field strengths over a broad time scale can be characterized by a single electric field distribution function. There is a small discrepancy in the value height of the maximum, but even with this scattering in the data the model delivers quite good results for the switching behaviour. Fig. 2a illustrates the distribution function calculated from the data of Fig. 1b. For the IFM simulation additional parameters are needed: $P_r$ the remanent polarisation value, $\tau_0$ the characteristic switching time constant and $E_a$ an activation field. The latter two are obtained by fitting the values of $E_{\text{max}}$ over the poling time $t_p$ with the
function $E_{th} = \frac{E_a}{\ln \left(\frac{t}{\tau_0}\right)}$ corresponding to the well known empirical function $\tau(E) = \tau_0 \exp\left[\frac{E_a}{E}\right] \alpha$ (with $\alpha = 1$) [5,6]. The fit is displayed in Fig. 2b.

The experimental data were obtained with 9 $\mu$m thick uniaxial stretched PVDF foils from Goodfellow GmbH. These foils have already oriented dipoles and hence are piezoelectric with a coefficient of $d_{33} \sim 18$ pC/N (in poling direction). An electrode of 100 nm aluminium was evaporated on both sides by PVD. The measurements of the polarisation reversal were done with the samples put in series with a measuring capacitor. From the charging of this capacitance the switched polarization was calculated.

As depicted in Fig. 3 the polarisation switches in two stages for high fields applied. At 180 kV/mm the fast part takes place within several tenths of a millisecond, whereas the complete switching tends to saturate above 100 s. This second slow part of the curve is due to screening charges accumulating at the interface layers and can be explained by a two component system as presented by Fedosov and von Seggern in 2004 [7]. The two components are a non-ferroelectric and a ferroelectric phase which are modelled in a sandwich-like layered structure. Charge carriers are travelling through the non-ferroelectric layers and build an interface charge layer at the phase boundaries. The accumulation is characterised by a Maxwell relaxation time $\tau = \varepsilon \varepsilon_0 / \gamma$ and is in the order of $10^{-3}$ – $10^{-5}$ s, which well represents the experimental results for longer time-scales. For lower field strength the fraction of the switched polarisation, which results from the applied electric field, is getting smaller until it is nearly suppressed at $E = 70$ kV/mm. These results are similar to the coercive field strength of PVDF of $E_c = 50$ kV/mm.
The IFM model finally describes virgin samples over a broad time-field domain covering nine orders of magnitude of the poling time and electric field values from 70-180 kV/mm (compare Fig. 3) satisfactorily. In the same way we can conclude that the IFM model is adaptive to ferroelectric ceramics and semi-crystalline polymers.

References:


**Surface Science**

The surface science division of the institute of materials science uses advanced surface science techniques to investigate surfaces and interfaces of materials and materials combinations of technological use. For this purpose integrated UHV-systems have been built up which combine different surface analytical tools (photoemission, electron diffraction, ion scattering, scanning probe techniques) with the preparation of thin films (thermal evaporation, close-spaced sublimation, magnetron sputtering, MOCVD) and interfaces. The main research interest is directed to devices using polycrystalline compound semiconductors and interfaces between dissimilar materials. The perspectives of energy conversion (e.g. solar cells) or storage (intercalation batteries) devices are of special interest. In addition, the fundamental processes involved in chemical and electrochemical device engineering and oxide thin films for electronic applications are investigated.

**The main research areas are:**

**Electrochemical Interfaces**
The aim of this research activity is the better understanding of electrochemical interfaces and their application for energy conversion. In addition, empirically derived (electro-)chemical processing steps for the controlled modification and structuring of materials is investigated and further optimized. In the center of our interest are semiconductor/electrolyte contacts.

**Intercalation Batteries**
The aim of this research activity is the better understanding of electronic properties of Li-intercalation batteries and of their degradation phenomena. Typically all solid state batteries are prepared and investigated using sputtering and CVD techniques for cathodes and solid electrolytes. In addition, the solid-electrolyte interface and synthetic surface layers are investigated as well as composite systems for increasing the capacity.

**Thin film solar cells**
The aim of this research activity is the testing and development of novel materials and materials combinations for photovoltaic applications. In addition, the interfaces in microcrystalline thin film solar cells are to be characterized on a microscopic level to understand and to further improve the empirically based optimisation of solar cells.

**Organic-inorganic interfaces and composites**
In this research area we are aiming at the development of composites materials for (opto-)electronic applications. The decisive factors, which govern the electronic properties of interfaces between organic and inorganic materials are studied.

**Semiconducting Oxides**
The aim of this research area is to understand electronic surface and interfaces properties of oxides. We are mainly interested in transparent conducting oxide electrodes for solar cells and organic LEDs but also in dielectric and ferroelectric perovskites.

**Surface analysis**
The UHV-surface science equipment and techniques using different and versatile integrated preparation chambers is used for cooperative service investigations.
For the experiments we use integrated UHV-preparation and analysis-systems (UPS, (M)XPS, LEISS, LEED), spectromicroscopy (PEEM) coupled with UHV-STM/AFM. We further apply synchrotron radiation (SXPS, spectromicroscopy), scanning probe methods (STM, AFM), and electrochemical measuring techniques. UHV-preparation chambers dedicated for MBE, CVD, PVD and (electro)chemical treatment are available.

The members of the group are involved in basic courses of the department's curriculum and offer special courses on the physics, chemistry and engineering of semiconductor devices and solar cells, on surface and interface science, and on thin film and surface technology and electrochemistry.

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Research Projects

Function and fatigue of conducting electrodes in organic LEDs, SFB 595-D3 (DFG 2003-2014)

Polarization and charge in electrically fatigued ferroelectrics, SFB 595-B7 (DFG 2007-2014)

Integriertes Graduiertenkolleg SFB 595 (DFG 2008-2014)

Tunable Integrated Components for Microwaves and Optics, Graduiertenkolleg 1037 (DFG 2004-2013)

Transparent organic phosphorescent devices for application in lighting systems (Osram 2009-2011)

Gradients in Cu(In,Ga)Se₂ thin film solar cells (BMBF 2009-2012)

P-I-N solar cells with alternative highly-absorbing semiconductors (BMBF 2010-2013)

LOEWE Schwerpunkt AdRIA (LOEWE-Hessen: 2008-2011)

Synthese, Charakterisierung und Testung von Katalysatoren für die regenerative Erzeugung von Wasserstoff („H₂-NanoSolar“, BMBF 2009-2012)

Inorganic-organic hybride materials for photovoltaic application (BMBF 2008-2011)

Organic Photovoltaics for Integrated Energy Supply (BMBF 2008-2011)


n-i-p CdTe Hochleistungs-Dünnschichtsolarzellen: Wissensbasierte Optimierung der Materialien, Bauelemente und Präparation (BMU 2008-2011)

Advanced buffer layers for CdTe solar cells (First Solar 2007-2010)

Elektrochemie für Elektromobilität – Verbund Süd (BMBF 2009-2011)

Funktionsmaterialien und Materialanalytik zu Lithium-Hochleistungsbatterien (2009-2011)

Hybridstrukturen aus Phosphoolivinen des Typs LiMPO₄ mit C-Nanofilamenten für Li-Ionen-Batterien, SPP Nanomat (DFG 2008-2012)

Insertionsverbindungen und Elektrolyte für Lithium-Ionenbatterien für solare Anwendungen, Verbundvorhaben LISA (BMBF 2008-2011)

Grenzflächen und dünne Schichten von Ionenleitern: elektronische Struktur, elektrochemische Potentiale, Defektbildung und Degradationsmechanismen, SFB 595-A3 (DFG 2003-2014)

Herstellung und Charakterisierung von Li-Ionen Dünnschichtbatterien SFB-D5 (DFG 2007-2011)
Publications

H. Hoche, C. Pusch, R. Riedel, C. Fasel, A. Klein, Properties of SiCN coatings for high temperature applications – Comparison of RF-, DC- and HPPMS-sputtering, SURFACE & COATINGS TECHNOLOGY 205 (2010), S21-S27.


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12 % efficient CdTe/CdS thin film solar cells deposited with low temperature close space sublimation

J. Schaffner, M. Motzko, A. Tüschen, A. Swirschuk, H.-J. Schimper, A. Klein, W. Jaegermann

CdTe is one of the most promising absorber materials for thin film solar cells. Efficiencies as high as 16.7 % have been reached [1]. The polycrystalline CdS and CdTe films can be prepared by a variety of different techniques like sputtering, chemical bath deposition (CBD), physical vapor deposition (PVD) and close space sublimation (CSS). CSS is a very attractive method for large scale manufacturing due to its high throughput. However, efficiencies of more than 10 % could only be realized with CdTe deposition temperatures above 450 °C with CSS so far [2].

We report 12 % efficient CdS/CdTe thin film solar cells prepared by low substrate temperature CSS. The CdTe deposition was carried out at a temperature of 340 °C, which is much lower than used in conventional CSS processes. The CdTe films were treated with a wet chemical CdCl\(_2\) activation process. Optimal annealing times and temperatures were found for low temperature cells and efficiencies of approximately 10.9 % with a copper free back contact and 12.0 % with a copper containing back contact were achieved using the low temperature process.

CdS and CdTe films were both deposited by high vacuum CSS in superstrate configuration on commercial fluorine doped tin oxide (FTO) substrates (Pilkington TEC15). The substrates were cleaned sequentially with a commercial detergent solution, isopropyl alcohol, and de-ionized water in an ultrasonic bath.

It is shown that CdS substrate temperature and deposition rate affect the morphology of the CdS film and the solar cell efficiency [3]. Therefore, three different sets of parameters for the CdS deposition (Tab. 1) were used in this work.

<table>
<thead>
<tr>
<th>CdS film</th>
<th>substrate temperature</th>
<th>source temperature</th>
<th>deposition time</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>470 °C</td>
<td>710 °C</td>
<td>15 s</td>
</tr>
<tr>
<td>B</td>
<td>520 °C</td>
<td>610 °C</td>
<td>16 min 10 s</td>
</tr>
<tr>
<td>C</td>
<td>380 °C → 420 °C</td>
<td>630 °C</td>
<td>2 min 10 s</td>
</tr>
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</table>

For all cells, a 4 µm thick CdTe layer was formed by CSS deposition with a substrate temperature of 340 °C and a deposition time of 2 min 10 s. For activation, the samples were covered with a CdCl\(_2\)/methanol solution followed by an annealing step in air. To form the primary Te back contact by selective etching, all cells were dipped into an aqueous solution of nitric and phosphoric acid (60 % H\(_3\)PO\(_4\) and 0.8 % HNO\(_3\) in water). The secondary back contact (≈ 100 nm gold) was deposited via sputtering. Finally, the back contact was separated from the front contact by mechanical scratching and the solar cells were divided into smaller cells, each of them having a size of 4 mm x 4 mm.

IV-curves under illumination (AM1.5) were measured and efficiency (\(\eta\)), fill factor (FF), short circuit current density (\(J_{sc}\)) and open circuit voltage (\(V_{oc}\)) were calculated.

The IV-curves and solar cell characteristics of the samples with the three different CdS films are compared in Fig. 1. We observed a higher \(V_{oc}\) but a lower \(J_{sc}\) by using a CdS film prepared with high deposition rate (CdS film A) compared to the solar cell with low deposition rate (CdS film B). This effect was already observed for solar cells with high
The best efficiency (10.9 %) was reached with CdS film C. During deposition of this film, the substrate temperature rises from 380 °C to 420 °C. This increase in sample temperature during deposition may lead to a more homogeneous and dense CdS film. However, to understand how the temperature profile during CdS deposition influences the solar cell efficiency, a systematic study of the CdS film properties before and after activation is still needed.

For the optimization of activation time and temperature, only samples with CdS film A, yielding the best for high temperature solar cells [3], were used. Two annealing temperatures, 380 °C and 400 °C, were tested with different annealing times. Tab. 2 shows the solar cell characteristics for these cells. With an annealing temperature of 380 °C and an annealing time of 35 min, the highest Voc of 0.8 V was obtained. The best Jsc of 22.1 mA/cm² and solar cell efficiency of 10.8 % were reached by annealing at 400 °C for 30 min.

Additionally, some solar cells with a copper containing back contact were prepared. For this, a 3 nm thick Cu film was added on the etched samples by sputtering and the gold deposition was followed by an annealing step at 150 °C for 40 min.

By using this copper containing back contact, we reached a high short circuit current density of Jsc = 23.9 mA/cm² and fill factor of FF = 64.9 %. The best efficiency so far obtained with...
low temperature CdTe and copper containing back contact is 12.0 %. The IV curve of this solar cell is shown in Fig. 3.

![IV curve under AM 1.5 illumination and solar cell characteristics for the best solar cell with low temperature CdTe and copper containing back contact. For the CdS deposition parameters, set A was used.](image)

Fig. 3: IV curve under AM 1.5 illumination and solar cell characteristics for the best solar cell with low temperature CdTe and copper containing back contact. For the CdS deposition parameters, set A was used.

It was thus shown that high solar cell efficiencies (12.0 %) can be reached with reduced CdTe deposition temperatures. The use of lower sample temperatures during CdS and CdTe deposition can reduce the production costs and enable the use of front contact materials with lower thermal stability like aluminum doped zinc oxide (AZO). Further investigations on AZO as alternative front contact material for CdTe thin film solar cells are planned.

The presented work was supported by the German Federal Ministry of Environment (grant no. 0329857B).

References:

The organic semiconductor 2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9’-spirobi- fluorene (Spiro-MeOTAD) is currently investigated as solid hole conductor replacing the liquid electrolyte contact in dye sensitized solar cells. Empirically it was found, that the efficiency of the solid dye sensitized solar cell is improved, when a thin layer of a transition metal oxide as WO$_3$ is inserted between Spiro and the external metal contact. In order to analyze the electronic function of the oxide, we investigate the electronic structure of the WO$_3$/Spiro contact using photoelectron spectroscopy at the synchrotron light source BESSY in Berlin.

In the course of stepwise evaporation of Spiro onto WO$_3$ we find a variation of the Spiro highest occupied molecular orbital HOMO, Fig.2 as well as of the spiro C1s emission, Fig.3, which clearly indicates band bending at the interface. WO$_3$ and Spiro are deposited by PVD in our integrated vacuum system SoLiAS at BESSY.

Figure 2: Valence band states and W4F emissions in the course of the WO$_3$/Spiro interface experiment. The binding energy of the HOMO of Spiro varies with Spiro coverage indicating band bending.
Figure 3: The Spiro C1s core level emission in the course of the WO$_3$/spiro interface experiment also indicates band bending.

Figure 4: In WO$_3$ no band bending is observed, the transferred electrons from Spiro form reduced W$^{5+}$ species at the interface. In contrast to the Spiro orbitals, the WO$_3$ emissions do not vary their binding energy in the course of Spiro adsorption. The electrons transferred from Spiro to WO$_3$ reside on W$^{5+}$ gap states at the interface as indicated in the growth of a reduced component in the W4f emission.

The photoelectron spectra of the interface experiment WO$_3$/spiro can be summarized in the band diagram displayed in Fig. 5. The band bending in Spiro-MeOTAD induced by a WO$_3$ interlayer helps extracting holes from Spiro to the metal contact. This is the mechanism of improving the efficiency of the solid dye sensitized solar cell.
Sn-doped In$_2$O$_3$ (ITO) is a transparent conducting oxide with a high transparency in the visible range of the optical spectrum and high electrical conductivity, which is widely used as transparent electrode material for organic light emitting diodes and organic photovoltaics. The work function of ITO is particularly important for the contact formation with organic semiconductors, as it determines the barrier height for hole injection. The desired high work function is typically achieved by oxygen-plasma or UV ozone treatments. Despite the almost exclusive use of polycrystalline ITO films, only a single value is commonly used for the work function. The fact that the work function can also depend on the surface orientation is thereby completely ignored. The ionization potential, which is the difference between the valence band maximum and the vacuum energy, is a better quantity for characterizing the orientation dependence, as it does not depend on the position of the Fermi level in contrast to the work function. The low index surfaces of In$_2$O$_3$ can be classified according to their polar nature following Tasker. Tasker type I and II surfaces have no electrical dipole moments perpendicular to the surface. They have a structure close to an ideal bulk termination and a low surface energy. In contrast, unreconstructed Tasker type III surfaces have permanent dipole moments, which make them electrostatically unstable. Consequently, the surfaces have a high energy and exhibit various types of reconstruction depending on the oxygen partial pressure.

The surface phase diagram of several In$_2$O$_3$ surfaces has been studied by density functional theory (DFT) as a function of oxygen chemical potential $\mu_O$, which corresponds to the effective oxygen partial pressure during deposition and/or treatment. According to these results only minor or no variations in stoichiometry and consequently of the ionization potential $I_p$ are possible for the (111) and (110) surfaces; practically over the whole stability region of the material the (111) surface has the lowest formation energy. In contrast, the In$_2$O$_3$ (100) surfaces exhibit a large variability with respect to changes in stoichiometry. At low oxygen chemical potentials the metallic termination is the stable (100) termination. For intermediate oxygen chemical potential the stoichiometric termination is most stable and for high oxygen chemical potentials oxygen dimers stabilize the surface.

In$_2$O$_3$ films were grown on (111) and (100) oriented Y-stabilized ZrO$_2$ substrates by using RF magnetron sputtering. The Ar/O$_2$ sputter process gas mixtures were varied between 0% and 10% O$_2$ content (reducing and oxidizing conditions). Epitaxial growth was verified using X-
ray diffraction. Ultraviolet photoelectron spectroscopy (UPS) was carried out in-situ in the DArmstadt Integrated System for MATerials research (DAISY-MAT). There are noticeable differences in valence band emissions around 6 and 11 eV binding energy for (100) or (111) oriented films, which are related to the different orientations and therefore provide a further hint for epitaxial growth and different surface orientations of the films. Measured and calculated values for the ionization potential are compared in Fig. 2. An explanation for the variation of ionization potential with oxygen content in the process gas is provided by the dependence of surface stability on the chemical potential of oxygen. The (111) surface is thermodynamically stable for almost all values of $\mu_O$ while the peroxide-terminated (100) surface becomes stable for strongly oxidizing conditions. A comparison of the ionization potentials for measured and calculated data shows good agreement for the (111) film deposited without oxygen and the calculated $I_p$ for the (111) surface, suggesting that growth took place in the stability region of the (111) surface. The same applies for the (100) film deposited with oxygen: the measured $I_p$ corresponds to the calculated one for the peroxide terminated (100) surface. By comparing the experimental and theoretical values we can conclude an ionization potential of $\sim 7.1$ eV for the In$_2$O$_3$(111) surface and an ionization potential of $\sim 7.7$ eV for the peroxide terminated In$_2$O$_3$(100) surface. These values are good agreement with the ionization potentials of preferentially oriented In$_2$O$_3$ and ITO films.

Fig. 2: (left) Normalized UP spectra of In$_2$O$_3$ films deposited using 0 % and 10 % O$_2$ in the process gas onto YSZ(100) and (111) substrates. The valence band maximum is taken as binding energy reference. (top right) Calculated ionization potentials. (bottom right) Comparison of calculated and measured ionisation potentials.

The results clearly demonstrate the importance of the surface orientation for the work function of polycrystalline ITO thin films. High work functions can only be achieved for the (100) surface orientation. The applied oxidative treatments of the ITO films in organic light emitting devices are also only effective for the (100) surface, as no dependence of surface termination occurs for the other surface orientations. ITO films with a preferred (100) orientation should thus perform better in organic LEDs. Polycrystalline films will also exhibit a large lateral variation of the work function and consequently a strongly inhomogeneous current injection.
The Advanced Thin Film Technology (ATFT) group works on advanced thin film deposition techniques of novel materials. The group is specialized on physical vapor deposition techniques such as pulsed laser deposition (PLD), advanced oxide molecular beam epitaxy (ADOMBE) and dc/rf-magnetron sputtering. The ADOMBE system has been jointly financed by Max-Planck-Institute for Solid State Research in Stuttgart and TU Darmstadt. PLD and ADOMBE are part of a cluster system allowing for in-situ sample exchange between the different deposition methods and characterization tools. The ADOMBE apparatus is a worldwide unique thin film deposition system which is dedicated to the growth of complex oxides beyond thermodynamic equilibrium. It allows for the simultaneous deposition of six elements from electron beam sources and further elements evaporated from effusion cells. The molecular beams of each element can be individually controlled by a feed back loop using electron impact emission spectroscopy (EIES).

The class of oxide ceramics, in particular with perovskite (derived) structures, comprises a stunning variety of new functional materials. Examples are high-temperature superconductors, magnetic oxides for spintronics, high-\(k\) dielectrics, ferroelectrics, and novel thermoelectric materials. As a vision for future, new solid state matter can be created by building hetero- and composite structures combining different oxide materials. While present day electronic devices heavily rely on conventional semiconducting materials, a future way to create novel functional devices could be based (completely) on oxide electronics. Oxide electronics and spintronics are also part of the research and graduate education program “Matronics” that is financed by the HMWK (Hessisches Ministerium für Wissenschaft und Kunst).

The group uses a Rigaku SmartLab x-ray thin film diffractometer with rotating anode ("synchrotron in house"). Other characterization tools located in the Advanced Thin Film Technology group include powder x-ray diffraction (XRD), x-ray photoemission spectroscopy (XPS), high-resolution scanning electron microscopy (HREM) with light element sensitive EDX, and SQUID magnetometry. A 16 Tesla magnet cryostat allowing measurements down to liquid helium temperature has been installed. Another magnet cryostat (10 T) lowering the available temperature range to below 300 mK is also available. This cryostat also contains high-frequency feed-throughs for electrical characterization (40 GHz). The group is also using external large scale facilities as synchrotron radiation (ESRF, Grenoble) and neutron reactors (ILL, Grenoble / HMI, Berlin) for advanced sample characterization.

Close cooperation exists in particular with the Max-Planck-Institute for Solid State Research in Stuttgart, with the Japanese company NTT in Atsugi near Tokio, with the University of Tokio, Chalmers University of Technology, and Hyderabad University. Throughout 2010 Lambert Alff was working also as a Dean of Studies in the faculty of Materials Science. In this time the new Master of Science program in Materials Science has been developed.

### Staff Members

<table>
<thead>
<tr>
<th>Role</th>
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**Research Projects**

Superconductivity in water intercalated Na$_3$CoO$_2$ thin films (TU Darmstadt, TU Braunschweig, and Max-Planck-Institute for Solid State Research, Stuttgart) (DFG 2006-2011)

Superconductivity and magnetism in the phase diagram of bulk La$_{2-x}$Ce$_x$CuO$_{4+\delta}$ investigated by muon-spin spectroscopy and neutron scattering (TU Darmstadt, PSI, Helmholtzzentrum Berlin) (DFG 2009-2011)

Novel arsenic free pnictide superconductors (SPP 1458) (DFG 2010 - 2012)

Doped SrTiO$_3$ for Microwave Applications and Multiferroics as novel materials for tunable components, within DFG Research Training Group 1037 “Tunable Integrated Components in Microwave Technology and Optics” (DFG 2008-2012)


HMWK graduate school for Matronics (HMWK 2008 - 2010)

Oxide-MBE (MPI-FKF/TUD 2007-2012)

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**Publications**


Advanced Oxide Molecular Beam Epitaxy (ADMOBE)

J. Kurian, E. Hildebrandt, L. Alff

MBE and oxide MBE [1] is a synthesis technique which enables the growth of even metastable phases which are not accessible by any other technique as one uses elemental sources for the film growth of complex compounds on a suitable substrate by reaction of the various elemental fluxes at the substrate surface. In addition, the substrate surface induced strain can be used to nucleate and stabilize such metastable phases. ADMOE is equipped with 6 electron beam evaporators and 4 effusion cells. A schematic of ADMOE is shown in Figure 1. Mostly effusion cells are used in the case of conventional MBE growth as the source for the generation/supply of the required atomic flux at the substrate surface. However, when it comes to refractory metals or elements with high melting point, the use of effusion cells become challenging, if not impossible and the solution is to resort to e-gun evaporation. A second enormous advantage of e-guns is that they respond ultra-fast to the feedback signals which are used for real-time flux rate control. Altogether, the use of combination of e-guns and effusion cells allows one to cover a large spectrum of compounds with a wide range of elements which are accessible by ADMOE. As the success of the growth of any complex oxides very much depend on the ability to precisely control the cation ratio (in other words the stoichiometry) with an accuracy better than 1% in real time during the entire growth process, one needs reliable and sensitive monitoring and control techniques. This demands the use of spectroscopic techniques like Electron Impact Emission Spectrometry (EIES) or Atomic Absorption Spectrometry (AAS). ADMOE uses EIES technique with the state-of-the-art gas compensating dual sensor heads with 6 channels allowing the monitoring and control of 6 elemental species simultaneously. (Gas compensation sensor heads eliminate the interference of the reaction gases and residual gases which significantly improves the accuracy and sensitivity of the flux measurement.) In addition, ADMOE houses three quartz crystal microbalance (QCM) monitors that utilize the state-of-the-art mode lock technology from Inficon for the monitoring and control of elements with weak emission lines which are difficult to monitor/control by EIES technique. QCM rate monitors also helps in the in situ calibration of EIES sensors. In addition to the precise rate control of the various cations involved, controlled oxidation of the various species also plays a vital role in the successful growth of complex oxides.

ADMOBE has the possibility to use either RF activated radical oxygen (enabling a wide range of control of the oxidation conditions by varying the RF power, flow rate, etc) or ozone. Both radical oxygen and ozone provide strong oxidation at low flow rates. The differentially pumped radical oxygen source also helps to keep the chamber pressure low which, in turn, enables the growth of thin films at lower substrate temperatures making the intermixing of the different layers due to bulk diffusion minimal. In ADMOE we use the IR laser heating of the substrates. This has numerous advantages: As it is possible to heat the substrate directly, one need not any gluing of the substrate making it a cleaner heating environment. Impurities are further minimized because there is no need for any hot heating element in the vacuum side. Since the substrate is heated directly, it is also possibly to heat or by the cool the substrate faster. This is particularly useful in case of ‘freezing’ a particular structure. In addition, laser heating of the sample allows the heating of the samples to higher
temperatures (only limited melting temperatures of the substrates) than in the case of conventional substrate heating. ADOMBE also utilises the conventional MBE in situ characterisation tools like Reflection High-Energy Electron Diffraction (RHEED), mass spectrometer, etc. for monitoring and characterisation of the films during growth. RHEED, in fact is an indispensable tool to the MBE growth as it provides vital information on the surface characteristics of the film in real-time, controlling the growth process and most notably helps in identifying the presence of undesired phases or precipitates formed during the growth. This information is useful in modifying the growth conditions accordingly in order to eliminate such undesired phases in real-time reaction.

In all fields of applications of oxides, more and more complex materials with more than 3 cations are coming into the focus of research. ADOMBE is a tailored synthesis tool to study the functional properties of such (metastable) complex multi-cation oxides as a function of doping and substitution. With this goal in mind, we have incorporated all our experience in thin film technology and the latest equipment developments into ADOMBE.

Reference
Dispersive Solids

The main research interests of the group Dispersive Solids are directed towards the development of novel strategies suitable for the synthesis of inorganic, oxidic and non-oxidic materials with properties beyond the state of the art. The materials of interest are advanced oxidic and non-oxidic ceramics with extraordinary properties in terms of thermal stability, hardness and electronic structure. Therefore, synthesis methods such as polymer-pyrolysis, non-oxidic and oxidic sol-gel methods, chemical vapour deposition and novel high pressure methods have been further developed.

The following topical issues are presently under investigation:

Polymer-Derived Ceramics
The thermolytic decomposition of suitable organosilicon polymers provides materials which are denoted as polymer-derived ceramics (PDCs). The main emphasis is on the synthesis and characterization of new ceramic materials in the B-C-N, Si-C-N, Si-O-C, Si-(B,C)-N and Ti-(B-C)-N systems. The structural peculiarities, thermochemical stability, mechanical and electrophysical properties of the PDCs have been investigated in a series of PhD theses and research projects. Due to their outstanding thermochemical stability as well as excellent oxidation and creep resistance at very high temperatures, the PDCs constitute promising materials for high temperature applications. Another advantage of the PDC route is that the materials can be easily shaped in form of fibres, layers or bulk composite materials. Finally the correlation of the materials properties with the molecular structure of the used preceramic polymer is elaborated.

Molecular Routes to Nanoscaled Materials
The aim is to develop concepts for the production of novel multifunctional inorganic materials with a tailor-made nanoscaled structure. In accordance with the so-called “bottom-up” approach, specific inorganic molecules are to be assigned to higher molecular networks and solid-state structures in the form of molecular nanotools by means of condensation and polymerisation processes.

High Pressure Chemistry
Ultra-high pressure techniques like laser heated diamond anvil cell (LH-DAC) or multi anvil devices have been applied to synthesise novel solid state structures which cannot be produced by other methods, for example, inorganic nitrides. Moreover, the materials behaviour under pressure such as phase transformations and decomposition can be analysed.

Functional Materials
Further research topics are related to the development of materials suitable for applications in the fields of microelectromechanical systems (MEMS), optoelectronics (LEDs), pressure, temperature and gas sensors as well as thermoresistant ceramic membranes for high temperature gas separation. The integration of state-of-the-art in situ and in operando spectroscopic methods is applied to understand the mechanisms responsible for sensing and catalytic properties.
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Research Projects


Nanocomposites as anode materials for lithium ion batteries: Synthesis, thermodynamic characterization and modeling of nanoparticulate silicon dispersed in SiCN(O) and SiCO-based matrices (DFG, Aug. 2010 – July 2013)

Nanostructure and Calorimetry of Amorphous SiCN and SiBCN (DFG, April 2010 – March 2013)


Indium oxide (In$_2$O$_3$) under high pressure: rational design of new polymorphs and characterisation of their physico-chemical properties (DFG, June 2009 – May 2012)


Polymerabgeleitete SiCO/HfO$_2$ und SiCN/HfO$_2$ Keramik-Nanokomposite für Höchsttemperaturanwendung (DFG, SPP 1181 – NANOMAT, Jan. 2007 - Sep. 2011)


Development and Structure Formation Mechanism of Self-Supported Ceramic Networks for Multifunctional Applications (Humboldt Fellowship, Aug. 2010 – July 2011)

Modelling of composite pressure cylinder rupture in aerospace application (Diploma Thesis in cooperation with Airbus Operation GmbH, Hamburg and Grenoble INP Phelma, SIMAP St Martin d’Heres, France, Nov. 2010 – April 2011)
Detailed characterisation of different grades of cast irons and cast steels – composition of subject cards (Diploma Thesis in cooperation with Ferry Capitain, Joinville, France, Sep. 2010 – March 2011)


Entwicklung neuer Prozesse für die Atmosphärendruckplasmadeposition zur Erzeugung industriell einsetzbarer Oberflächen (Diploma Thesis in cooperation with Siemens AG, Erlangen, Sep. 2010 – Feb. 2011)


5th International Workshop on Spinel Nitrides and Related Materials, Rüdesheim (DFG, Aug. 2010 - Sep. 2010)


Hybrid materials consisted of electroactive polymers and metal hexacyanometallates as electrode materials for supercapacitors (Training program of "Development of interdisciplinary studies at Gdansk University of Technology within the scope of modern technologies")


Free-standing ultrathin ceramic foils (Diploma Thesis in cooperation with ETH Zurich, Nov. 2009 – April 2010)
Hochdrucksynthese neuartiger binärer und ternärer superharter Phasen im System Si-C-N (DFG, SPP 1236, May 2008 – April 2010)


Publications


**Books**

Nanodomain Structure of Carbon-Rich Silicon Carbonitride Polymer-Derived Ceramics

Gabriela Mera, a Aitana Tamayo, a Hong Nguyen, a Sabyasachi Sen, b and Ralf Riedel a

a Technische Universität Darmstadt, Institut für Materialwissenschaft, Darmstadt, D-64287, Germany
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The presence of nanodomains in polymer-derived ceramics constitutes one of the most intriguing features of this class of materials. In the present work, the nanostructure of novel carbon-rich silicon carbonitride (SiCN) ceramics synthesized via thermolysis of poly(methylphenylsilylcarbodiimide), –[Ph(CH3)Si-NCN]n–, at 1300°, 1500°, 1700°, and 2000°C is investigated by micro-Raman spectroscopy, X-ray powder diffractometry, and small-angle X-ray scattering (SAXS). The structural information obtained from these experimental methods is combined together with theoretical modeling of the SAXS data to obtain a detailed model of the temperature-dependent evolution of nanodomains comprised of free carbon, SiC, and Si3N4 in SiCN-based ceramics.

Fig. 1: Results of the simulation of the particle size distributions in the SiCN ceramics annealed at different temperatures as based on the experimental small-angle X-ray scattering data.

In conclusion, several characterization techniques have been used in order to investigate the nanostructure and nanodomains present in poly(methylphenylsilylcarbodiimide)-derived ceramics synthesized at 1300, 1500, 1700 and 2000°C. At 1300°C, the sample is X-ray amorphous. By Raman spectroscopy, a lateral carbon particle size Lc of 2.01 nm was determined, and the value coincides with the 2.08 nm (spheroid shape) evaluated by...
modeling the SAXS data. Moreover, nanodomains of amorphous Si$_3$N$_4$ (2.33 nm, spheroid shape) and an amorphous interphase of SiC domains (0.98 nm, spheroid shape) were identified. At 1500 °C, the amorphous SiCN starts to crystallize to give rod-like SiC (1.56 nm), while the remaining Si$_3$N$_4$ phase persists to be amorphous (1.45 nm, spheroid shape). Nanodomains of spherical SiC domains (0.79 nm) are still present at this temperature. The divergence between the nanodomain size calculated from the Raman spectra and that derived from the SAXS data is probably due to experimental and modeling errors. At 1300° and 1500 °C the modeled shape of the samples is predominantly spherical. At 1700 °C, the clusters of crystalline carbon and SiC are embedded in the matrix of carbon. The amorphous nanodomains of rod-like carbon determined by SAXS modeling is 0.75 nm and 7.4 nm length while the Raman-determined cluster size of carbon is 1.35 nm. No more amorphous SiC and Si$_3$N$_4$ nanodomains are present after annealing of the SiCN sample at this temperature. The crystalline SiC phases are analyzed as rods and spherical particles, with 2.61 and 1.12 nm in size, respectively. Rod-like particles of SiC (15.99 nm length) simulated from SAXS are assimilated to crystallites with 14.27 nm lateral size determined by Rietveld refinement. Moreover, the SAXS simulation shows the presence of rods of turbostratic carbon with 0.75 nm lateral size and 9.85 nm length. XRD analysis is probably not sensitive enough to detect such small sizes and, therefore, the presence of t-C cannot be experimentally identified. At the highest temperature of 2000 °C, the nanostructure is composed of amorphous carbon (3.09 nm by SAXS), crystalline SiC (rods with 5.14 nm and spheroids with 1.01 nm in size) and turbostratic rod-like carbon with 0.99 nm. The Raman analysis gives a carbon cluster size of 1.11 nm. The length of the crystallite obtained from the Rietveld refinement is 57.23 nm while particles of 60.8 nm are analyzed from the SAXS data. In general, the results derived from X-ray diffraction are similar to that of the SAXS measurements; the differences in the particle size determination are due to the impossibility to distinguish the shape of the particles. Information on size, composition, shape, orientation, and volume fraction of the nanodomains are provided by SAXS analysis. The Rietveld refinement of the XRD diffractometry data assume that all the particles are spherical, which is not true. Therefore, a dissimilarity of the sizes can be observed. However, an excellent correlation in the determination of the particle size exists between the Raman spectroscopy and the SAXS analysis.

To conclude, Raman spectroscopy, XRD and SAXS results indicate that the structure of polymer-derived carbon rich SiCN ceramics consists of nanodomains. The carbon-rich ceramics derived from [PhMeSi-NCN]$_n$ reveal the presence of more than one type of nanodomain in the microstructure, compared to the low-carbon poly(methylsilylcarbodiimide)-derived ceramicsobtained from [HMeSi-NCN]$_n$. These results clearly show that excess carbon in the SiCN composition plays an important role in the temperature dependent formation of the nanodomain structure of these polymer-derived ceramics. An increase in the nanodomain volume fraction in the SiCN ceramics implies an increase in the intergranular surface area and consecutively in the “reactivity” of the PDCs. However, despite the pronounced nanodomain structure, the PDCs are thermally stable, resistant to corrosion and chemically inert as has been shown by a number of experimental studies reported in the past. According to these studies nanostructured polymer-derived ceramics such as these carbon-rich PDCs are excellent candidate materials for high-temperature applications in the fields of catalyst supports, MEMS/NEMS or advanced ceramic fibers and protective coatings. Therefore, further studies are needed in future to understand the relationship between the nanodomain structure of PDCs and their unusual physical-chemical properties.
A static pressure-induced decomposition of indium hydroxide into metallic indium that takes place at ambient temperature is reported. The lattice parameter of c-In(OH)₃ decreased upon compression from 7.977(2) to 7.45 Å at 34 GPa, corresponding to a decrease in specific volume of 18%. Fitting the second-order Birch-Murnaghan equation of state to the obtained compression data gave a bulk modulus of 99 (3 GPa for c-In(OH)₃. The c-In(OH)₃ crystals with a size of 100 nm are comminuted upon compression, as indicated by the grain-size reduction reflected in broadening of the diffraction reflections and the appearance of smaller (5 nm) incoherently oriented domains in TEM. The rapid decompression of compressed c-In(OH)₃ leads to partial decomposition of indium hydroxide into metallic indium, mainly as a result of localized stress gradients caused by relaxation of the highly disordered indium sublattice in indium hydroxide. This partial decomposition of indium hydroxide into metallic indium is irreversible, as confirmed by angle-dispersive X-ray diffraction, transmission electron microscopy imaging, Raman scattering, and FTIR spectroscopy. Recovered c-In(OH)₃ samples become completely black and nontransparent and show typical features of metals, i.e., a falling absorption in the 100-250 cm⁻¹ region accompanied by a featureless spectrum in the 250-2500 cm⁻¹ region in the Raman spectrum and Drude-like absorption of free electrons in the region of 4000-8000 cm⁻¹ in the FTIR spectrum. These features were not observed in the initial c-In(OH)₃, which is a typical white wide-band-gap semiconductor.

Fig. 1: Optical microscopy images of c-In(OH)₃ samples loaded in DACs (Re gasket with Pt foil): (A) initial sample (white) at ambient pressure; (B) sample after compression to 33 GPa; (C) sample after rapid decompression to ambient pressure from the first compression experiment; (D) sample recovered to ambient pressure after two successive loadings from the second experiment (see the text). Images A-C were taken under transmitted light and image D under reflected light.
Fig. 2: Second experiment: in situ energy-dispersive XRD patterns of c-In(OH)$_3$ that was compressed in a DAC to $\sim$20 GPa and quickly decompressed to ambient pressure. The bottom pattern (labelled as “after decompression from 20 GPa”) is for the sample in the DAC at ambient pressure. The next six patterns are for samples compressed to pressures in the range 6-34 GPa (as indicated), and the top pattern is for the sample recovered to ambient pressure after compression up to 34 GPa. In the top pattern, the ($hkl$) planes of c-In(OH)$_3$ and a (011) plane of t-In are indicated.

Fig. 2: a) Scanning electron microscopy image of the initial white c-In(OH)$_3$ sample. (b, c) TEM micrographs of the recovered black In/c-In(OH)$_3$ sample. The inset in (c) reveals an inverse FFT image of the boxed region. The measured distance obtained from the inverse FFT image is 2.74 Å, which is in good agreement with the $d_{011}$ distance in t-In.
In summary, a partial decomposition of indium hydroxide into metallic indium induced by a static pressure at ambient temperature has been observed. This unique process is initiated by rapid decompression, is irreversible, and seems to be intimately related to the disordering of the indium sublattice in indium hydroxide. The instability of c-In(OH)$_3$ as well as of any other metal hydroxide/oxohydroxide toward decomposition under high pressure conditions has not been reported previously.
Structure Research

In the year 2010, Dr. Helmut Ehrenberg accepted a position as a Full Professor of Anorganic Chemistry at the Karlsruhe Institute of Technology. We wish him the best for his new position. The collaborative research program about “Fatigue in electrical functional materials” was extended for another four years, and so was the project of the Structure Research Group. The diffraction equipment is being gradually renewed: we installed a Guinier Camera with an integrated image plate system and a closed cycle cryostat.

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Research Projects

Design, realisation and operation of the new neutron structure powder diffractometer SPODI at the FRM-II, TU München in Garching (BMBF, 1998-2010).

Electron and magnetization density in the transition metal oxide Co₃V₂O₈ (DFG, 2005-2010).

Heterogeneously catalyzed partial oxidation of acrolein to acrylic-acid structure, influence of water of the V-Mo-W mixed oxides (DFG 2007-2010)
DAAD exchange program with Slovakia (2006-2011).

Structural investigations into the electric fatigue in PZT (DFG-SFB, 2003-2010)

In-situ investigations of the degradation of intercalation batteries und their modelling (DFG-SFB, 2003-2010)

Spinel cathode materials LiM$_{2}$Mn$_{2-x}$O$_{4}$, M=Cr, Fe , Co, Ni, optimized for high-power Li-ion batteries with high cell voltages (DFG, 2007-2010)

The electronic structure of TiO$_{2}$, VO$_{2}$ and related transition-metal oxides: A joined electron-density study of materials in position, momentum and phase space (DFG, 2009-2011)

Correlated momentum, charge and magnetization density in the kagome staircase system Co$_{3}$V$_{2}$O$_{8}$, (DFG, 2009-2011)

**Publications**

Alyoshin, V.A.; Romanova, I.P.; Mikhailova, D.; Oswald, S.; Senyshyn, A.; Ehrenberg, H., Oxygen nonstoichiometry of tetragonal La$_{2-x}$Sr$_{x}$CuO$_{4-δ}$ (x = 0.15–1.2) and in situ XPS studies at elevated temperatures, J. Phys. Chem. A, 114:13362–13369 (2010)


Bhaskar, A.; Bramnik, N.N.; Senyshyn, A.; Fuess, H.; Ehrenberg, H., Synthesis, characterization and comparison of electrochemical properties of LiM$_{0.5}$Mn$_{1.5}$O$_{4}$ (M=Fe, Co, Ni) at different temperatures, J. Electrochem. Soc., 157(6):A689-A695 (2010)


Zuniga, F.J.; Garcia-Garcia, F.J.; Hoelzel, M.; Reller, A., *Al_{14}Ba_{8}La_{26.3}Ru_{0.18}Sr_{53.7}O_{167}: a variant from the cubic perovskite with isolated RuO_{6} units*, Acta Cryst. C 66:150-154 (2010)

Additional 89 publications in Acta Cryst E
Epitaxial Strain-Induced Chemical Ordering in La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ Films on SrTiO$_3$


La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (LSCO) has been considered as one of the best candidate for cathode materials in solid-state oxide fuel cells (SOFCs) and for oxygen separating membrane applications. In order to reduce the working temperature of SOFCs and thereby save costs and enhance the lifetime of the cells, it is necessary to enhance the ion conductivity of the cathode. It has been suggested that one way of enhancing the mobility of oxygen ions is to provide disorder-free channels of oxygen vacancies by using compounds with perovskite structure that exhibit cation ordering. Although LSCO has otherwise desirable properties, it does not show cation ordering in bulk powder samples. Electron microscopy studies on thin films demonstrated the occurrence of superstructures in small regions of the sample, but those have been generally attributed to particular patterns of oxygen vacancy ordering, not to chemical ordering of the cation sublattices. The choice of the right substrate and favorable oxygen partial pressure and temperature should be able to provide the conditions for cation ordering, thereby inducing vacancy ordering and enhanced oxygen transport properties. In this letter, we report on the chemical ordering in LSCO films epitaxially grown on [001]-oriented SrTiO$_3$ (STO) and the structure and epitaxy of these films in different oxygen partial pressure environments.

![Fig. 1: X-ray diffraction $\theta$-2$\theta$scans along the surface normal ([001]-direction) of a 40 nm thin LSCO film on STO. Closed symbols are for a pressure of 1 atm air and a temperature of 300 K; open symbols are for 0.1 atm air and a temperature of 650 K. Note the large shift of the film peak from the right side of the substrate peak to its left side.](image-url)
Figure 1 shows a θ-2θ scan along the surface normal of a 40 nm thin as-grown LSCO film inside the mirror furnace at 300 K and 1 atm air (closed symbols); the scan is calibrated in terms of the substrate reciprocal lattice. Only the (00l) reflections of LSCO together with those of STO appear in the diffraction pattern. (The center of the STO (002) reflection is left out of the scan because of a detector non-linearity.) This scan illustrates that the LSCO film has its c-axis oriented normal to the substrate surface. The lattice parameter c determined from the scan in figure 1 is 0.3804 nm. After pumping down the furnace volume to 0.1 atm air, no change of the diffraction pattern was detectable within the first hour. Subsequent heating at this pressure first led to a slight lattice parameter change visible at 500 K but then when the temperature was raised to T=650 K at a heating rate of 1 K/sec a massive change occurred. The open symbols in figure 1 represent a scan at a steady-state condition of T=650 K. The LSCO (002) reflection had moved from the right side of the STO reflection to its left side (l=1.942). This corresponds to an expansion of the film lattice of 5.7% along the c-direction; 0.7 % of that value can be attributed to thermal expansion, the rest results from a structural change described below. At the same time, an additional reflection corresponding to a doubling of the unit cell appeared with a maximum intensity of about 10 % of the fundamental (002) reflection. This enormous lattice expansion is reversible at a temperature of 650 K: venting of the furnace to 1 atm air leads to a shift of the (002) peak back to its original position together with the disappearing of the half-order reflections.

We derived the structural models in figure 2 from the intensities of the observed film reflections in the pseudo-cubic and the expanded, tetragonal phase. Figure 2a shows two unit cells of the pseudo-cubic phase with the La and Sr cations randomly distributed. The Co ions are octahedrally coordinated by oxygen ions and each oxygen ion is shared by two cobalt ions. Heating the sample under a lower oxygen partial pressure leads to the removal of the apical oxygen (one out of six oxygen atoms) together with the chemical ordering of the cations. La$^{3+}$ (small spheres) ions move into the oxygen-deficient planes, whereas Sr$^{2+}$...
ions (large spheres) are located within the oxygen-containing planes (figure 2b). The intensities of the half-order reflection cannot be explained with oxygen vacancy ordering alone, but require cation ordering to be taken into account. In the particular example shown above, the degree of chemical ordering within the cation sublattices is about 66%. The cobalt coordination changes to square-pyramidal, leaving the Co in a mixed-valence (oxidation state 2.5) state, slightly lifted from the pyramid base (see parameters in table 1). The size difference between the La$^{3+}$ (1.16 Å (VIII)) and Sr$^{2+}$ (1.44 Å XII) ions together with the Coulomb repulsion between the Co ions leads to the huge lattice expansion of 5.7%.

References:
Materials Analysis

The Materials Analysis group participates in two of the five Research Clusters of the Technische Universität Darmstadt: New Materials and Nuclear and Radiation Science. On the one hand the group is concerned with the characterization of self-synthesized modern materials, on the other hand with effects on materials caused by exposition to detrimental influences like ion irradiation. The research aims for clarification of the correlation of materials properties and synthesis or exposition parameters, respectively, by investigation of the elemental composition and the chemical binding.

Current research topics are:

**Nanochannels, nanowires and nanotubes:** Utilizing polymer foils which were irradiated by high energy ions, a set of nanostructures can be produced with a variety of applications. Nanochannels, produced by chemical etching of the irradiated foils, can be transformed into bio-specific sensors or into devices with selective transport properties, depending on the functional groups that are attached to their surfaces. The research is concerned with facile and versatile ways to achieve this attachment as well as with applications, e.g. as sensors for protein analytes or as logic gates.

By filling the channels nanowires can be obtained which can be freed from the template by dissolution of the latter. Nanowires can be used for fundamental research, e.g. the investigation of the Kondo effect, but also as nanowire arrays in sensor applications, e.g. as gas sensors.

By altering the filling process the resulting structure is not a wire but a tube. The correlation of synthesis conditions, morphological parameters and properties is investigated and optimized towards the utilization in catalysis, particle separation and sensor technology.

This work is conducted in collaboration with the GSI Helmholtzzentrum für Schwerionenforschung.

**Materials in Radiation Fields:** The degradation under intense ionizing radiation is investigated for different materials, such as semiconductors, amorphous magnetic alloys, polymers, graphite and scintillators. Many of those materials will be used in components (beam guiding magnets, beam dump, detectors) of the next generation accelerator facility at the GSI Helmholtzzentrum für Schwerionenforschung. In situ characterization is performed at the M-branch of the UNILAC experimental hall in the GSI by various analytical tools, e.g. FT-IR and UV/VIS measurements as well as mass spectrometry.

**Thin film preparation:** Surface coatings and surface modifications are prepared on a scale from single molecular layers to films of about 200 nm thickness. The preparation technique depends on the purpose of the treatment, which can be, to name a few: 1) the synthesis of a functional material, e.g. a gas sensor prepared by electrochemical deposition, or a lead-free piezoelectric thin film prepared by spin- or dip-coating of a sol-gel solution. 2) the synthesis of an additional top-layer to improve certain parameters, e.g. the corrosion protection of light metals and their alloys by atomic layer deposition, or the friction coefficient by addition of a diamond-like carbon layer via plasma based ion deposition. 3) alteration of the surface layer, e.g. increase of hardness or adhesion by implantation of ions.

**Thin film analysis:** Apart from the analysis of the self-synthesized samples mentioned above a variety of in-house techniques as well as externally available measurement facilities are used for characterization and fault analysis in collaboration with other research groups and institutes. This includes for example oxygen and hydrogen diffusion measurements in bulk samples of ferroelectrics by SIMS or the investigation of the binding states of thin
carbonitride films with the substrate by NEXAFS at Bessy II, jointly with the PTB. Other techniques involved are mainly ion beam based – like RBS, NRA and ERDA – but not exclusively so, e.g. positron annihilation spectroscopy is also applied.

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Research Projects


Degradation of plastics in superconducting magnets by heavy ion irradiation (GSI, 2007 – 2010)

Radiation stability of graphite as production target and ion beam dump of the Super-FRS (GSI, 2007 – 2010)

Interdiffusion and crystallinity of advanced thin film systems for spintronic applications (DAAD, 2009– 2010, jointly with Pedagogical University Krakow, Poland)

High Resolution in situ characterization of structure alteration in solids, extreme non-equilibrium conditions induced via high energy heavy ion radiation (BMBF/DESY, 2007–2010)

Preparation of lead free piezo electric thin films (LOEWE Adria, 2008–2011)

Preparation of thick actuator films on the basis of lead free piezo materials (LOEWE Adria, 2010–2011)

Investigation of scintillators for high current applications at UNILAC (GSI, 2008–2011)

FAIR accelerator: Investigations of alterations of material properties by beam losses (BMBF/GSI, 2009–2012)

FAIR accelerator: Scintillator materials for diagnostics of high currents (BMBF/GSI, 2009–2012)

Investigation of the chemical bindings in interfaces of boron- and siliconcarbonitrides with the substrate (DFG, 2010–2012, jointly with PTB Berlin)

NanoC – Preparation, modification and characterization of nanochannels in polymer membranes (Beilstein-Institut, 2009–2011)

NanoMag – Spin-dependent scattering in magnetic and Kondo nanowires (Beilstein-Institut, jointly with Goethe Universität Frankfurt am Main, 2009–2011)

Publications


W. Ensinger, R. Sudowe, R. Brandt, R. Neumann; Gas separation in nanoporous membranes formed by etching ion irradiated polymer foils; RADIATION PHYSICS AND CHEMISTRY, 79 (2010) 204-207.


D. Severin, E. Balanzat, W. Ensinger, C. Trautmann; *Outgassing and degradation of polyimide induced by swift heavy ion irradiation at cryogenic temperature*; JOURNAL OF APPLIED PHYSICS, 108 (2010) 024901.


Protection of tantalum against hydrogen embrittlement during corrosion by platinum ion implantation

S. Flege, W. Ensinger

Hydrogen embrittlement may cause catastrophic failure of otherwise stable metallic devices. Tantalum vessels, for example, are used for storage and handling of mineral acids in the chemical industry. Normally, the natural oxide layer of the tantalum provides sufficient protection against corrosion; at higher temperatures, however, there is a certain rate of corrosion which releases hydrogen as a by-product. This in turn might diffuse into the metal and cause embrittlement.

Platinum can act as a remedy in this situation due to its catalytic activity for hydrogen recombination. The recombined hydrogen desorbs rather than diffusing into the Ta. While the use of additional Pt sheets within the reaction vessel is highly effective it is also expensive. If the Pt is brought into contact with the Ta surface via ion implantation, considerably less Pt is required for a long term protection.

Pt\(^+\) ions were implanted at both faces of tantalum sheets with an energy of 70 keV and fluences between \(5 \times 10^{15}\) and \(5 \times 10^{16}/\text{cm}^2\). The Pt profiles were measured with depth via secondary ion mass spectrometry using \(4 \text{kV} \text{O}_2^+\) primary ions. Fig. 1 shows one of the recorded isotopes of Pt in an oxidized Ta sample. The implantation zone comprises several ten nm with the highest intensity near the surface, the amount depending on the Pt fluence.

![Pt implantation profiles](image)

Fig. 1: \(^{194}\text{Pt}\) implantation profiles (with two different fluences) into oxidized Ta samples, as measured by secondary ion mass spectrometry.
The samples were stored under corrosive conditions (immersion into concentrated sulphuric acid at a temperature of 500 K) for up to 180 days. The percentage of embrittlement was determined by bending tests of 180° with 1 Hz. The number of bends until fracture occurred was recorded. The results are presented in Fig. 2. An untreated sample only took 9 days until it reached such a state of embrittlement that it fractured at the first bending. The implanted samples exhibited a considerably lower degree of embrittlement. Even after half a year the embrittlement was only about 50%, a value the untreated sample reached after only four days. Comparing metallic and oxidized samples, no difference was found, i.e. the oxide film of about 200 nm does not lead to an improvement.

Fig. 2: Percentage of embrittlement vs. corrosion time in concentrated sulphuric acid at 500 K

For a detailed discussion of the Pt influence and the corrosion reactions see the corresponding publication [1].

A further reduction of the amount of Pt is probably feasible if only parts of the sample are implanted. Future experiments will determine the minimum required surface area for an effective embrittlement protection.

References:

Electroless synthesis of metal nanotubes for catalytic applications

F. Muench, C. Neetzel, W. Ensinger

As part of our investigations on nanopore modification and template-assisted nanomaterial synthesis [1, 2], we fabricate metal nanotubes and nanowires utilizing ion track etched polycarbonate templates and the electroless metal deposition technique [3, 4]. This wet-chemical method has several complementary advantages over electrochemical plating [5]. Due to its ability to simultaneously cover a complex-shaped non-conducting surface with a homogeneous metal nanoparticle film, it is especially suited for the synthesis of metal nanotubes. In combination with the highly flexible template approach, tubes with tailored properties such as length, diameter, wall thickness, material composition and nanostructure can be obtained. Besides metals, we work with nanotubes consisting of functional oxides [6] to introduce properties such as ferromagnetism or gas-sensitivity.

Fig. 1: SEM images of a single free-standing gold nanotube (left) and a gold nanotube field (right).

Fig. 2: Cyclic voltammograms of different platinum-ruthenium nanotubes and a commercial C-supported platinum-ruthenium fuel cell catalyst.

Fig. 3: SEM images of a small platinum nanotube (A) and a field of free-standing large platinum nanotubes. The arrow in the inset of (B) shows a polycrystalline grain of the tube wall. In (C), a TEM image of a platinum nanowire is shown next to a corresponding X-ray (EDS) spectrum.
Metal nanotubes are fascinating materials which have been applied in different fields ranging from catalysis to sensing and separation. Recently, we developed a refined electroless gold plating procedure [3]. The synthesis shows significantly enhanced control of both nanoparticle size and deposition rate and enables the synthesis of filigree and highly homogeneous nanotubes (Fig. 1). These parameters can be easily adjusted by changing the concentration of the auxiliary reagent 4-(N,N-dimethylamino)pyridine and by altering the pH value of the plating bath. Additionally, the template-supported nanotubes were applied as flowthrough reactors. In a UV-vis monitored model reaction – the reduction 4-nitrophenol by sodium borohydride – the gold nanotubes proved to be microfluidic devices of excellent catalytic activity [3].

In another experimental series, we developed an electroless plating procedure to fabricate platinum and platinum-ruthenium nanostructures in ion track etched polycarbonate [4]. The obtained nanostructures were tested as unsupported catalysts in the electrooxidation of methanol, revealing a distinct effect of the preparation method and the platinum-ruthenium nanostructure on the catalyst performance (exemplary cyclic voltammograms of the different nanostructures are given in Fig. 2). Considering the surface normalized current density at a potential at 0.7 V vs. RHE as a measure of the catalytic activity, the platinum-ruthenium nanotubes can surpass commercial catalysts [4]. As mentioned in the introduction, the used method allows the independent variation of several important product parameters. In Fig. 3, electron micrographs of platinum nanotubes with diameters of approximately 120 and 450 nm and platinum nanowires of 100 nm diameter are shown. All structures have a rough surface and consist of platinum nanoparticles of less than 5 nm size.

References:

Theoretical Materials Science

Teaching by this division addresses the atomistic foundations of materials science, including the concepts underlying their representation, from the theoretical physics point of view. Research focuses on materials modelling, being a powerful tool for materials development. Experimental results will be understood, and predictions of further observations given, in the light of theoretical evidence, both to aid the optimization of the properties or the performance of materials already in use and to guide the design of novel materials with properties, or behaviour, required in future engineering applications.

Current investigations centre on the following classes of materials:

**Transition metals and related alloys**
For this class of materials, represented by Ta and Fe or, respectively, steels, the goal is examining their suitability for structural components of high-power spallation neutron sources that are exposed to intense proton beams. Irradiation-induced hydrogen production under the operating conditions of the envisaged European spallation source is predicted to generate high internal concentrations of atomic hydrogen which, further enhanced by stress-driven hydrogen accumulation near microstructural cracks, may lead to a severe degradation of the mechanical properties of steel, whereas no noticeable deterioration is to be expected in the case of tantalum.

**High-temperature superconductors**
For this class of materials, typified by YBa$_2$Cu$_3$O$_7$ and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ in thin-film or bulk form, great interest is directed towards investigating extended defects (e.g. low-angle grain and twin boundaries) which are considered as weak-links between superconducting grains. There are two principal aims: (i) exploring the connection between the electromagnetic response (e.g. the current-voltage relation) and the characteristic defect morphology so as to obtain insight into constitutive parameters of superconducting films; (ii) searching for possibilities to improve the current-carrying capability of superconducting materials, which is limited by the above-mentioned types of defect. Preliminary studies of novel heterostructures involving superconductor strips with a single grain boundary defect, placed in open magnetic cavities, show that magnetic shielding here is a promising way forward. Another field of research addresses the interaction between electromagnetic radiation and multilayered heterostructures made up of highly anisotropic superconductors as well as a range of different classes of materials with a view to examining their suitability for novel photonic crystals. Of special interest are materials whose properties can be controlled by external parameters and fields.

**Organic semiconductors**
For this class of materials, represented by Alq$_3$ and PPV, emphasis is placed on modelling of bipolar charge carrier injection, transfer and recombination as well as on a theoretical analysis of thermally stimulated luminescence phenomena with the aim of extracting, in conjunction with experiments, information about the electronic structure of inherent traps so as to assist technological exploitation and further materials development. Some of the most important features to be taken into account hereby are the field dependence of the injection barriers present, apart from allowing for the variation of the distribution of traps in space and depth.
**Ferroelectrics**

For this class of materials, typified by BaTiO$_3$ and PZT, attention is focussed on the process of aging, i.e. the gradual change of materials properties with time, isothermal conditions and absence of external mechanical loads implied. This process manifests itself in alterations of static and, respectively, kinetic characteristics such as the clamping pressure exerted on the walls of ferroelectric domains, the electric permittivity and the asymmetry of the electrical conductivity regarding current flow parallel or antiparallel to the direction of the spontaneous polarization; phenomena, which may be explained in terms of migration of charged point defects under the influence of internal or external electric fields. Preliminary results obtained with a drift-diffusion approach suggest that the experimentally observed drastic rise of the clamping pressure and the decrease of the electric permittivity with time may indeed be controlled by a mechanism of this kind.

The theories underlying these investigations range from microscopic to macroscopic; their realizations employ analytical as well as computational techniques.

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**Staff Members**

- **Research Associates**: Dr. Yuri A. Genenko, D.Sc.; Dr. Galina I. Yampolskaya; Dr. Sergey V. Yampolskii
- **Diploma Student**: Philipp Krüger
- **Secretary**: N.N.
- **Visiting Scientists**: Prof. Dr. Antonio Badía; Harold Ruiz, M.Sc.

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**Research Project**

Kinetic Modelling of the Charge Transfer in Organic Semiconductors and Ionic Conductors (Collaborative Research Centre (SFB) "Electric Fatigue in Functional Materials", 2007-2010, with Prof. Dr. H. v. Seggern, Darmstadt University of Technology).

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**Publications**

Y.A. Genenko; H. Rauh: *Hysteretic ac losses in a superconductor strip between flat magnetic shields*; SUPERCOND. SCI. TECHNOL. 23 (2010) 075007/1-5.

H. Rauh; G.I. Yampolskaya; S.V. Yampolskii; Optical transmittance of photonic structures with linearly graded dielectric constituents; NEW J. PHYS. 12 (2010) 073033/1-23.


Finite-element simulations of hysteretic ac losses in a bilayer superconductor/ferromagnet heterostructure subject to an oscillating transverse magnetic field

Y.A. Genenko, H. Rauh, P. Krüger

Reducing hysteretic ac losses is a problem of utmost importance for both actual and future superconductor applications. Second-generation high-temperature superconductor wires rest upon a coated-conductor technology which – because of manufacturing needs – usually employs Ni alloy tapes as supports. The role of these ferromagnetic constituents is not yet unequivocally perceived since magnetic shielding can, in principle, assist or inhibit the penetration of magnetic flux, and hence the dissipation of electromagnetic energy, depending on the geometrical and material characteristics of the magnetic environment. It is for this reason that we take a look at the principal effects of a ferromagnetic support on hysteretic ac losses in a superconductor strip by making recourse to Bean’s model of the critical state, when utilizing the ANSYS commercial finite-element software program for computing scalar, vector and tensor fields.

Let us define our model by considering a planar superconductor/ferromagnet heterostructure of bilayer geometry, viz. an infinitely extended type-II superconductor strip of width $2w$ and thickness $d$ on a ferromagnetic support of respective thickness $D$, buffered by a non-magnetic layer in between, and subject to an oscillating transverse magnetic field with strength $H_a$. We choose materials and dimensions that second-generation coated conductors typically display, i.e. YBa$_2$Cu$_3$O$_7$ for the superconductor strip and Ni$_{95}$at.%W for the ferromagnetic support delineated by a finite permeability $\mu$, apart from an oxide buffer (to simplify matters here: a vacuum having permeability $\mu_0$), with $w = 5\, \text{mm}$, $d = 2\, \mu\text{m}$, and $D = 100\, \mu\text{m}$, at the temperature of 77 K. Since $d << w$, we ignore spatial variations of the induced current on a length scale less than $d$ and, for mathematical convenience, regard the strip as infinitesimally thin, so that its physical state can be characterized by the sheet current $J$ alone. In conformity with Bean’s model of the critical state duly adapted to the geometry of the strip, magnetic flux penetrates from both edges of the strip; a flux-free region prevails in the central part of the strip, where the normal component of the magnetic field $H_n$ disappears, whereas in the marginal, flux-penetrated parts of the strip, of depth $s$, the sheet current $J$ adopts its critical value $J_c$, taken as independent of the magnetic field.

Fig. 1. Distribution of the magnetic field $H$ around the magnetically shielded superconductor strip, for the relative permeability of the ferromagnetic support $\mu/\mu_0 = 20$, as calculated by means of ANSYS. The strength of the magnetic field is characterized stepwise by regions of different colour depths, whose boundaries define lines of the magnetic field. The support together with the strip is indicated by black contour lines.
Fig. 1 illustrates the distribution of the magnetic field $H$ around the magnetically shielded superconductor strip, for a fixed relative permeability $\mu/\mu_0$. Two antagonistic effects of the ferromagnetic support come to the fore: on the one hand, it tends to concentrate the magnetic field both in the centre and near the edges of the strip, promoting penetration of magnetic flux; on the other hand, it guides the magnetic field around the superconductor strip, impairing penetration of magnetic flux, as in closed geometries.

The variation of the normalized flux penetration depth $s/w$ with the normalized amplitude of the applied magnetic field $H_a/H_c$, depicted in Fig. 2 for a range of values of the relative permeability $\mu/\mu_0$, confirms ambiguous traits: above $H_a/H_c \approx 0.4$, penetration of magnetic flux is seen to abate monotonically with increasing $\mu/\mu_0$ from its extreme for $\mu/\mu_0 = 1$, the latter exactly coinciding with the theoretical forecast for the unshielded superconductor strip; around $H_a/H_c = 0.4$, however, curves pertaining to different values of the relative permeability $\mu/\mu_0$ of the ferromagnetic support intersect and exchange positions below $H_a/H_c \approx 0.4$, disclosing the tendency of the curve for $\mu/\mu_0 = 100$, the highest relative permeability taken into account, to even cross the curve for $\mu/\mu_0 = 1$, the intersection point lying outside the computationally accessible regime.

Fig. 2. Dependence of the normalized flux penetration depth $s/w$ on $H_a/H_c$, the normalized amplitude of the magnetic field applied to the magnetically shielded superconductor strip, in the computationally accessible regimes, when the relative permeability of the ferromagnetic support $\mu/\mu_0 = 1$ (black curve), $\mu/\mu_0 = 20$ (red curve), $\mu/\mu_0 = 50$ (green curve), and $\mu/\mu_0 = 100$ (blue curve). The dashed line represents the analytical result for the unshielded superconductor strip.

Fig. 3 shows the variation of the normalized hysteretic ac loss, per cycle and unit length of the strip, $U_{ac}/H_a$ with the normalized amplitude of the applied magnetic field $H_a/H_c$, introducing the characteristic magnetic field $H_c = J_c/\pi$, for the same range of values of the relative magnetic permeability $\mu/\mu_0$. Above $H_a/H_c \equiv 0.6$, hysteretic ac losses obviously wane monotonically with increasing $\mu/\mu_0$ from their extreme for $\mu/\mu_0 = 1$, the latter matching the theoretical prediction for the unshielded superconductor strip in the whole range of $H_a/H_c$; below $H_a/H_c \equiv 0.6$, however, curves for different values of $\mu/\mu_0$ cross each other and, eventually, also intersect the curve for $\mu/\mu_0 = 1$. A comparison with measured data reveals that empirical values obtained for the magnetically shielded superconductor strip, around the
maximum of $U_{ac}/H_a^2$, lie between the simulated results for $\mu/\mu_0 = 20$ and $\mu/\mu_0 = 50$; a fact which correlates satisfactorily with the estimate $\mu/\mu_0 \approx 30$, noting $H_c \equiv 8$ A/mm, from experiments.

Fig. 3. Dependence of the normalized hysteretic ac loss $U_{ac}/H_a^2$ on $H_a/H_c$, the normalized amplitude of the magnetic field applied to the magnetically shielded superconductor strip, in the computationally accessible regimes, when the relative permeability of the ferromagnetic support $\mu/\mu_0 = 1$ (black curve), $\mu/\mu_0 = 20$ (red curve), $\mu/\mu_0 = 50$ (green curve), and $\mu/\mu_0 = 100$ (blue curve). The full and open circles bear witness to the experimental database for the magnetically shielded and, respectively, unshielded superconductor strip, whereas the dashed line represents the analytical result for the unshielded superconductor strip.

Nevertheless, perceptible differences between numerical forecasts and empirical findings in the low- and high-value regimes of $H_a/H_c$ remain. Thus, the curve for $\mu/\mu_0 = 1$, whilst manifesting perfect coincidence with analytical results in the whole range of $H_a/H_c$ and fair consent with measured data in the medium-value regime of $H_a/H_c$, increasingly deviates from experiment below $H_a/H_c \approx 0.6$. This discrepancy might be due to the assumption of an infinitesimally thin superconductor strip, both in the analytical theory and in the numerical analysis, as opposed to the finite thickness of the superconductor strip; a simplification known to distinctly underestimate hysteretic ac losses in superconductor strips of rectangular cross section with an aspect ratio $2w/d$ even larger than the one at hand. The difference in the asymptotic behaviour above $H_a/H_c \approx 5$, exhibiting an overestimate by theory of hysteretic ac losses in superconductor strips on a non-magnetic support, could be attributed to the decrease of the critical sheet current at high fields. By contrast, the extending underestimate of simulated hysteretic ac losses in a magnetically shielded superconductor strip below $H_a/H_c \approx 0.8$ as compared to those found experimentally seems to demonstrate the importance of additional, ferromagnetic ac losses in the support, not accounted for here as yet.

In conclusion, our finite-element simulations underpin an equivocal effect of the ferromagnetic support on hysteretic ac losses in a bilayer superconductor/ferromagnet heterostructure, these losses being enhanced in the low-field regime and reduced in the high-field regime as compared to those for a non-magnetic support.
Materials Modelling Division

The research of the Materials Modelling Division is focused on multi-physics modelling of defect structures in functional oxides and nanostructured metals. Materials of interest include ferroelectric materials, transparent conductive semiconductors as well as nanocrystalline alloys and bulk metallic glasses. We are combining electronic structure calculations with atomistic modelling methods and continuum descriptions depending on time and length scales involved. Quantum mechanical calculations based on density functional theory are used for electronic structure calculations. Large-scale molecular dynamics with analytical interatomic potentials are the method of choice for studying kinetic processes and plastic deformation. Kinetic lattice Monte-Carlo simulations are extensively used for simulations of diffusional and transport processes on extended time scales. The group is operating several HPC-computers and has access to the Hessian High Performance Computers in Frankfurt and Darmstadt. The current research areas are:

- Electronic structure, thermodynamics and kinetics of defects in functional materials
- Size-effects in nanomaterials
- Energy materials
- Reactive interatomic potentials for compound systems

Within the bachelor program the Materials Modelling Division is offering classes on thermodynamics and kinetics as well as defects in materials. Lectures and lab classes on simulation methods and programming techniques are offered as electives

Staff Members

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Research Projects

HMWK, Loewe-AdRIA (2008 – 2011)

Forschergruppe 714, Plasticity of nanocrystalline metals and alloys, (DFG AL 578/7-2, 2009 - 2012)

Quantenmechanische Computersimulationen zur Elektronen- und Defektstruktur oxidischer Materialien (SFB 595, Teilprojekt C1, 2007-2014)

Atomistische Computersimulationen von Defekten und deren Bewegung in Metalloxiden (SFB 585, Teilprojekt C2, 2003-2014)

Erforschung der Phasenstabilität und Niederdrucksynthese von festem Stickstoff mittels atomistischer Computersimulationen und Experimenten (DFG AL 578/3-2, 2009 – 2011)

Plastizität nanokristalliner Metalle und Legierungen: Atomistische Computersimulationen zu Mechanismen der Verformung (DFG Forschergruppe 715, TP 2, AL 578-7, 2006-2012)

Beyond Ni-Base Superalloys: Atomistische Modellierung des Einflusses von Legierungszusätzen auf die Korngrenzeigenschaften in Mo-Si-B und Co-Re Superlegierungen (DFG Forschergruppe 727, AL 578/9-1, 2010 – 2013)

Nanosilicon dispersed in SiCN(O) and SiCO-based ceramic matrices derived from preceramic polymers: new composite anode materials for lithium ion batteries. (DFG SPP 1473 „Wendelib“, DFG AL 578/10-1, 2010 – 2013)


Atomic scale modeling of metallic nanoparticles embedded in nanoparticle carbon structures (DFG KO 3861/2-1, 2009 – 2011)

Bleifreie Piezokeramiken, LOEWE-Schwerpunkt ADRIA (HMWK, 2008-2011)

BMBF-GRACIS, Chemische Gradienten in CU(In,Ga) Se2 Solarzellen: Grenzflächen-untersuchungen und theoretische Modellierung (03SF0359E, 2009 - 2011)

PPP Finnland, Atomic level simulations of structure and growth of nanoalloys (DAAD 2007 – 2010)

Publications


J. Kling, S. Hayn, L. Schmidt, M. Gröting, H.-J. Kleebe, K. Albe, A-site occupancy in the lead-free (Bi$_{1/2}$Na$_{1/2}$TiO$_3$)$_{0.94}$ (BaTiO$_3$)$_{0.06}$ piezoceramic: Combining first-principles study and TEM, J. Appl. Phys. 107 (2010) 114113


A. Stukowski, Visualization and analysis of atomistic Simulation of OVITO was given with the Open Visualization Tool, Mod. Sim. Mat. Sci. Eng. 18 (2010) 01501
Extracting dislocations and non-dislocation crystal defects from atomistic simulation

Alexander Stukowski, Karsten Albe

Crystal plasticity and fracture of materials are closely linked to dislocation activity. Atomistic simulation methods, like molecular dynamics (MD), allow us to simulate the deformation behavior of virtual samples by numeric integration of atomic trajectories. While standard visualization techniques in principle can help to identify deformation processes by visual inspection of atomic configurations, a quantitative analysis as well as a detailed investigation of dislocation lines and other crystal defects in atomistic simulation data remain a challenge.

In a recent paper [1], we have proposed a novel algorithm, which follows a simple, but rigorous idea as illustrated in Fig. 1. This new method directly translates the network of disordered core atoms into a network of connected dislocation segments, thereby preserving its true topology. The output provided by this algorithm is a network of discrete dislocation lines and nodes, which entirely conforms to the Burgers vector conservation rule, and which reflects the shape of the underlying dislocation lines with atomic-scale precision. Moreover, the new algorithm delivers a geometric description of all other (non-dislocation) crystal defects (e.g. grain boundaries, surfaces, pores, etc), which is very useful for visualization purposes and other applications. The basic algorithm requires only a single control parameter, making its usage extremely simple. In the following, we describe the principal steps of the algorithm and finally give an example.

Fig. 1: Schematic illustration of the new DXA. First a manifold surface enclosing the dislocation cores is constructed. Then elastic ‘Burgers circuit bands’ are swept over the manifold along each dislocation segment. Finally, nodal points are generated where multiple Burgers circuits meet on the manifold.
The dislocation extraction algorithm (DXA) presented here consists of three principal steps:

I. The CAN method [2] is used for identifying crystalline atoms. We call the remaining atoms, which form crystal defects, ‘disordered atoms’.

II. A closed, orientable, two-dimensional manifold (referred to as interface mesh) is constructed that separates the crystalline atoms from the disordered ones. For each dislocation segment, an initial Burgers circuit is generated on this manifold.

III. The closed circuit is moved in both directions to the two opposing ends of the dislocation segment to capture its shape (Fig. 1). While the circuit is advanced in each direction, a one-dimensional line representing the dislocation segment in the output is constructed.

Note that the DXA is in most parts a generic algorithm, independent of the underlying crystal structure. Figure 2 shows an example demonstrating the complete transition process from the atomistic input data to the final dislocation lines. The input is a snapshot taken from an MD simulation of a nanocrystalline tungsten structure, which is being deformed in a simulated tensile experiment.

![Fig. 2: Stepwise conversion of three atomistic dislocation cores into a geometric line representation. (a) Atomistic input data. (b) Bonds between disordered atoms. (c) Interface mesh. (d) Smoothed output.](image-url)
The first picture of figure 2 displays a section of the atomistic input, which contains three dislocation segments (red atoms) that have been nucleated from a nearby grain boundary junction (gray atoms). Note that the CNA has been applied to remove ideal bcc atoms in this picture, and dislocation core atoms have been highlighted manually for the sake of clarity. For the CNA, the cutoff radius \( R_{\text{CNA}} = 3.8145 \text{Å} \) was used, which is halfway between the second and third neighbor shells of tungsten. Figure 2(b) displays the bonds between disordered atoms, which are used to generate the interface mesh. The final interface mesh is shown in figure 2(c). The colored parts of the mesh have been swept by Burgers circuits during the dislocation analysis, i.e. they have been identified as dislocation segments. Their colors correspond to the three different Burgers vectors as depicted inside the bcc unit cell in figure 2(d). The last figure shows the final results of the analysis algorithm: the one-dimensional dislocation lines, which merge at a nodal point; their Burgers vectors (transformed into the coordinate system of the real crystal) and the defect surface, which represents the surrounding grain boundaries.

The DXA yields a geometric description of the dislocation network contained in an arbitrary crystal. The network of one-dimensional continuous dislocation lines generated by the algorithm is guaranteed to have the same topology as the real dislocation network. In particular, it always conforms to the Burgers vector conservation rule. The shape of dislocation loops is resolved with up to atomic precision. All other crystal defects (grain boundaries, surfaces, etc), which cannot be represented by dislocation lines, are converted into a polyhedral representation by the algorithm. This representation is ideal for visualization purposes, even for applications which do not involve dislocations.

The DXA was designed to reliably divide the wealth of information stored in a snapshot of an atomistic simulation into relevant and dispensable parts. The complexity of the relevant part, the crystal defects, is reduced as far as possible by transforming them into a higher-level description, which consists of only dislocation lines (and their Burgers vectors) and defect surfaces. In summary, the DXA provides a simple-to-use and robust method to analyze and visualize atomistic simulations of crystal plasticity. An implementation of the described algorithm is available from the authors on request.

References


Acknowledgements

This work was performed with financial support of the Deutsche Forschungsgemeinschaft (FOR714) and computing time grants from HHLR Darmstadt, FZ Jülich and bwGRiD, member of the German D-Grid initiative. Test datasets have been kindly provided by J. Schäfer. Three dimensional visualizations have been created with OVITO and PARAVIEW.
Plastic deformation of nanocrystalline PdAu alloys: On the interplay of grain boundary solute segregation, fault energies and grain size

J. Schäfer, A. Stukowski, K. Albe

The active deformation mechanisms governing the plastic behavior of nanocrystalline (nc) metals strongly depend on grain size and strain rate \([1, 2]\) and are distinct from coarse grained materials. In the past, computer simulations have revealed that grain rotation and sliding, dislocation emission and absorption in grain boundaries, twinning and faulting as well as diffusional creep and grain boundary migration are deformation mechanisms operational in nanocrystalline fcc metals \([3]\). Experimentally, this has been confirmed by analyzing the “kinetic fingerprint” (i.e. strain rate sensitivity and activation volume) \([3]\) of the dominating processes.

In pure nc metals, however, a grain size in the nanometer range is difficult to stabilize, whence segregating solutes have been used to prevent grain growth and their influence on the mechanical properties has been addressed \([4]\). Much less attention, however, has been paid to miscible solutes that in principle allow to specifically tune certain material properties: The nucleation of partial dislocations, for instance, is stimulated by miscible solutes \([5]\). Allopying also affects the thermal stability of grain boundaries (GB) and leads to a variation of the generalized planar fault energy (GPFE) of the bulk material. Dislocation nucleation and slip in fcc materials, in turn, depend on the GPFE \([6]\), which also affects the twinability of the material. Moreover, it is well known that the grain boundary structure and energy depend on the type and concentration of solutes, and therefore chemical equilibration of GBs should influence the mechanical properties of alloyed nanocrystals.

In this work, we present molecular dynamics (MD) studies of nanocrystalline miscible Pd–Au. Samples of various grain sizes are constructed according to the Voronoi tessellation method, alloyed with a hybrid MD/Monte-Carlo (MC) scheme and finally tested in tensile straining experiments. We perform a detailed analysis of the element distribution in the nanocrystalline GB network and investigate its influence on the interplay of intergranular and intragranular deformation mechanisms. The observed stress-strain behavior for structures with two different grain sizes and three different concentrations is shown in Fig. 1.

Fig. 1: Stress-Strain behavior of nc Pd-Au as a function of composition for two different grain sizes.
Here, the yield stress shows a clear dependence on the concentration. This is particularly pronounced for the intermediate concentrations. As discussed above, the stable and unstable fault energies predicted by our model potential for the Pd–Au alloy are composition-dependent. For investigating this dependence, we analyzed the activity of dislocations in the samples during deformation using the automated on-the-fly dislocation detection algorithm [7]. This method allows to monitor the dislocation lines in all grains and to determine their Burgers vector. A statistical analysis of this data gives the total dislocation density, which continuously increases during plastic deformation after dislocation nucleation from the grain boundaries has started (not shown).

While the composition-dependent fault-energies and derived properties like the resistance parameter \( R \) [8] for partial nucleation can explain the measured defect density at a given strain, they can not explain the increase in stress at the onset of plastic deformation for the presented case. If the nucleation of a partial dislocation into the grain was the barrier to overcome at the onset of plastic deformation, one would expect a correlation between the maximum stress and the resistance parameter. Fig. 2 shows that the contrary is the case, namely, that the observed maximum stress in the stress-strain behavior correlates inversely with the resistance parameter. Therefore, we can reason that it is not the nucleation of leading partial dislocations, which controls the maximum strength of this nc alloy.

Fig. 2: Correlation between maximum stress, flow stress and the resistance parameter \( R (\gamma_{uf}/Gb) \) for 15 nm grain size.

Since we can exclude the composition dependent bulk material properties (controlling the intragranular deformation), we focus on the influence of the intergranular region in the following. Here, we employ a Voronoi tesselation method to compute the atomic volume of each atom. The excess volume per atom is then the difference between the calculated volume and the average volume of an atom of the same type within a single crystal of identical global composition. We define the free volume of the grain boundary atoms as the sum over the excess volumes of all atoms within the GB. Monitoring the change in free volume in the GB during straining yields a similar composition dependent trend as observed for the stress-strain behavior (not shown).

Fig. 3 shows, that the observed maximum stress in the stress-strain behavior correlates to the increase in atomic volume in the GB during deformation for all observed relaxation states and grain sizes. That is, the more free volume needs to be generated, the higher the maximum strength. According to our observations, one can reason, that the energetic state of the GB is correlated to the free volume in the GB and depends on the treatment of the structure and equilibrating processes (e.g. the positional configuration of solutes within the GB).
During the course of plastic deformation (Fig. 4), this energetic state of the GB (and the atomic volume in the GB) has to be raised to a steady state deformation level. The initial energetic state of the GB in turn controls the barrier for the onset of the deformation mechanisms, which is correlated to the maximum strength (inset of Fig. 4). The properties of the bulk material (e.g. shear modulus, burgers vector) appear to have a less significant influence.

Fig. 3: Correlation between maximum stress and the ratio between free volume during straining and the initial free volume for 5 and 15 nm grain size and different states of relaxation. Open symbols refer to the 5 nm grain size and crosses to the 15 nm grain size. Shown is the data for chemically equilibrated samples (red, blue), only structurally equilibrated samples (green, pink) and the restrained samples (black, turquoise).

Fig. 4: Schematic of the energetic state of the grain boundary and its dependence on initial relaxation, GB segregation and deformation. The inset shows, how the energetic state of the GB influences the barrier for the onset of plastic deformation or the maximum stress, where properties of the bulk material play a minor role (see text).

References:

Materials for Renewable Energies

Research in the Renewable Energies group focuses on nanoscaled catalysts applied predominantly in low and intermediate temperature fuel cells, but also in heterogeneous catalysis applications, using advanced ex situ, in situ, and, in particular, operando techniques. The systematic structural and electrochemical characterization is carried out in order to unravel the structure-properties correlation. Techniques used for structure analysis include X-ray absorption spectroscopy (XAS), transmission electron microscopy (TEM), and X-ray diffraction (XRD), whereas electrocatalytic activities are measured by cyclic voltammetry (CV) and in single cell fuel cell tests. The group’s recent scientific activities can be divided into the following areas:

• New catalyst concepts
  Our main focus is on the design of alternative support materials, e.g. electron conducting oxides and polymers, which do not suffer from corrosion in the severe conditions of the cathode side and may be promising candidates to replace the standard carbon support. Different morphologies, e.g. fibres or hollow spheres, contribute to an improved control in 3D electrode design.

• Functional electrode design
  Beyond the conventional preparation techniques, advanced layer-by-layer (LbL) techniques are applied in the fabrication of membrane-electrode assemblies (MEA) allowing for a well-defined 3D architecture of porous electrodes. Electron microscopy is applied for the electrodes’ detailed characterization. For this specific purpose, new techniques have been developed and established in the group starting from sample preparation by ultramicrotomy to very sophisticated mapping methods. For the first time, these can also be used at the interface between electrode surface and gas diffusion layer despite the very different mechanical properties of porous electrode and flexible polymer membrane.

• In situ studies
  In situ and operando X-ray absorption studies play an important role in our recent activities with respect to the systematic investigation of catalyst poisoning and degradation processes. A special in situ sample environment has been designed and successfully implemented at various synchrotron facilities. It enables the spatial and time resolved study of different areas of the membrane-electrode assembly (MEA). By this approach, electrode areas with more severe degradation can be identified. In addition to the conventional EXAFS analysis the novel delta \( \mu \) XANES technique is applied in cooperation with Prof. David Ramaker, George Washington University. This technique enables us to study adsorbates attached to the active catalyst surface, so that reaction mechanisms can be followed directly during operation. The results provide important insights, which will help with further catalyst optimization.

Financial support is provided by DFG, BMWi, BMBF, and EU as well as by the respective synchrotron facilities and industrial partners. The group’s research interests are covered by a lecture on “Fuel Cells – from fundamentals to application” and a practical course “X-ray absorption spectroscopy – fundamentals and data analysis”. Furthermore, a workshop on “Scientific work and presentation skills” is offered on request.
## Staff Members

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<td>Prof. David Ramaker (1 week)</td>
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## Research Projects

- Synchrotron- and neutron-based investigation of PEM fuel cells (RunPEM) (BMBF project 2007-2010)
- German-Canadian fuel cell cooperation (BMBF project 2010-2012)
- New developments in intermediate temperature fuel cells (EU project 2010-2012)
- New concepts for a controlled 3D design of porous electrodes (DFG project 2010-2013)

## Publications


3D visualization of PEMFC electrode structures using FIB nanotomography

Susanne Zils, Melanie Timpel, Tobias Arlt, André Wolz, Ingo Manke, Christina Roth

Introduction
Membrane electrode assemblies (MEA) for polymer electrolyte membrane fuel cells (PEMFC) consist of a proton conducting membrane and two electron- and proton conducting electrodes. Beyond the electron- and proton conducting part, the electrodes have to provide for the reactant supply of the fuel cell. This results in a rather complex electrode structure. The so-called triple phase boundary, (TPB) where the electrochemical reactions in the PEMFC take place, can be improved by optimizing the ratio between electron conducting parts (e.g. carbon supported Pt), proton conducting parts (e.g. Nafion® ionomer), and gas phase ( pores in the electrodes). This will lead to an increased PEMFC performance. Previous studies showed that well hydrated Nafion® membranes maintain a high proton conductivity. Zhang et al. [1] claim that reactants and products use the same pathways through the hydrophobic pores of the electrodes, whereas hydrophilic pores only facilitate the liquid water removal. They also suggest that a reduction of the pore diameter and an increase of the hydrophobicity will decrease flooding effects which are a severe problem. Hence, porosity and pore size distribution of the electrode play a major role in the fuel cell's water management [1]. In order to improve the porosity and pore size distribution, it is important to analyze and optimize the electrode's structure.

In recent years, several analyzing techniques have been used to reveal the electrode structure of PEMFC MEAs. Most of the previous studies were based on electron microscopy as the method of choice, though Hg porosimetry gives information about the electrode's porosity as well. Rolison et al. [2] analyzed the advantages of catalytic nanoarchitectures by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Both methods are fully capable of displaying the 2D structure of the samples, which are investigated. 3D properties, such as pore elongation or information on the so-called open porosity, however, cannot be determined by any of these techniques, neither by electron microscopy, nor by Hg porosimetry. Consequently, a method has to be found, which allows for 3D characterization of the electrode structure.

In 2001 Inkson et al. [3] published the 3D characterization of a metallic nanocomposite by Focused Ion Beam (FIB) tomography. Starting from there, FIB tomography was developed further and first results in 3D reconstruction concerning PEMFCs were published by Ostadi et al. [4] in 2010. In the work presented here, two differently prepared MEAs were sectioned by FIB and the reconstructed volumes were analyzed regarding porosity, pore size and tortuosity. Polarization curves of the MEAs were recorded in order to point out the structural influence on the PEMFC performance.

Experimental
Membrane electrode assembly preparation
In this study, MEAs were manufactured using two different fabrication processes. A reference MEA was prepared by a slightly modified airbrushing method (hereinafter referred to as AB), which was first published by Wilson et al. [5]. For the second MEA (multilayered MEA, hereinafter referred to as ML) a novel fast spraying technique [6] was used.

Characterization
FIB nanotomography was performed using a Zeiss 1540EsB CrossBeam®. A FIB serial sectioning and SEM imaging sequence based on the work of Holzer et al. [7] was used for
obtaining slices of nominally 12.5 nm (AB MEA) and 14.5 nm (ML MEA) thickness. The voxel sizes of the reconstructed AB MEA (9.3 nm × 9.3 nm × 12.5 nm) and the ML MEA (14.8 nm × 14.8 nm × 14.5 nm) differ due to adjustments of the FIB software. Alignment of the image stacks was obtained via a recursive method using the software ImageJ with StackReg Plugin [8]. A representative subvolume was defined and binarized using the Otsu thresholding algorithm [9]. For the 3D visualization of the 2D binarized image datasets, the commercial visualization software package VGStudioMax 2.0 was employed. Determination of the MEAs’ platinum loading was performed by thermogravimetric analysis (TGA). Fuel cell tests were carried out on fresh MEAs using an in-house built manually operated single cell test bench in hydrogen/oxygen operation. Polarization curves were recorded galvanostatically after several days of conditioning using an electronic load and a potentiometer.

Results and discussion
Focused Ion Beam nanotomography
After alignment and reconstruction of the SE images, 3D visualizations of the two MEAs were assembled and are shown in Figures 1a and b. The z-direction represents the FIB milling direction. The green color in Figure 1 represents the solid phase (carbon supported Pt), the free volume corresponds to the pore space. The 3D reconstruction of the ML MEA (Figure 1b) features a more homogeneous and also higher porosity compared to the reconstructed AB MEA volume (Figure 1a). This assumption is confirmed by measurements performed with the software package VGStudioMax 2.0. Figure 2 displays the position of the two 3D reconstructions within the MEA.
Porosity, pore size distribution and tortuosity

Based on the 3D reconstruction of the MEAs’ microstructure, an analysis of the porosity, pore size distribution and tortuosity of both samples could be processed as a volume analysis. The ML MEA reaches a porosity of about 62%, which is 15 to 20% higher compared to the AB MEA's porosity of about 45%. The mean pore size of the ML MEA (118 nm ± 76 nm) is half of the AB MEA’s mean pore size (233 nm ± 143 nm). In combination with the higher porosity this has a positive effect on the Pt utilization of the ML MEA. A recent study by Zhang et al. [1] demonstrated the positive influence of higher electrode porosity on the water management in PEMFCs. Furthermore, a higher porosity is linked to an increase of the TPB and, therefore, a higher Pt utilization. This was confirmed by the Pt utilization analysis of the two MEAs by TGA measurements. The Pt utilization of the ML MEA is 1962 mW mg⁻¹, exceeding the AB MEA's Pt utilization of 879 mW mg⁻¹ by far. Hence, the 20% higher porosity leads to an increase of the Pt utilization by a factor of about 2. Beyond that, TGA analysis showed that only 40% of the carbon supported Pt catalyst used for the AB MEA (40.6 mg) was needed for the ML MEA (16.3 mg) to reach the same performance. This represents a cost reduction of 60% for MEA fabrication.

The mean tortuosities in the main gas flow direction (y-direction) of both MEAs of 1.09 (AB MEA) and 1.11 (ML MEA) indicate a high number of pores with a nearly direct connection between gas diffusion layer and the Nafion® membrane. A direct connection enhances the gas transport within the electrodes and is favored for the removal of liquid water out of the cell.

Single cell tests

Polarization curves were recorded and power density curves were calculated on the basis of the polarization curves (Figure 4). The polarization curves show a higher open circuit voltage for the ML MEA compared to the AB MEA. In contrast, the AB MEA reached slightly higher current densities. With respect to the maximal power densities, the two MEAs reached almost the same values (p_{ML,max} = 210 mW cm⁻², p_{AB,max} = 218 mW cm⁻²). Mean maximum power densities were calculated from polarization curve measurements recorded over five days of operation by summing up the individual values and dividing it by the number of values. A higher mean maximum power density is obtained for the ML MEA (p_{ML,mean} = 189 mW cm⁻² ± 18 mW cm⁻²) compared to the AB MEA (p_{AB,mean} = 179 mW cm⁻² ± 22 mW cm⁻²).

Figure 5: Polarization and power density curves of the a) AB MEA and the b) ML MEA.
Furthermore, the maximum power densities of the ML MEA decrease less drastically over time. This can be explained by the electrode structure and the improved water management of the ML MEA compared to the AB MEA. The ML MEA may therefore be better suited for long-term applications than the AB MEA. This has to be further confirmed in future degradation studies.

Conclusion

Two MEAs, one airbrushed and one fabricated by the novel layer-by-layer inspired fast spray coating technique, were investigated with respect to their porosity, pore size distribution, tortuosity, Pt utilization and performance. FIB nanotomography, TGA measurements and single cell tests were performed. To our knowledge, we were the first to apply the FIB nanotomography technique to differently prepared MEAs for PEMFCs [11]. The investigations showed that the ML MEA features a more homogeneous porosity and pore size distribution. The Pt utilization of the ML MEA (1962 mW cm$^{-2}$) was more than 2 times higher than the Pt utilization of the AB MEA (879 mW cm$^{-2}$). Furthermore, the advantages of the novel spray coating technique show in a high homogeneity of the electrode with respect to pore size and Pt distribution, which lead to a cost reduction of 60% due to the decreased catalyst amount in the electrode.

Acknowledgments

Financial support of the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged. Parts of the project were funded by the German Federal Ministry of Education and Research (BMBF) under Grant No. 03SF0324. The authors thank C. Fasel for the thermogravimetric analysis measurements.

References

Physics of Surfaces

Physical properties of surfaces and interfaces are relevant in nearly all areas of science and engineering. The fundamental interactions between surfaces, the surrounding fluid and small objects in the fluid play an important role, for example in biology, biotechnology, mechanical engineering, or petroleum geology. The common research question can be expressed as “How does the interplay between physical surface properties, surface and interface chemistry, and fluid flow affect the entire system?”

We follow an interdisciplinary approach focusing on physical, chemical and biological properties of surfaces. The connection between surfaces and fluids is of particular interest because it is essential in various technological systems. Our research targets at a better understanding of the interplay between surface patterning (morphological and chemical) and modification with the fluid flow. Experimental methods such as microscopy, microfluidics, or spectroscopy are important tools.

The research group Physics of Surfaces has been established in April 2010. The nanoanalytic lab became operational in December 2010. Further experimental equipment will be transferred from Munich to Darmstadt in 2011.

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Research Projects

Titanomagnetite STA 1026/2-1(LMU, DFG 2007 – 2011)

Nanostruktur und Benetzungseigenschaften von Porenraumoberflächen (LMU, BMBF 2008 – 2011)

Funktionale Polymer-Peptidoberflächen (CSI, 2010 – 2012)

Influence of elasticity, density and chemical composition of extracellular matrices on the spatiotemporal dynamics of plasma membranes (CSI, 2010 – 2012)

Wafer cleaning (LMU, Industrie 2007 - 2010)

Low friction coatings (LMU, Industrie 2008 – 2011)
Publications


Optical Properties of Collagen

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ABSTRACT Collagen is the main connective tissue protein of vertebrates. It shows exceptional mechanical and optical properties. The alignment of the collagen fibrils correlates to the function of the specific tissue and leads to optical anisotropy. The effect of the molecular alignment on Raman scattering, however, is barely investigated. We found that the peak intensities of the C-C, C=O, and N-H vibrational modes, which are typical for the Raman bands of the protein backbone, change with the orientation of the collagen fibrils. These observations demonstrate that Raman spectra contain molecular and fibre alignment specific information.

INTRODUCTION
Collagen is the most abundant structural protein of vertebrates and features unique properties. It is known for its exceptional durability and tensile strength, which are results of the hierarchical structure [1-3] and the fibril alignment. According to its specific function, it is organized in bundles or in a random meshwork determining the tensile stress, elasticity, and geometry of skin, tendon, ligament, artery walls or the organic matrix of bones. In tissue that is subject to unidirectional forces such as tendon, single collagen fibrils are equally oriented and organized in bundles (see e.g. Fig. 1). The bundles are aligned with the direction of the load, which leads to anisotropic mechanical properties.

Fig. 1: (a) High-resolution images of individual collagen fibrils, showing fibrils stacked in sheet-like structures. Each fibril shows the periodic banding pattern. (b) Typical fibril profiles that were measured along line AB, perpendicular to the fibril axes (line CD). The distance between sequential bands (e.g., from I to II) was 68 nm. The height (III and IV) averaged to 32 nm and the fibril width (V and VI) was 90 nm.
Collagen also features remarkable optical properties. Optical anisotropy such as birefringence or differences in light scattering and propagation [4, 5] evoke from the structure and alignment of the fibrils. This makes the collagen fibril orientation an exceptional indicator for the properties of a biological tissue. Regularly arranged collagen bundles are transparent. Raman spectroscopy is a promising technique to characterize the degree of order. We found that there is a strong dependency between the intensity of certain Raman bands (e.g. the amide bands around 1271 cm$^{-1}$ and 1668 cm$^{-1}$) and the orientation of aligned collagen fibrils with respect to the polarisation of the laser light.

Two-micrometer-thick transverse sections of bovine Achilles tendon (Sigma-Aldrich) and human skin were investigated. Both tissues are rich in type I collagen. As exemplarily shown for the human skin (figure 1), highly ordered collagen structures with well-defined uniaxial, parallel aligned collagen fibrils were present. Raman spectra were recorded on collagen fibril bundles. The spectra shown in figure 2 were obtained on fibrils whose long fibril axis was parallel and perpendicular aligned in respect to the polarisation of the incident laser. The spectra were normalised to the most intense Raman band around 2939 cm$^{-1}$ which features a steady intensity and peak centre position throughout the measurements and is far away from the finger print region of collagen (700 to 1800 cm$^{-1}$).

![Fig. 2: Raman spectra taken on collagen fibrils oriented parallel and perpendicular to the incident laser beam. The gray areas indicate bands that show strong anisotropy. The inset details the fingerprint region.](image)

![Fig. 3: Polar diagrams of selected bands of collagen from human skin (yellow) and bovine tendon (black).](image)
The polar diagram in figure 3 outlines the varying peak intensities for a total rotation of 360°, illustrating the intensity variation as a function of the collagen orientation. From the asymmetric intensity distribution the alignment of the collagen fibrils on the specimen can be derived. The shape of the intensity distribution indicates strong anisotropic Raman scattering. The amide I and amide III bands, that represent the peptide bonds within proteins and in the collagen, indicate the stabilization of the subfibrillar triple helical structure by the formation of inter-chain hydrogen bonds between the N-H groups of glycines with the C=O groups of prolines in neighbouring chains [6,7]. The anisotropic Raman scattering at these amide groups indicates that they are oriented in the direction of the fibril backbone (long axis).

The polarisability typically varies if the electrical field is applied parallel or perpendicular to the molecular axis or in different directions relative to the molecule. Hence, the Raman scattering in the collagen fibres depends on the fibre alignment and the orientation of the polarised laser beam. The anisotropy is expressed by the nonzero elements of the Taylor expanded susceptibility tensor for Raman scattering. Therefore, a rotation of aligned collagen fibrils with respect to the incident laser causes intensity variations in several Raman bands. Thus, the orientation of the intensity distribution pattern in the polar diagrams characterizes the uniaxial orientation of the collagen bundles. The shape of these isointensities can act as an indicator for fibril structure of parallel aligned bundles.

CONCLUSION
In summary, the conformation and orientation of hierarchical molecules can be characterized by Raman spectroscopy. Intensity variations of several Raman bands were observed while rotating aligned collagen fibrils with respect to the polarisation of the incident laser beam. This result implies that the orientation of Raman active subunits of an ordered macromolecular protein in a tissue can be determined by Raman scattering. The orientation dependent scattering not only enables to optically characterize the alignment of collagen fibrils but also has to be considered in the analysis of the spectra. In general our study shows that Raman spectroscopy can determine the orientation of collagen fibrils with excellent sensitivity. This recommends Raman spectroscopy for the analysis and diagnosis of tissue alterations such as for the discrimination between healthy or diseased tissue and as a promising method for medical diagnostics.

References:
Joint Research Laboratory Nanomaterials

The Joint Research Laboratory Nanomaterials was established in 2004 to enhance the cooperation between the Institute for Nanotechnology at the Karlsruhe Institute of Technology and the Institute of Materials Science at the Technische Universität Darmstadt. Start-up funds to establish the laboratory were provided by both institutions. Scientific personnel is financed by the Institute for Nanotechnology at Karlsruhe Institute of Technology and by external grants of funding agencies in Germany and of the EU as well as by industrial cooperations. The laboratory interacts in several areas with research groups in Materials Science and Chemistry. The research activities are concentrated in the area of nanoparticulate systems, their synthesis and processing, microstructural characterization and their properties. The focus is currently on developing nanoporous structures as bulk materials and as thin films for the development of tailored and tuneable nanomaterials with applications ranging from printable electronics to energy materials. An additional engineering focus of the research is on the stability of nanostructured materials under operation conditions, such as high temperatures and gas environments, as well as the study of mechanical performance of nanoporous structures. The nanomaterials are prepared using Chemical Vapor Synthesis and Nebulized Spray Pyrolysis starting from metal-organic precursors and metal salts. Using these methods a wide range of nanostructures can be synthesized. In addition to several synthesis systems, characterization equipment is available including X-ray diffraction, nitrogen adsorption, light scattering and Zeta potential, gas chromatography and, in cooperation with the Surface Science Group, special equipment for in-situ characterization of battery materials using surface analytical techniques.

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Dr. Virgil Provenzano, NIST Gaithersburg
Research Projects

EU-Projekt, 7th Framework, MAHEATT FP7-ENERGY-NMP-2008-1
Plastizität in Nanokristallinen Metallen und Legierungen (DFG HA 1344/22-2, 2009-2011)


Investigation of non-equilibrium phonon populations in biased metallic single-walled carbon nanotubes (DFG OR 262/1-2, 2009-2010)

MIME – Molecule Interferometry and Metrology (DFG HH 1344/24-1, 2008-2011)

Reversibles Durchstimmen der elektronischen Transporteigenschaften in oxidischen leitfähigen Nanostrukturen zur Anwendung im Bereich der druckbaren Elektronik (DFG HA 1344/25-1, 2010-2013)

HMWK III.3.2 – 408/07.001, Investitionsfonds und Forschungsförderung (2008-2010)

Förderung durch Mittel des Helmholtz Institut Ulm (2010-2014)

Publications


Nisha P, Pillai SS, Darbandi A, Misra A, Suresh KG, Varma MR, Hahn H, *Magnetism and magnetocaloric effect in nanocrystalline La0.67Ca0.33Mn0.9V0.1O3 synthesized by nebulized spray pyrolysis*, JOURNAL OF PHYSICS D-APPLIED PHYSICS 43 (2010) 135001.


Clusters are organized aggregates of atoms or molecules with sizes ranging from single up to several hundred entities. In recent years, various studies have shown that especially smaller clusters have unique electronic, magnetic and catalytic properties being often totally different from the characteristics of the corresponding bulk. These specific properties are strongly correlated with the size of the clusters. Therefore, mass-selected clusters could be used as building blocks for new types of alloys with tailored properties. For the investigation of such cluster-based alloys a beam line was recently designed and constructed. The main focus was the possibility of controlled deposition of mass-selected clusters with high deposition rates.

In addition, this beam line will also be used for a so called Poisson spot experiment. The Poisson- or Arago spot is a bright spot visible within the center of the “shadow” of a circular object illuminated with a collimated beam of light. The phenomenon is based on wave interference and can therefore also be utilized in matter wave experiments in order to determine if particles show wave characteristics. In our experiment a collimated beam of heavy clusters (> 1000 amu) in combination with small spheres (D ≈ µm) as obstacles in the beam will be used to explore the mass limits of matter wave experiments.

In the experimental setup clusters of variable size are generated by a source (1) which combines magnetron sputtering and gas aggregation (Haberland et. al). To achieve the combination of these techniques the magnetron sputter head is mounted inside a liquid nitrogen cooled tube and immersed in a helium stream. The sputtered atoms are cooled down via collisions with cooled helium atoms and aggregate to clusters of various sizes. Finally, the clusters are extracted to the adjacent chamber by the helium stream.

Depending on the mode of operation either anions or cations are then attracted and collimated to a beam by subsequent electrostatic lenses. By means of the applied electrostatic fields the energy of the cluster beam can be adjusted in a range from 0 to 1 keV.

Downstream of the cluster source, the beam enters the mass separator section. Its key element is a large 90° sector magnet (R = 500mm) with a resolution better than 1/50 and a maximum magnetic field of 1,4 T (3). In combination with the variable beam energy this allows the selection of defined clusters within a huge mass range. In front and behind of the magnet the cluster beam passes electrostatic quadrupole triplets (2, 4). In the first triplet the beam is guided and focused into the magnet. The second triplet serves for guiding, collimation and shaping. The mass separator is followed by an electrostatic bender (5). At this point the cluster beam is guided into the two different experimental setups.

The deposition setup (6) used to deposit selected clusters on defined targets is straight ahead. To prevent the destruction of the clusters during the deposition process the last step has to take place under soft landing conditions. Therefore, the clusters are first decelerated in a stack of two electrostatic lenses and finally landed on a liquid nitrogen cooled substrate. Thereby the impact energy on the target will be below 1 eV per atom.
The setup for the Poisson Spot experiment is to the left side (7). Here the clusters are decelerated, neutralized and then collimated. The resulting neutral beam with a speed of less than 1 m/s and a collimation of $10^{-6}$ is finally diffracted by spherical obstacles.

The construction of the beam line has been finished recently and first promising test runs are currently being performed.
Collaborative ResearchCenter (SFB)

“Electrical Fatigue in Functional Materials”

2003 – 2014

www.sfb595.tu-darmstadt.de

The center for collaborative studies (Sonderforschungsbereich) has been awarded by the Deutsche Forschungsgemeinschaft in 2002 to TU Darmstadt and is centered in the Department of Materials and Earth Sciences with important contributions from the Department of Chemistry as well as the Mechanical Engineering Department of the University of Karlsruhe. The center was renewed in 2006 and again in 2010 and is now in the third and final four-year funding period.

It is comprised of a total of 17 projects and financial resources for the current four-year period of about 8 Mio. The center has an active guest program with guests visiting from 2 days to 3 months. In 2008, an integrated graduate school was also implemented with graduate students visiting from other Universities for time frames between 1 to 12 months. For specific information, please contact either the secretary of the center, Mrs. Gila Völzke, or the director of the center, Prof. Jürgen Rödel.

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Electrical fatigue in functional materials encompasses a set of phenomena, which lead to the degradation of materials with an increasing number of electrical cycles. Electrical cycling leads to both reversible and irreversible currents and polarisations. Ionic and electronic charge carriers interact with each other and with microstructural elements in the bulk as well as at interfaces (grain boundaries and domain walls) and interphases (electrode/electrolyte). This in turn causes local changes in the distribution of electric currents and electric potentials. As a consequence local overloads and material degradation ensues and leads to irreversible loss of material properties. This material degradation can lead finally to mechanical damage as well as to dissociation reactions. The basic phenomena of electrical fatigue are not yet understood on a microscopic level.

A key feature of the center is therefore the steady comparison between theory and experiment. This is utilized to find the physico-chemical origins of electrical fatigue as well as to develop strategies for new materials and improved material combinations. The materials of interest are ferroelectrics, electrical conductors (cathode materials for lithium batteries and transparent conducting oxides) and semiconducting polymers.

The goal of this center of excellence is the understanding of the mechanisms leading to electrical fatigue. An understanding of the experimental results is supported by concurrent materials modelling which is geared to encompass different time and length scales from the material to the component. In the third phase next to a quantitative modelling the development of fatigue-resistant materials and in the case of ferroelectrics, lead-free piezoceramics, is of particular focus.
Projects:

**Division A: Synthesis**

**A1**  
P.I.: Prof. J. Rödel  
Topic: Manufacturing of textured ceramics actuators with high strain

**A2 [ended 2010]**  
P.I.: Prof. M. J. Hoffmann  
Topic: Manufacturing and characterization of PZT-ceramics under dc loading

**A3**  
P.I.: Prof. W. Jaegermann  
Topic: Boundary layers and thin films of ionic conductors: Electronic structure, electrochemical potentials, defect formation and degradation mechanisms

**A4**  
P.I.: Prof. R. Riedel  
Topic: Novel functional ceramics using anionic substitution in oxidic systems

**A5**  
P.I.: Prof. M. Rehahn  
Topic: Synthesis of semiconducting model polymers and their characterization before and after cyclic electric fatigue

**Division B: Characterization**

**B1 [ended 2010]**  
P.I.: Dr. R.-A. Eichel  
Topic: EPR-Investigations of defects in ferroelectric ceramic material

**B2 [ended 2010]**  
P.I.: Dr. A. G. Balogh  
Topic: Investigations of the defect structure and diffusion in ferroelectric materials

**B3**  
P.I.: Prof. H.-J. Kleebe / Prof. H. Fueß  
Topic: Structural investigations into the electrical fatigue in PZT

**B4**  
P.I.: Prof. H. Ehrenberg  
Topic: In-situ investigations of the degradation of intercalation batteries und their modelling

**B7**  
P.I.: Prof. H. v. Seggern / Prof. A. Klein  
Topic: Dynamics of electrical properties in fatigued PZT

**B8**  
P.I.: Prof. Christian Hess  
Topic: In situ characterization of intercalation batteries using Raman spectroscopy
B9
P.I.: Prof. Gerd Buntkowsky / Dr. Hergen Breitzke
Topic: Characterization of structure-property relationships of functional materials using solid state NMR

Division C: Modelling

C1
P.I.: Prof. K. Albe
Topic: Quantum mechanical computer simulations for electron and defect structure of oxides

C2
P.I.: Prof. K. Albe
Topic: Atomistic computer simulations of defects and their mobility in metal oxides

C3 [ended 2010]
P.I.: Prof. R. Müller / Prof. W. Becker
Topic: Microscopic investigations into defect agglomeration and its effect on the mobility of domain walls

C5
P.I.: Dr. Y. Genenko / Prof. H. v. Seggern
Topic: Phenomenological modelling of bipolar carrier transport in organic semiconducting devices under special consideration of injection, transport and recombination phenomena

Division D: Component properties

D1
P.I.: Prof. J. Rödel / Dr. Torsten Granzow
Topic: Mesoscopic and macroscopic fatigue in doped ferroelectric ceramics

D3
P.I.: Prof. A. Klein
Topic: Function and fatigue of conducting electrodes in organic LEDs and piezoceramic actuators

D4
P.I.: Dr. C. Melzer / Prof. H. v. Seggern
Topic: Fatigue of organic semiconductor components

D5
P.I.: Prof. W. Jaegermann
Topic: Processing and characterization of Li-ion thin film batteries
Division T: Industry transfer

T1 [new in 2011]
P.I.: Prof. H. Ehrenberg
Topic: In operando investigations of fatigue of commercial battery types using neutron tomography and diffraction

T2 [new in 2011]
P.I.: Prof. M. Hoffmann
Topic: Influence of PbO stoichiometry on microstructure and properties of PZT ceramics and multilayer actuators

Integrated Graduate school

MGK
P.I.: Prof. A. Klein
Diploma Theses in Materials Science

Bekhet, Maged; Indium-based Perovskites and Spinels for Magnetic and Multiferroic Application, 08.09.2010

Bischler, Ruben; Tailored Nanostructured Metal Borides, 17.09.2010

Bleith, Peter; Titandiborid (TiB₂) als Trägermaterial für die Brennstoffzellenkathode, 26.10.2010

Cao, Shaoyong; Sintern von bioaktivem Glas, 03.05.2010

Cheng, Sumeng; R-Kurve Verhalten von La-Dotiertem BFPT, 06.04.2010

Dauermeier, Jonas; Charakterisierung reaktiv kathodenzerstäubter Kuperoxid-Schichten und deren Grenzfläche zu Zinn-dotiertem Indiumoxid, 18.10.2010

Diehm, Manuel; Finite-Size Effects in Oxide Nanoparticles, 22.03.2010

Ehmke, Mattias; Electric fatigue and aging processes in lead-free BNT-BT-KN ferroelectrics, 30.04.2010

Fehse Marcus; Light Metal Hydrides in Nanoporous Cabon Confinement, 10.05.2010

Fuchs, Marina; Termische Stabilität gefüllter und ungefüllter Polysiloxane für die Anwendung im Bereich der Elektrotechnik, 08.02.2010

Gorczak, Natalie; Charge transfer in PbS-QDs: PCBM: P3HT investigated by ultrafast laser spectroscopy, 26.10.2010

Härter, Johanna; Synthesis and characterization of mesoporous Co/N/C based cathode catalyst materials for PEM fuel cells, 04.10.2010

Hirsch, Alexander; Untersuchungen zu Phasen- und Mikrostrukturentwicklung polymer-abgeleiteter SiOC/MB₂ keramischer Nanokomposite bei T>1000°C, 07.05.2010

Hohmann, Mareike; Herrstellung und Charakterisierung epitaktischer Indiumoxid-Schichten und Zinndotierter Indiumoxid-Schichten, 10.05.2010

Kaspar, Jan Hans; Elektrochemical Characterization of Polymer-Derived Carbon-Rich SiCN Anode Materials for Lithium-Ion Batteries, 30.04.2010

Krüger, Philipp Andreas; Finite-Elemente-Simulationen der Feld- und Stromverteilungen sowie hysteretischer Wechselstromverluste in Supraleiter/Ferromagnet-Heterostrukturen 12.04.2010

Lange, Annika; Al₂O₃/ Cu-Verbundwerkstoffe: Reaktive Infiltration mit Cr-/Mo-Karbidi, 05.10.2010

Lilge, Britta; Sintern strukturierter Aluminiumoxid-Schichten mit einer Gasphase, 25.10.2010

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Seiß, Martin; Thin Films of magnetic iron oxides, 07.09.2010

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Gassmann, Andrea; Stabile und effiziente Kathoden für organische Leuchtdioden, 16.07.2010

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Mankel, Eric; Elektronische Eigenschaften von Heterosystemen organischer und anorganischer Halbleiter: Präparation, Modifikation und Charakterisierung von Grenzflächen und Kompositen, 29.09.2010

Melke, Julia; Study of the ethanol oxidation in fuel cell operation using x-ray absorption spectroscopy and electrochemical methods, 29.10.2010

Menapace, Ilaria; Photoluminescence properties of heat-treated silicon-based polymers: promising materials for LED applications, 10.03.2010

Narayanan, Narendirakumar; Physical properties of double perovskites La_{2-x}Sr_x CoIrO_6 (0≤x≤2), 24.09.2010

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Schierholz, Roland; Konvergente Elektronenbeugung an PbZr_{1-x}Ti_x O_3 -Keramiken, 19.03.2010

Seifert, Klaus; Development of new Lead-Free Piezoelectric Ceramics, 07.12.2010

Stukowski, Alexander; Atomic-scale modeling of nanostructured metals and alloys, 02.07.2010

Yekehtaz, Mehdi; Evaluation of Porosity and Corrosion Protection Ability of Sol-Gel Deposited Oxide Thin Films on Magnesium, 08.10.2010
Mechanical Workshop

The mechanical workshop of the Institute of Materials Science is designing, manufacturing and modifying academic equipment for a broad range of projects. In the year 2010 the workshop was involved in the following major projects:

- Design and realisation of a new neutron structure powder diffractometer (SPODI) at the FRM-II, TU Munich, Garching

- UHV-preparation chambers dedicated for MBE, CVD, PVD and (electro)chemical treatment

- Design and manufacturing of a protection chamber for x-rays with up to 150keV photons

Staff Members

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<th>Head</th>
<th>Jochen Korzer</th>
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<td>Technical Personnel</td>
<td>Frank Bockhard</td>
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<td>Volker Klügl</td>
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Electrical Workshop

The electrical workshop of the Institute of Materials Science was involved in the following projects:

- Maintenance and repair of various academic equipment like the Electron Probe Micro-Analyzer (EPMA), Secondary Ion Mass Spectrometry (SIMS), sintering furnace, Transmission Electron Microscopy (TEM), X-Ray powder Diffractometer (XRD) and Molecular Beam Epitaxy (MBE)

- Design and development of electronic components for specific research projects like temperature control unit, data logging, power controller, high voltage amplifier, high voltage power supply, measuring amplifier, high temperature furnace for impedance measurements

- Development of testing software (V-Basic / LabView / i-Tools)

Staff Members

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<th>Michael Weber</th>
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Institute of Applied Geosciences

Preface

Global change of climate, environment and land cover poses a challenge specifically for geosciences. Expanding energy needs, economy and population cause stress in all of the compartments of the Earth System, far beyond long-term sustainability. Geosciences are in the forefront to investigate resources, cycles and temporal aspects of natural changes in the Earth Systems as well as the anthropogenic impact on it.

In order to meet future demands for skilled professionals in Applied Geosciences, the Institute of Applied Geosciences offers new BSc and MSc courses focusing on three main topics: (i) Water, (ii) Energy and (iii) Environment. The new BSc degree course in Applied Geosciences (Bachelorstudiengang "Angewandte Geowissenschaften") was accredited by ASIIN in July and successfully launched in October with 40 freshmen. A new MSc degree course in “Applied Geosciences” is currently started with the winter term 2010/2011 and will clearly pursue this new concept and, therefore, allow our future students to address topics that will affect next generations.

The international master's course TropHEE (Tropical Hydrogeology, Engineering Geology and Environmental Management) continued in its fifth year with twelve new students from Bangladesh, Belgium, Germany, India, Kenya, Nepal, Nigeria, Sri Lanka, Tanzania and Thailand. TropHEE is internationally accredited and certified by ASIIN since March 2005 and supported by grants from DAAD and BMBF. TropHEE is considered an integral part of our efforts to focus our future-oriented research as well as teaching activities on applied geoscience topics with particular emphasis on water, energy and environment.

The research group of Prof. H.-J. Kleebe, Geomaterial Science, further extended their activities in the area of biomaterials and biomineralization. Moreover, with respect to the extension of the electron microscopy laboratory, a dual-beam FIB, a TEM with field emitter, and a Cs-probe corrected HR-TEM was purchased. The installation of the field emitting TEM started in November 2010.

![Fig. 1: Number of students (without Ph. D. students) in Geosciences at TU Darmstadt over the last 10 years](image-url)
The Hydrogeology of Prof. C. Schüth continued their research efforts in the field of hydrogeology of arid areas with GTZ-IS, UFZ, and the Ministry of Water and Electricity of Saudi Arabia as cooperation partners. Three field sites are currently operated in Saudi Arabia in the framework of the BMBF project IWAS, for which another 2 years of funding were granted by the BMBF.

In the field of Geothermal Energy, the industry-funded Chair for Geothermal Science and Technology was established at the TU Darmstadt – the first foundation professorship in energy science of the university. Since September 2009 Prof. I. Sass holds this chair and his research group, in cooperation with the Institute and Laboratory for Geotechnics, successfully conducted the Fourth Geothermal Summer School with 19 participants. In addition, in cooperation with the "Hessisches Ministerium für Wirtschaft, Verkehr und Landesentwicklung" the Fourth Forum on Deep Geothermal Systems ("4.Tiefengeothermie-Forum") took place at our institute in September 2009 with about 160 participants.

In the research group of Prof. S. Kempe (Physical Geology and Global Cycles) the cooperation with colleagues in Jordan was extended, focussing on the 100 km long Roman water tunnel in the north and on neolithic features in the east of the country. Mrs. S. Abu Ghazleh submitted her thesis about the Dead Sea/Lake Lisan terrasses. The study was supported by the DAAD and DFG and has implications for the planned Red-Sea Dead Sea Channel, that promised sustainable hydroelectric generation due to the large elevation change.

The research group of Prof. Hoppe (Geo-Resources and Geo-Hazards) led an interdisciplinary working group on sustainable development of cities within the so called LOEWE program of excellence about the “Intrinsic Logics of Cities”. Prof. Prem Thapa from Kathmandu University joined as a Research Fellow of Alexander von Humboldt Foundation this group to develop models of landslides within the Himalayas.

Prof. R. Ferreiro Mählmann gave an Erasmus lecture for applied clay mineralogy at the Sofia University St Klement Ohridski (Bulgaria) and initiated LLP-Erasmus bilateral agreement for cooperation for the academic year 2010/11-2013/14. Through Erasmus a science and consulting cooperation focus on the hydrocarbon and geothermal potential of intramontanous and foreland basins in Bulgaria.

In October, the Institute hosted the GeoDarmstadt 2010 conference in the Darmstadtium, with about 800 attendees, 450 oral, and 150 poster presentations organized by Prof. A. Hoppe and Prof. C. Schüth. Themed ‘Geosciences Secure the Future’, the conference brought together nearly all geoscientific disciplines. In numerous plenary sessions, leading experts in their fields gave overview presentations on the most pressing problems of our today’s society, i.e., the loss of biodiversity, decreasing natural resources and climate changes.

As it is the tradition in Geosciences to conclude the year with the ‘Barbara Fest’, all faculty, staff and students got together to discuss the events of the year as well as the future in a very friendly and positive atmosphere.
Physical Geology and Global Cycles

In the solar system, Earth is a unique rocky planet with an ocean and an atmosphere. It is inhabited by bacteria since about 4 billion years and by higher life – plants and animals – since ca. 600 million years. Organisms, air, water, and rocks are interconnected in a never ending cycle of matter and energy: The Earth System.

The crustal plates of Earth are driven by radioactive heat. This causes creation of new crust at mid-oceanic ridges at rates of several centimeters per year. On the other side, plate margins become subducted into the mantle again or fold up vast mountain ranges, like the Alps and the Himalayas, combining rocks of very different origin. During subduction the basaltic crust is partially melted, generating more felsic magmas which rise to form plutons and to cause lines of andesitic volcanoes such as occurring around the entire Pacific Rim. This is called the endogenic cycle of rocks.

At the same time Earth receives solar radiation which moves air and water in gigantic cycles around the planet. Specifically the water cycle causes the denudation of mountains by mechanical erosion and the leveling of plains by chemical weathering, the latter aided tremendously by vegetation and its CO\(_2\)-input to soils. This is called the exogenic cycle of rocks.

This exogenic cycle is increasingly impacted by mankind. The radiation balance of the atmosphere has been upset by the emission of carbon dioxide, methane, and other trace gases. Earth is warming. Industrially produced chlorinated hydrocarbons have risen to the stratosphere, weakening the protective ozone layer. Dust from traffic, industry and agriculture produces reagents which alter air chemistry, causing unprecedented interactions with the marine realm, vegetation and even rocks through acidification, excessive deposition of nutrients and salts. Dry and wet deposition of anthropogenic (i.e. produced by humans) particles can be measured world-wide. The population explosion caused the intensification of agriculture and an alarming loss of topsoil while reducing the extent of natural ecosystems at the same time. Artificial fertilization of soils causes wide-spread nitrate pollution of shallow ground waters. Urbanization alters the water cycle above and below ground. Local leakage of chemicals impacts soil, rivers and ground water. Civil engineering causes alterations in almost all rivers world-wide, and even coastal oceans show increasing eutrophication, siltation and ecosystem changes in the water column and in their shallow sediments. Scars left by mining of minerals and fossil energy are visible everywhere and cause increasing problems. Throughout the globe man has changed the rate of natural processes. He spreads ever further into the landscape, utilizing regions and building in areas which are not suitable for construction, considering their natural risks. Thus, damage of natural catastrophes rise each year, endangering the world insurance system. These processes and their consequences are topics in Environmental Geology.

Understanding Global Change and accepting the responsibility of mankind to conserve the planet and its resources for future generations are prerequisites for ensuring a sustainable development. The division of Physical Geology and Geological Cycles at the Institute for Applied Geosciences addresses questions important to environmental geology both in the present and in the geological past.
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<td>Global quantification of the CO$_2$-sink chemical weathering and the resulting riverine transports of dissolved solids into coastal waters (DFG).</td>
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<td>Tectonic structure of the southern boundary of the Harz mountain and its development since the Permian.</td>
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Within the frame of a PhD-Study Hans-Peter Hubrich will carry out a new geological mapping of the southern Harz mountain range. Objective is a regional map in the scale 1:10 000 that will cover an area of 5 x 100 km. The approach includes:

- Compilation of about 40 unpublished maps carried out as diploma thesis.
- Compilation of results obtained during students mapping courses.
- Assimilation of existing geological maps (small sub-areas and ‘GK 25’) after careful consideration of own mapping results.

First results are already available covering the area Badenhausen (near Osterode) to Bad Sachsa. These include the petrographic characterisation of the carbonates, maps of Karst features and Quaternary deposits as well as a fault map. It turns out that about 50 % of the faults are striking around 120°. The project is expected to be completed in 2012.

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Lake Van, Turkey: Evidence for a lake level drop of 500 m in the period 20-15 ka BP

Günter Landmann and Stephan Kempe

Lake Van, the largest soda lake on Earth, is located on the Eastern Anatolian High Plateau, Turkey. It is a terminal lake, thus its level reacts very sensitive to climate changes. The large water depth of 451 m allows the lake to survive periods with strong negative water balance for a long time before drying up. A high stand, 70-80 m above the present water level, is documented by a lake terrace dated to about 20.3 ka BP. At that time varved sediments were deposited with an average accumulation rate of 9 mm a\(^{-1}\) at a location close to an ancient river mouth.

Sediment cores from Lake Van cover the last 15 ka. A core taken from a water depth of 420 m is continuously varved back to 14.7 ka BP. Only the lowermost 40 cm are not laminated and contain large clasts, ooids, coated grains (Fig. 1) and iron oxide schlieren.

![Fig. 1: Backscatter REM picture from a sand layer at a core depth of 823-825 cm, showing ooids (horizontal arrows) with a nucleus consisting of clay minerals and an aragonitic cortex, a coated grain (vertical arrow, nucleus: clay minerals; cortex: Fe and S) and a secondary mineral (circle) consisting mainly on Fe and traces of S, Si, Na, F, and Mg.](image)

These textures are interpreted as being the result of a lake level regression to below 428 m and its consecutive transgression. This interpretation is supported by the pollen record and the geochemistry of the unvarved section revealing very dry conditions and a maximum concentration of terrigenous material. Furthermore the accumulation rate in a section representing this shallow lake phase is 10.8 mm a\(^{-1}\), that is more than 20 fold higher than the average accumulation rate for the past 14.7 ka (Fig. 2).

![Fig. 2: Picture of the section 962-969 cm of K6 (top). Shrinking of the sediments due to water loss was about 14% at the time the picture was taken. Vertical average of pixels within the marked area are extracted and presented as grey value versus distance (below). The section 3-60 mm is interpreted to represent six varves.](image)

Evidence for this regression in the period 20-15 ka BP is also derived from pore water chemistry. Salinity in all cores reveals a linear increase downcore reflecting upward diffusion of salt (Fig. 3). During the regression increasingly concentrated brines formed that penetrated into the pore space of the sediment by replacing older pore water of lower salinity. The deeper the lake level...
dropped, the more concentrated was the brine that penetrated into the pore space thus explaining the depth dependence of the Cl-gradient as shown in the inset of Figure 3.

Water balance calculation suggest that a lake level drop of 500 m within less than 5000 years can not be explained by a low precipitation alone but must also have been caused by a higher evaporation than today. A simultaneous lake level drop is also reported for Lake Lisan, the precursor of the Dead Sea.

**Fig. 3:** Cl-concentration of pore water of cores from different water depths. The dotted lines give the linear regression. The shaded area marks a section of core K6 that was replaced by older slump sediments. Inset: The solid line shows the Cl-gradient (lower X-axis) versus basin depth. The dotted line provides the salinity increase (upper X-axis) during a lake level decrease by keeping the total salt amount constant.
Geomorphological and sedimentological evidence for a high stand of Lake Lisan of up to 150 m higher than previously reported

Shahrazad Abu Ghazleh and Stephan Kempe

Along the eastern escarpment of the Dead Sea rift, Middle Cambrian, unconsolidated siltstones outcrop repeatedly in Wadi Al-Tayan due to branches of the Dead Sea Transform Fault. On these siltstones, terraces have been preserved at altitudes of -150 to 0 m, ca. 150 m higher than the previously reported high-stand of glacial Lake Lisan. The terrace altitudes were determined using DGPS and remains of calcareous stromatolitic crusts were U/Th-dated and analysed for stable isotope mineral composition (XRD) and Mg/Ca ratios.

Based on the newly derived data, the history of Lake Lisan can now be reconstructed much more precisely: The lake stood at -56 m at ~80 ka BP and at -66 m at 76 ka BP, reflecting an extraordinary humid climate during MIS 5a in the southern Levant. In two profiles, terraces up to 0 m occur suggesting that the lake stood even up to this level prior to 80 ka BP. After this high stand period the lake level dropped dramatically until it reached -350 m at ~63.6 ka BP, implying a cold and dry climate of the Jordan valley during H6 and MIS 4. Following a low level period between ~63 and 57 ka BP, the lake recovered again, reaching a high stand of >-137 m just before 32 ka BP. This suggests a once again more humid climate and a high water input to Lake Lisan during MIS 3.

By the beginning of MIS 2, the lake receded from its high stand of -137 m at 32 ka BP to -148 m at ~30 ka BP associated with H3. The lake level continued to drop to -152 m at ~27 ka BP and to -154 m at ~23 ka BP. Then, the lake level dropped sharply to -200 m at ~22.5 ka BP, consistent with the dry cold climate of H2. During the LGM, Lake Lisan recovered again to a high stand of -160 m at ~19 ka BP, implying a return to a positive water balance. The correspondence of Lake Lisan regressions to the cold MIS 4 and 2, as well as to Heinrich events 6, 5, 4, 3 and 2 implies a cold, dry climate of the Levant during these periods. On the other hand, the lake high stands during MIS 5a and the sharp transgression of the lake during MIS 3 suggest a warm, wet climate of the Jordan valley during these periods, most likely caused by an invasion of the Monsoon from the south.

Fig. 1: Reconstruction of Lake Lisan level curve during the last 80 ka according to our U/Th and OSL dates (blue and red points). The pink points refer to U/Th ages of the lake stromatolites from the western coast reported by Lisker et al. (2009). Heinrich events are according to Hemming (2004), Vidal et al. (1999) and (GISP2).
Hydrogeology

The Hydrogeology group focuses on 3 main research areas, (I) the fate of organic contaminants in the subsurface, (II) the development of novel methods to remediate soil and groundwater contaminations, and, (III) on water resources management on a regional scale.

(I) In our two field projects that study the fate of polycyclic aromatic hydrocarbons in soils and sediments (in alpine valleys as well as in selected catchments in the Taunus close to Frankfurt) monitoring equipment is in routine operation. Over the year data for atmospheric deposition of contaminants, soil contamination and also for contaminant output through evaporation and water discharge were gathered. In addition, through a co-operation with the Environmental Mineralogy group (Prof. Stefan Weinbruch), particle input into the Taunus field sites were determined using various particle samplers and Environmental Scanning Electron Microscopy.

(II) The mobile water treatment plant ‘Treatment Train’ is still in operation at the Greppin site north of Bitterfeld. A complex contamination is tackled with the elimination of CS2 by selective oxidation in the gas-phase as the crucial step. The developed method is now in its final testing phase and we expect that it can be an economically interesting alternative to replace the current treatment approach based on activated carbon adsorption.

(III) The first phase of the IWAS initiative, that focuses on water resources in Saudi Arabia, was completed by the end of 2010. A second phase will be financed by the BMBF to continue the project. This is especially encouraging as in 2010 the field installations in Saudi Arabia were completed and data are generated now on a regular basis for groundwater recharge estimation. An additional PhD student for this project was funded by the IPSWAT program of the BMBF to study the geochemistry of the large aquifer systems on the Arabian Peninsula.

In addition, our studies of groundwater-surface water interactions at our test site at the Schwarzbach continued. The test sites are equipped with several multi-level groundwater wells to allow high resolution water sampling.

Staff Members

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<td>Mustafa Yasin Reshid</td>
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Research Projects


SAFIRA 2: The treatment train approach (BMBF: 2009-2011)

The hydrogeology of the Taunus area, Hessia (HLUG: 2007-2010)

Improved management of contaminated aquifers by Integration of source tracking, monitoring tools and decision strategies – INCOME (EU-Life program: 2008-2011)

Ermittlung der Relevanz von ‘Cold Condensation’ Prozessen in Mittel- und Hochgebirgen (DFG 2008-2011)

Publications


Use of chemical probes and passive samplers for the determination of the atmospheric input and fate of persistent organic pollutants (POPs) in soil

Michaela Laxander, Thomas Schiedek, Christoph Schüth

Introduction

Persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) can be found ubiquitously in the environment. They are typically emitted from local and diffuse sources and enter the atmosphere either in their gaseous form or sorbed to carbonaceous particles. Removal from the atmosphere is due to wet and dry deposition and this can lead to an accumulation of the POP’s in soils and sediments. However, after deposition climate controlled desorption and evaporation processes may lead to a contaminant remobilization. It was speculated that especially in high altitudes remobilized contaminants may accumulate and contaminant patterns may change, due to the contaminants chemical and physical properties. These processes are summarized as cold condensation or cold trapping (Wania and Mackay, 1993, 1996, Daly and Wania, 2005).

We used PAH and PCB as model compounds to study climate and altitude triggered fractionation processes in detail. In two remote alpine valleys (Sarntal, Martelltal) and in a valley in the Black Forest (Großes Tal) test sites were equipped to (i) quantify wet and dry deposition using bulk deposition samplers and air samplers, and (ii) to determine evaporation rates using chemical probes.

Results

Fig. 2 shows deposition rates for PAH and PCB in the three valleys, depending on the season and altitude. It could be shown, that measured deposition rates were in general two orders of magnitude higher for PAH (sum of 16 EPA PAH) compared to PCB (sum of 6 EPA PCB). However, while higher deposition rates for PAH were found in winter, presumably due to increased combustion in the heating period, PCB deposition rates were, especially in the Black Forest valley (Großes Tal), higher in summer, indicating increased evaporation from sources at higher temperatures. Also, a general trend of decreasing deposition with altitude was observed.
Deposition rates for PAH showed a large variation between the three valleys. In general lowest deposition rates were found for the Martelltal. This valley is one of the oldest nature conservation areas in the alps, indicating the absence of significant local PAH emission sources. On the contrary, PAH deposition rates in the Black forest valley were on average highest, due to the adjacent densely populated Rhine valley.

In the three valleys also soil samples were taken and the concentrations of PAH and PCB were determined. Fig. 3 shows the results of the PAH analysis in dependency of the altitude the samples were taken. It can be clearly seen, that soil samples from the Black Forest valley show substantially higher PAH concentrations compared to the alpine valleys. This again underlines the urban influence in this valley compared to the more remote alpine valleys. Maximum concentrations in the soil reached 2.3 mg/kg. This value is already close to the threshold value of 3 mg/kg defined by the German soil protection law for soils with low organic carbon content (< 3%). A further accumulation of PAH in the soil due to atmospheric deposition would eventually lead to an exceedance of the threshold value.

**Outlook**

Four additional 3 month sampling periods will be realized to further increase the data base. With this a time frame of two years will be covered to better elaborate the differences of deposition in winter and summer. Also, the chemical probes will be analyzed to directly measure evaporation rates. For this, various sorbents were preloaded with selected PAHs and PCBs (several mg/kg), filled into mesoporous ceramic tubes and deployed at the test sites. It is expected, that the results will lead to a better understanding of deposition, evaporation and accumulation of organic contaminants in soil depending on climatic conditions.

**Literature:**


Geothermal Science and Technology

Geothermal Energy is defined as the heat of the accessible part of the earth crust. It contains the stored energy of the earth which can be extracted and used and is one part of the renewable energy sources. Geothermal Energy can be utilized for heating and cooling by applying heat pumps as well as it can be used to generate electricity or heat and electricity in a combined heat and power system.

The field of Geothermal Science has natural scientific and engineering roots. Geothermal Science connects the basic knowledge with the requirements of practical industry applications. Geothermal Science is in interdisciplinary exchange with other applied geological subjects such as hydrogeology and engineering geology and therefore is a logic and proper addition to the research profile of the Technische Universität Darmstadt.

The broad implementation of geothermal energy applications and the utilization of the underground as a thermal storage will help to reduce CO$_2$ emissions and meet the according national and international climate protection objectives. Furthermore, the utilization of geothermal energy will strengthen the independency on global markets and the utilization of domestic resources. Geothermal Energy will be an essential part of the decentralized domestic energy supply and will contribute an important share of the desired future renewable energy mix.

Regarding the worldwide rising importance of renewable energy resources, Geothermal Science is one of the future's most important field in Applied Geosciences. In 2009, the industry-funded Chair for Geothermal Science and Technology was established at the TU Darmstadt – the first foundation professorship in energy science of the university. Since September 2009 Prof. Sass holds this chair and in October 2009 the position of associate professor was filled. This position is hold by PD Dr. Götz, focussing on the facies-related characterization of geothermal reservoirs.

The Chair of Geothermal Science and Technology deals with the characterization of geothermal reservoirs, starting from basic analyses of thermo-physical rock properties, which lead to sophisticated calculation of the reservoir potential of distinct rock units. Reliable reservoir prognosis and future efficient reservoir utilisation is addressed in outcrop analogue studies world-wide. Organisation of a highly qualified geothermal lab and experimental hall (TUD HydroThermikum) started already in 2007 and was continued in 2010. Field courses and excursions in 2010 focused on geothermal energy in China, Island, Indonesia, Germany and the Netherlands.

Staff members

<table>
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<tr>
<th>Head</th>
<th>Prof. Dr. Ingo Sass</th>
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<tr>
<td>Associate Professor</td>
<td>PD Dr. Annette E. Götz</td>
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<td>Dipl.-Geol. Philipp Mielke</td>
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<td>Dr. Wolfram Rühaak</td>
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<tr>
<td>Technical Personnel</td>
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Michael Thomson (RES)
Bastian Welsch
Marcin Wronowski (RES)

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Prof. Dr. Axel Björnsson, University of Akureyri

Guest Lecturers
Prof. Dr. Yuri Popov, Academy of Sciences Moscow
Prof. Dr. Thomas Rüde, RWTH Aachen
Prof. Dr. Ingrid Stober, Universität Freiburg
Prof. Dr. Ákos Török, TU Budapest
Prof. Dr. Stefan Wohlnich, Ruhr-Universität Bochum

Research Projects started in 2010

Experimentelle Untersuchungen zur Verifizierung eines Mehrphasenmodells für das Wärmetransportverhalten im Untergrund. Funding: 3 years, Bundesministerium für Wirtschaft und Technologie.

Rock and Hydrothermal Fluid Interactions and Their Impacts on Permeability, Reservoir Enhancement and Rock Stability. Funding: 3 years, DAAD.

Machbarkeitsstudie „Machbarkeit und Nutzung von tiefer geothermischer Energie am Flughafen Frankfurt. Funding: 2011, FRAPORT AG.


Auswirkungen oberflächennaher Geothermie auf den Zustand des Grundwassers - Empfehlungen für eine umweltverträgliche Nutzung. Research proposal Umweltbundesamt.
Optimizing the arrays of shallow borehole heat exchangers for large buildings such as high rise buildings with limited ground property to utilize for geothermal installations in expanding cities. Research proposal Deutsche Forschungsgemeinschaft.

**Research Projects continued and finalized in 2010**

Rock mechanical and geothermal evaluation of basaltic rocks in Harrat Al-Shaam, Jordan–DAAD-funded project in collaboration with Hashemite University of Jordan, Zarqa.


Scientific consulting and supervision of an enhanced hydrothermal power plant system, Upper Rhine Valley – private client, confidential.

Soil abrasion effects on tunnel boring machines – Industry-funded project (CDM Inc. Seattle) in collaboration with PennstateUniversity, Institute of Soil and Rockmechanics.

Long-term effect of a seasonal thermal storage on the subsurface: a case study from the Upper Muschelkalk, SW Germany – Industry-funded project (CDM Consult GmbH, Crailsheim) in collaboration with ITW, University of Stuttgart.

Evaluation of thermal response tests using a cylinder source approach (Type Curve Fitting Method) – Industry-funded project (Geotechnisches Umweltbüro Lehr).

Development of a thermal conductivity measuring device for soil or cuttings. In collaboration with DIN-Innovation of normalisation and standardization.

Cooperation with the School of Renewable Energy Science (RES), Akureyri, Iceland. The cooperation between the Chair of Geothermal Science and Technology and RES was established in 2008. In 2009, the TU Darmstadt Energy Center signed to collaborate with RES in energy research and education. Prof. Sass continued his lectures as part of the RES Master Programme in Geothermal Energy. Two students from RES joined the group of Prof. Sass at TUD in 2010 to prepare their Master theses.


Engineering Geology

Engineering Geology is an applied earth science and a branch of the applied geology which requires multidisciplinary knowledge within both, natural sciences (geology, chemistry, physics, mathematics) and engineering sciences. The common aims of all special subjects contributing to engineering geology are the investigation, the use, the protection and the remediation of the upper parts of the earth's crust.

Engineering Geology seizes the behaviour of rocks and rock masses according to the genetic material properties and their development in earth's history. It quantifies the mechanical, physical and hydromechanical characteristics and the behaviour of soils and rocks in detail and in the assembly.

Important corresponding special subjects are soil and rock mechanics, civil services, foundation engineering, tunnel and cavity construction, drilling technology, measurement engineering and applied subjects of hydrology and hydrogeology, petrology and geochemistry. Engineering geology has thus strong relations with geotechnical engineering. It translates the results and knowledge of the geosciences into the engineering requirements.

Engineering Geology contributes to the fact that buildings of all kinds can be built and heated surely and economically. For this purpose the building ground and other underground conditions for engineering structures, such as geothermal power plants, traffic routes (e.g. roads, bridges, tunnels) as well as other infrastructure such as caverns, dams, pipelines as well as buildings such as high rise buildings, halls, wind power stations as well as water-structural plants such as water gates, dams, and dykes, are investigated.

At present the Chair of Engineering Geology is represented by the Chair of Geothermal Science and Technology. The appointment of a candidate for the advertised professorship is still pending.
Sedimentary rocks cover about 75% of the earth’s surface and host the most important oil and water resources in the world. Sedimentological research and teaching at the Darmstadt University of Technology focus on applied aspects with specific emphasis on hydrogeological, engineering and environmental issues. One key issue in this context is the quantitative prediction of subsurface reservoir properties which is essential in modelling of regional groundwater hydrology, oil and gas exploration, and geothermal exploitation. However, also basic sedimentological research is carried out, e.g. the use of sediments as archives in earth history to reconstruct geodynamic, climatic and environmental processes and conditions in the past. To predict groundwater movement, pollutant transport or foundations of buildings in sedimentary rocks a detailed knowledge about the hydraulic, geochemical or geotechnical properties is needed which often vary about several magnitudes. This kind of subsurface heterogeneity can be related to distinct sedimentological patterns of various depositional systems. In addition, changes of depositional systems with time can be explained by specific controlling parameters e.g. changes in sea level, climate, sediment supply and are nowadays described by the concept of sequence stratigraphy. The research in applied sedimentology also includes modelling of erosion and sediment transport and its implication for the management of rivers and reservoirs with the help of GIS.

To detect subsurface heterogeneities at a high resolution, the sedimentology group hosts a georadar equipment for field measurements. This geophysical device is composed of various antennas and a receiver unit. Sophisticated computer facilities are provided to process the data and construct real 3D subsurface models. The group shares their equipment and facilities with the Universities of Frankfurt (Applied geophysics), Tübingen (Applied sedimentology), Gießen (soil sciences), the RWTH Aachen and industrial partners. These institutions founded the Georadar-Forum which runs under the leadership of Dr. Jens Hornung (http://www.georadarforum.de/). Funding via a DFG research grant will allow to renew and extent the equipment in 2011. For quantification of reservoir properties a self-constructed facility for permeability measurements of soil and rock materials exists which is further developed. This lab is also fundamental to geothermal research.

In 2010, the group participated in the DFG Research Unit RiftLink (http://www.riftlink.de/) and two European Research Groups within the EUCORES Programme (TOPOEurope, SedyMONT). The topic of these research projects are in the context of earth surface processes, palaeoenvironmental reconstructions and georisk assessments. Field work is running in East Africa and the Alps. In April, Prof. Hinderer was in Saudi Arabia to continue the cooperation with GIZ (Gesellschaft für International Zusammenarbeit; früher GTZ), UFZ (Umweltforschungszentrum Halle-Leipzig), and the Ministry of Water and Energy of Saudi Arabia (MOEWE). The aim is to investigate the storage properties of large sedimentary aquifers and their relation to amount and quality of substracted groundwater in a hyperarid area suffering from water scarcity.

Based on previous work of the group several research initiatives are running at the moment, e.g. past environmental pollution in Central Europe as reconstructed from lake sediments, early history of the Transmexican Volcanic Belt (visit in August 2010 UNAM), Mesozoic palaeoenvironmental evolution in NW China (visit 2009 Jilin University Changchun), and high-resolution palaeoclimatic studies in Messel and similar maar lakes. In September, Jianguang Zhang commenced with his PhD work in the sedimentology group supported by a Chinese grant.
Prof. Hinderer has been member of the DFG senat commission of common geoscientific research (DFG-Senatkommission für Geowissenschaftliche Gemeinschaftsaufgaben) and is speaker of the "Wissenschaftlicher Beirat Beschleunigungmassenspektrometer, DFG University of Cologne. He is also the representative of the German-speaking sedimentologists (Section of Sedimentology in Geologische Vereinigung and SEPM-CES) and he organized a workshop of this group in December 2010 in Neustadt/Weinstraße.

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**Technical Personnel**  
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**Secretary**  
Kirsten Herrmann

**Research Projects**

Linking source and sink in the RuwenzoriMountains and adjacent rift basins, Uganda: landscape evolution and the sedimentary record of extreme uplift: Subproject B3 of DFG Research Group RIFT-LINK “Rift Dynamics, Uplift and Climate Change: Interdisciplinary Research Linking Asthenosphere, Lithosphere, Biosphere and Atmosphere” (DFG HI 643/7-1).


Spatial distribution of modern rates of denudation from cosmogenic Nuclides and Sediment Yields throughout the Alps (EUCORES programme TOPOEurope, Research Unit TOPO Alps, IP 3, DFG HI 643/9-1).

High resolution 3D architectural analysis and chronology of alluvial fan deposits in mountain landscapes: A case study of the Illgraben fan, Switzerland (EUCORES programme TOPOEurope, Research Unit SedyMONT, IP 6, DFG HI 643/10-1).

Monitoring of soil water content with ground penetrating radar (PhD thesis).

Climatic and tectonic interplay in central Asian basins and its impact on paleoenvironment and sedimentary systems during the Mesozoic (2 PhD theses).

Publications


LakeMessel, a high resolution archive for early Middle Eocene climate variability

Olaf K. Lenz

The Middle Eocene oil shale of the Messel pit near Darmstadt (Hesse, Germany) is worldwide known for an exceptionally well preserved fossil assemblage. A continuous core from the center of the basin proved that the oil shale was deposited in a meromictic maar lake which formed due to a phreatomagmatic eruption 47.8 ± 0.2 Ma ago [1, 2]. The core included a complete reference section of the Middle Eocene lake deposits (Messel Formation) thus representing a unique climate archive for the early Middle Eocene in Central Europe.

The classical “Messel oil-shale” of the Middle Messel Formation is characterized by a continuous succession of finely laminated bituminous claystones, representing long-term stable meromictic conditions. They show a very fine light and dark lamination, which was caused by annual algal blooms of the coccal green alga *Tetraedron minimum* (Fig. 1) forming light spring and summer layers that were superimposed on the terrigenous background sedimentation, as represented by the dark autumn and winter layers (Fig. 2).

![Fig 1: SEM image of a single cell of the coccal green alga Tetraedron minimum from the Eocene Messel Oil Shale.](image)

Since varved maar lake deposits are commonly used as accurate archives of climate change during the Quaternary, the core Messel 2001 was used to test whether subtle changes during the stable greenhouse phase of the Eocene are recorded. Now it is possible to show that short-term fluctuations in lacustrine sedimentation are reflected in Messel which can be attributed to an “Eocene ENSO”. Today ENSO (El Niño-Southern Oscillation) is one of the most important factors in global climate dynamics. The Messel studies now confirm a robust ENSO for the Eocene which has previously only been postulated by climate modeling [3].
Fluctuations in varve sedimentation are significant in the quasi-biennial (2.1-2.5 yr) and low-frequency band (2.8-3.5 yr, 4.9-5.6 yr) thus showing that algal growth as well as the background sedimentation were controlled by ENSO effects at least over a time interval of 600 k.y (Fig. 3). Significant signals of quasi-decadal (10-12 yr), interdecadal (17-22 yr) and multidecadal fluctuations (~52 yr, ~82 yr) show the enduring influence of more or less cyclic instabilities which are comparable to modern instabilities like the PDO, the Pacific Decadal Oscillation.

High resolution palynological analysis of the oil shale of the Middle Messel Formation in the core now provides an insight into the dynamics of a paratropical climax vegetation during the Middle Eocene greenhouse climate. Pollen and spores show that the vegetation...
surrounding Lake Messel did not change substantially in qualitative composition, but a change from a more humid climate with relatively high water levels in the lake to less humid conditions and lower water levels may be reflected by changes in the quantitative composition of the assemblage towards the top of the section. In addition to these long-term changes in the vegetation, short-term fluctuations in the frequency of individual taxa and certain clusters of taxa are recognizable.

Accepting an annual lamination, time series analyses of palynological data suggest that pollen assemblages reflect periodicities within the range of eccentricity, obliquity, long precession and short precession. This implies that orbital control of climate change was sufficient to impose quantitative changes in the composition of the terrestrial vegetation in the area though no taxonomic turnover occurred.

According to the cyclicity of the palynological data and with the availability of the astronomical solutions of La2004 [4] and Va2003 [5], it is now possible to implement an astronomical tuning to the 640 kyr record of the Middle Messel Formation. When tuning the pollen data to the La2004 Earth's orbital solution, the age of the Middle Messel Formation can be astronomically fixed between 46.6 and 47.3 Ma.

Reference


Geo-Resources and Geo-Hazards

In times of rapid population growth and the resulting exhaustion of the resilience of natural systems, geosciences have become an increasingly important research area. Geo-scientific knowledge about material flows from and back into the environment as well as the possibly catastrophic consequences of big natural phenomena are often not taken into account by decision makers, who were not able to spend long years on understanding the four-dimensional space-time-development of our earth. Nevertheless, the metabolism of cities, with their growing need for clean water, construction material and safe building areas, while simultaneously egesting waste into their neighbourhood, requires a thorough understanding of their underground and their geo-scientific environment. Geo Information Systems and 3D-techniques like gOcad are powerful tools to qualify and quantify resources and hazards as they enable the aggregation of complex geological and spatial data to thematic maps for a better understanding, interpretation and visualization of the results.

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Dipl.-Geol. Ina Lewin

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Guest Scientist
Prof. Dr. Prem Thapa (Georg Forster Research Fellow, Alexander von Humboldt Foundation)
Research Projects

The “Intrinsic Logic of Cities (Eigenlogik der Städte)” is an interdisciplinary project supported within the Hessian LOEWE program (Landesoffensive zur Entwicklung Wissenschaftlich-ökonomischer Exzellenz). Andreas Hoppe (as speaker of one of three groups) and Constanze Bückner investigated Mainz and Wiesbaden to identify significant natural framework conditions, elaborated an electronic data base and took part in a Research Group (Forscherguppe) applying support from the German Research Council (DFG).

Prem Thapa from Tribhuvan University in Nepal has started his research on GIS-based predictive hazard modelling to investigate the increased landslide activity in mountainous terrains, central Nepal Himalaya. The investigation aims to derive spatial characteristics of landslides and develop appropriate hazard mapping techniques in different geo-environments.

Rouwen Lehne and Marie-Luise Mayer started a 4D reconstruction of the uppermost layers in the northern Upper Rhine Graben in a project supported by the Hessian Geological Survey (HLUG) in order to evaluate the geopotentials of near-surface resources and hazards. A geodetic measurement program to detect recent movements in the Northern Upper Rhine Valley in cooperation with the Czech Academy of Sciences (Prague) and supported by DFG was continued.

Rouwen Lehné served as guest lecturer at the University of Christchurch (New Zealand) and “participated” in the 7.1 magnitude Canterbury earthquake on September 4. As a result of his guest lecture he is co-supervisor of two MSc-theses, dealing with assessment of geo-hazards (here mass movements) in the Southern Alps.

Rouwen Lehné started a research project in Estonia in cooperation with Tallinn University of Technology to compile a geological 3D-model of the northern part of the country in order to evaluate geo-resources, i.e. oil shale and black shale, in the context of given frame conditions (national directions, EU directions, etc.). Since Estonia covers more than 90% of its energy consumption by oil shale, the intention of the project is to offer spatial decision support.

Ina Lewin continued with investigation in the Neogene Hanau-Seligenstadt Basin between the Odenwald and Spessart Mts in cooperation with the Chair of Hydrogeology (Christoph Schüth) and supported by the local water distributor (Zweckverband Gruppenwasserwerk Dieburg). In a small area near Babenhausen georadar profiles have been measured to optimize the place for wells where high precision measurements of temperatures and other parameters can be carried out in order to understand relations between local sedimentology and hydraulic conditions.

Dirk Arndt completed a goCad based 3D model of the State of Hesse which is the base for the evaluation to decipher the deep seated geothermal potential for Hesse. The project runs together with the Chair of Engineering Geology (Ingo Sass), is financed by the Hessian Ministry of Economy (HMWVL) and accompanied by the State Geological Survey (HLUG).

Mass movements in terms of gully erosion in the northern periphery of Belo Horizonte (Minas Gerais, Brazil) have been modelled by Monika Hofmann in an ongoing project evaluating geo-resources and geo-hazards for a sustainable growth of the city. An integration of all relevant geoscientific data into a spatial decision support system was started.
Mass movements in a narrow valley within the Sierra Madre Oriental in northwestern Mexico which have blocked sediment transport have been mapped. The resulting quiet water deposits were investigated by two Diploma students (Dennis Brüsch & Yuki Weber) and could be dated to late Pleistocene and Early Holocene events.

Andreas Hoppe, Rouwen Lehné and Ulrike Simons together with three BSc students started investigations in Olympia (Greece) in cooperation with the German Archeological Institute (DAI). Several shallow drillings and geoelectric measurements have been carried out with technical and scientific support of Andreas Voett (University Cologne) and a first digital elevation model was developed to support a reconstruction of the historical landscape and environment.

Andreas Hoppe organized together with Christoph Schüth (Chair of Hydrogeology) at Darmstadt Conference Centre a national geoscientific congress (GeoDarmstadt2010) with the participation of nearly all German geoscientific organizations and institutions under the title “Geosciences Secure the Future”; more than 450 lectures and 250 posters were offered to approx. 800 participants. One of the most frequented sessions was that about GIS and 3D-modeling in geosciences, organized by Rouwen Lehné as chairman of the geoinformatics section of the German Geological Society.

As speaker of the Evenarí Forum for German-Jewish Studies at Technische Universität Darmstadt, Andreas Hoppe organized a series of lectures on “The Intrinsic Logic of Cities” (2009-2010) and “The Technische Universität Darmstadt between 1920 and 1960” (2010-2011). In addition, he served as chief-editor of the “Zeitschrift der Deutschen Gesellschaft für Geowissenschaften” (ZDGG).

**Publications**


Predictive landslide hazard modelling in mountainous terrain

P. B. Thapa\textsuperscript{1,2}, A. Hoppe\textsuperscript{2}, R. Lehne\textsuperscript{2}

\textsuperscript{1}Department of Geology, Tribhuvan University, Kathmandu, Nepal
\textsuperscript{2}Institut für Angewandte Geowissenschaften, Technische Universität Darmstadt, Germany

Frequent occurrence of landslides in the mountainous terrains is one of the most damaging natural hazards and often occurs during or after heavy rainfall. Landslides claim people’s lives almost every year and cause huge property damage in mountainous areas. In order to assess the potential for landslides, it is a requirement to identify and analyze the influencing factors. For this purpose, both qualitative and quantitative methods have been used in the process of creating landslide hazard maps. The qualitative method was widely used during the late 1970s by engineering geologists and geomorphologists. Quantitative methods, however, became popular in the last few decades because of the numerical expressions of the relationship between controlling factors and landslides by using geographic information system (GIS) techniques. Due to the large spatial variability of mechanical, hydrological and geometrical parameters involved in the equations of physically based models, the current study applies statistical analysis of landslide prediction modelling in the central Nepal Himalaya which is particularly suited to determine landslide hazard over large and complex area. The analysis is greatly optimized by extensive field data based on engineering geological evaluation, GIS automation and logical combination of modelling parameters.

Database and spatial characteristics

Spatial database comprises landslides inventories and landslide triggering geomorphological-geological variables that acquired from different sources: existing digital data, image processing, and detailed field surveying. Quality and reliability of the landslide distribution map should be considered high, as the entire slope movements were directly identified and mapped in the field to define landslide types, soil characteristics, failed-material thickness, soil depth and lithology. Landslides are also verified by processing remote sensing data like Landsat images. Regarding analysis of Landsat data, per-pixel classification methods for landslide detection are not applicable since the spectral response of a landslide is not unique and can correspond to the aggregation of pixels with different spectral properties. Land cover extraction was carried out by calculating normalized difference vegetation index (NDVI) which provides a standardized method of comparing vegetation greenness between satellite images (Eq. 1).

\[
\text{NDVI} = \frac{(B4 - B3)}{(B4 + B3)}
\]  

(1)

where B3 (red) and B4 (near infrared) are digital numbers in each pixel corresponding to Landsat bands 3 and 4 respectively. Boolean decision function within the class descriptor was used to delineate land-use.

GIS technique automatically or semi-automatically captures most of the parameters related to slope failures by executing algorithms for quick extraction of variables from large areas and regionalization of mapping information. Spatial analysis involves managing and manipulating interactions between landslide data and causative factors which provide the patterns, relationships and trends of landslide occurrences. The quantitative relationship between landslides and causative spatial data was obtained by evaluation of physical variables contributing to the initiation of landslides. The inter-relationship of multilayered data has been computed and effects of each parameter on landsliding as well as the triggering mechanisms have been investigated.
Cause, mechanism, and characteristic features of landslides have been concluded from the detailed spatio-temporal database by correlating a set of considered variables with slope instability from the precise landslide inventory. Results indicate that the factors such as slope gradient and orientation of rock discontinuities are statistically significant instability factors (explanatory variables) that contributed to landslides. Natural slope angle is the distinct pre-disposing factor for maximum likelihood occurrence, distribution and characteristics of landslides. In this study, slope angles for landslide initiation varied from 25° to 35° with critical slope angle of 27°. Correlation of landslides with the slope aspect factor indicated particular geological structure forming hill-slope form that might trigger landslides. Bedrock geology is another important significant explanatory variable which caused the spatial localization of slope failures. Therefore, it is confirmed that landslides occurred in a variety of engineering geological settings; (1) soils consisting of colluvium, (2) stratified rocks with contrasting competency and (3) slip zones with largely structurally orientation along either soil-rock contacts or bedding planes rocks that are about parallel to or gentler than slopes, frequently slide in translational form.

**Quantitative prediction and validation**

The probability function was used to assess future landslides as the quantitative measures of the hazard. In prediction model, the optimum mapping units were defined and preliminary selection of variables was carried out by univariate analysis. Bivariate and multivariate analyses were used to compute landslide hazard. Results were compared and validated. The bivariate statistical analysis was carried out to generate statistically derived numerical weights for all classes of the variable maps (Eq. 2). The weight calculation procedure is apparently complex but it can easily be coded and automated.

\[
W_i = \ln \frac{N_{pix}(SX_i)}{N_{pix}(X_i)} = \ln \left(\frac{\text{Number of pixels with landslide within variable class } X_i}{\text{Number of pixels within variable class } X_i}\right)
\]

where \(W_i\) = the weight of certain variable class (e.g. slope class), \(N_{pix}(SX_i)\) = Number of pixels with landslide within variable class \(X_i\), and \(N_{pix}(X_i)\) = Number of pixels within variable class \(X_i\).

Due to subjectivity of parameter selection in the bivariate analysis, the modelling procedure was extended to multivariate analysis, a logistic regression analysis that uses input factors as independent variables and presence/absence of landslides as a dependent variable. In the process, an important aspect is the conversion of various nominal parameters (e.g., lithology, land-use) to numeric values. This has been done automatically by creation of dummy variables matrix. The regional GIS database has been exported to statistical software (SPSS) for computation of logistic regression equations. Quantitatively, the relationship between landslide occurrence and its dependency on several variables can be expressed as (Eq. 3):

\[
Pr(\text{event}) = \frac{1}{1 + e^{-Z}}
\]

where \(Pr(\text{event})\) is the probability of an event to occur. In the present situation, the \(Pr(\text{event})\) is the estimated probability of landslide occurrence. As \(Z\) varies from \(-\infty\) to \(+\infty\), the probability varies from 0 to 1 on an S-shaped curve. \(Z\) is the linear combination (Eq. 3):

\[
Z = B_0 + B_1X_1 + B_2X_2 + \cdots + B_nX_n
\]
Where $B_i (i=0, 1,\ldots, n)$ is the coefficient estimated from the sample data, $n$ is the number of independent variables (i.e. landslide-related physical parameters), and $X_i (i=1, 2,\ldots, n)$ is the independent variable.

The final coefficients of logistic regression from SPSS were imported back into the GIS to calculate landslide hazard probabilities. The predicted probabilities were classified into five different hazard categories (very low, low, medium, high, and very high) and verified by crossing the predicted image and spatial occurrences of landslide events from 1993 to 2010. The verification showed sufficient (satisfactory) agreement between the presumptive hazard/susceptibility map and the existing data on landslide areas (locations), i.e. good correlation between areas defined as representing ‘high to very high’ hazard and the known landslides. The areas in high hazard zones that are devoid of landslides indicate potential landslide zones.

Success and prediction rates were computed for quantitative validation of landslide hazard model (Fig. 1). The AUC (area under the curve) varied from 0.7413 to 0.8656 indicating that rates ranged from 74% to 86% and thus the model is valid with prediction accuracy of 0.5 to 1 (total area).

Acknowledgment: The first author is grateful to the Alexander von Humboldt Foundation (AvH), Germany for the research fellowship.
Geomaterial Science

Geomaterial Science (Applied Mineralogy) explores the formation/processing conditions, composition, microstructure and properties of minerals, rocks in addition to synthesized compounds, while the study of the latter material group focuses on industrial applications. Research activities include a comprehensive characterization of relevant natural and synthetic phases, their performance under pressure, temperature, deformation and local chemical environment as well as tailored synthesis experiments for high-tech materials.

The experimental studies comprise the crystal chemistry of minerals and synthetic materials, in particular, their crystal structure, phase assemblage, deformation behaviour and microstructure evolution. The microstructure variation (e.g., during exposure to high temperature) has an essential effect on thermo-mechanical and electrical properties of synthetic materials as well as natural minerals, which in turn can be used to reconstruct the mechanical and thermal history of rock formation during sub- or obduction processes.

An important facet of the Fachgebiet Geomaterial Science at the Institute of Applied Geosciences is the application of transmission electron microscopy (TEM) techniques for the detailed micro/nano-structural characterization of solids. TEM in conjunction with spectroscopic analytical tools such as energy-dispersive X-ray spectroscopy (EDS), electron energy-loss spectroscopy (EELS) and energy filtered imaging (GIF) are employed for detailed microstructure and defect characterization. High-resolution imaging of local defects on the atomic scale in addition to chemical analysis with high lateral resolution (down to a few nanometers) is similarly applied to high-performance ceramic materials and natural minerals.

Recent research projects involve topics such as fatigue of ferroelectrics, re-calibration of the clinopyroxene-garnet geothermometer with respect to small variations in the $\text{Fe}^{2+}/\text{Fe}^{3+}$-ratio, defect structure in Bixbyite single crystals (and their corresponding exaggerated grain growth), morphology of $\text{In}_2\text{O}_3$ nanocrystals, transparent ceramics (spinel, YAG), interface structures in polycrystals, high-temperature microstructures, and the study of biomineralisation and biomaterials.

Staff Members

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<tr>
<th>Head</th>
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<td>Dr. Ingo Sethmann</td>
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<tr>
<td>Postdoctoral Students</td>
<td>Dr. Ana Ljubomira Schmitt</td>
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<td>PhD Students</td>
<td>Jens Kling (co-supervision with</td>
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<td>Prof. H. Fueß)</td>
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<td>Horst Purwin</td>
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<td>Eric Detemple</td>
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<td>Scientific Assistant</td>
<td>Dr. Gerhard Miehe</td>
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Institute of Applied Geosciences – Geomaterial Science
Senior Scientist  
Prof. Dr. Wolfgang F. Müller

Diploma Students  
Mathis M. Müller
Melanie Rohm

Technical Personnel  
Bernd Dreieicher

Secretary  
Angelika Willführ

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Research Projects

TEM Investigations on Cubic Crystal Shapes of Corundum-Type Indium Oxide; Novel High-Pressure Phases


Polymer-derived SiCO/HfO$_2$ and SiCN/HfO$_2$ Ceramic Nanocomposites for Ultrahigh-temperature Applications, SPP-1181 (DFG 2007-2012)

Investigation of Strengthened Hydroxyapatit/β-Tricalcium Phosphate Composites with Tailored Porosity (DFG 2008-2010)

Nanostructure and Calorimetry of Amorphous SiCN and SiBCN Ceramics (DFG 2009-2012)

Indium oxide (In$_2$O$_3$) under high pressure: rational design of new polymorphs and characterisation of their physico-chemical properties (DFG 2009-2012)


Temperature and Pressure Dependence of the Fe$^{2+}$/Fe$^{3+}$-Ratio in Omphacite for Recalibration of the Fe-Mg Geothermometer (DFG 2007-2011)


Investigation of the Atomic and Electronic Structure of Perovskite-Multilayer-Heterojunctions (in collaboration with the MPI Stuttgart, Prof. P. van Aken)

Phase Developments and Phase Transformations of Crystalline Non-Equilibrium Phases (in collaboration with the MPI Stuttgart, Prof. P. van Aken).
Publications


Crystallographic Orientation Relationship between Bastnaesite, Fluocerite and Cerianite in a Single Crystal from the Pikes Peak Pegmatites

Mathis M. Müller, Hans-Joachim Kleebe, Stefan Lauterbach, Technische Universität Darmstadt
Gary Zito, Colorado School of Mines

A unique crystal of fluocerite and bastnaesite, found in the Pikes Peak area in Colorado, was investigated by transmission electron microscopy in conjunction with electron diffraction. Fluocerite appears as a yellowish stripe within the middle of the crystal and bastnaesite as light brown slabs left and right parallel to the (0001) plane (Fig 1).

During the examination, unexpectedly a third phase, cerianite, was observed near irregular bastnaesite/fluocerite interfaces.

The orientation relationship between bastnaesite, fluocerite and cerianite can be determined by the generation of three corresponding orientation matrices. With the established matrices, representing the transformation of one crystal system into the other, all orientation relationships between the three mineral phases can be determined, as shown below, where parallel lattice planes and prominent lattice directions of one crystal are related to the equivalent planes and directions of the other phase.

| Bastnaesite || Fluocerite | Bastnaesite || Cerianite | Cerianite || Fluocerite |
|-------------|------------|-------------|------------|------------|------------|
| (2\(\bar{1}\)0)[10\(\bar{1}\)0] || (2\(\bar{1}\)0)[10\(\bar{1}\)0] | (1\(\bar{2}\)1)[01\(\bar{2}\)1] || (1\(\bar{2}\)1)[01\(\bar{2}\)1] |
| (\(\bar{1}\)2\(\bar{1}\))[01\(\bar{1}\)0] || (\(\bar{1}\)2\(\bar{1}\))[01\(\bar{1}\)0] | (1\(\bar{2}\)1)[01\(\bar{2}\)1] || (1\(\bar{2}\)1)[01\(\bar{2}\)1] |
| (0002)[0001] || (0002)[0001] | (0002)[0001] || (0002)[0001] |

In contrast to the main phases fluocerite and bastnaesite, the third phase cerianite occurred only in isolated grains, in the vicinity of fissures in fluocerite. The orientation of cerianite was monitored by electron diffraction patterns, when fluocerite/bastnaesite was oriented with the incident electron beam being parallel to prominent zone axis (Figure 1).

Fig. 1: Optical micrograph of fluocerite overgrown by bastnaesite of cerianite with both fluocerite and bastnaesite.

Fig. 2: Electron diffraction patterns of fluocerite (a), bastnaesite (b) and cerianite (c), verifying an orientation relationship of cerianite with both fluocerite and bastnaesite.
The diffraction patterns of cerianite (Figure 1c) also reveal an orientation relationship to both fluocerite and bastnaesite. Equivalents (hkil)-planes of fluocerite/bastnaesite versus cerianite are indicated by grey labels.

All three phases are structurally related to each other and are oriented in a way that the prominent lattice directions and planes of both hexagonal and the one cubic phase are parallel to each other, i.e., the hexagonal c-axes of bastnaesite and fluocerite run parallel to the body-diagonal [111] of the cubic cerianite.

Taking the mineral associations carbonate, fluorite and fluocerite into account and assuming a REE-transport via a hydrothermal fluid, the formation of an epitaxial overgrowth of bastnaesite on fluocerite can be rationalized, as given in equations (1,2). Here, fluoride acts as a stable ligand for REE up to 300°C (Haas, 1995). When the $\text{CO}^2-$ content in the hydrothermal fluid increases (which is assumed to initially have fluocerite composition), the epitaxial growth of bastnaesite would then be controlled by the following reactions:

$$\text{(Ce,La)}_3\text{F}_5 + \text{CO}^2- \Rightarrow \text{(Ce,La)}_3\text{(CO}_3\text{)}_2\text{F}_2 + 2\text{F}^-$$  \hspace{1cm} (1)

fluocerite + carbonate $\Rightarrow$ bastnaesite + excess fluorine

$$\text{Ca}^{2+} + 2\text{F}^- \Rightarrow \text{CaF}_2$$  \hspace{1cm} (2)

calcium + excess fluorine $\Rightarrow$ fluorite

Note that equation 1 reflects a solid state reaction leading to the formation of bastnaesite pseudomorph after fluocerite. However, the formation of a pseudomorph can be excluded here, since the overgrown bastnaesite is a perfect, transparent crystal (see Figure 1). Considering the crystal studied here, it is concluded that fluocerite was the first phase precipitated in an early stage of mineral formation, followed by the formation of bastnaesite. The presence of a third phase, the Ce-oxide cerianite, can be explained based on the observed chemical gradient within bastnaesite. It is suggested that this variation in REE content within the bastnaesite is a result of a local surface oxidation of $\text{Ce}^{3+}$ to $\text{Ce}^{4+}$ (Styles and Young, 1983), leading to the simplified reaction (3):

$$(\text{Ce}^{3+}\text{La})_3\text{F}_5 \Rightarrow \text{La}_3\text{(CO}_3\text{)}_2\text{F}_2 + 2\text{Ce}^{4+}\text{O}_2 + \text{fluid}$$  \hspace{1cm} (3)

The above reaction might be caused by a gradual change of the local chemical environment during growth; e.g., a more oxidizing fluid, resulting in the precipitation of cerianite. In contrast, the clean interface between the fluocerite and the Ce-rich bastnaesite (without any cerianite precipitation) indicates the epitaxial overgrowth due to a first variation in fluid chemistry becoming enriched in carbonate ions. In a second alteration step, the formed bastnaesite, being initially enriched in $\text{Ce}^{3+}$, is oxidized at inner surfaces (small cracks and fissures), leading to the local precipitation $\text{CeO}_2$ cerianite.

References and details are found in
Nanocalcination of In(OH)₃ Probed Locally in One Nanocrystal During in-situ High Resolution Transmission Electron Microscopy: a Frame-by-Frame VideoSequence Analysis

Stefan Lauterbach, Hans-Joachim Kleebe, Aleksander Gurlo, Gerhard Miehe

In-situ TEM has gained more attention in recent years, allowing for a broad range of applications, e.g. the in-situ characterization of phase transformations in materials under external stimuli. In the case of a highly focused probe, the inelastic scattering of electrons can cause radiation-induced damage of the specimen especially hydrogen-containing specimens such as metal hydroxides/oxohydroxides, accompanied by specimen heating, mass loss. Thus, radiolysis damage effects have been used to study metastable intermediate phases in the dehydroxylation of aluminum hydroxides and oxohydroxides, i.e. gibbsite, \( \gamma \)-Al(OH)₃, and boehmite, \( \gamma \)-AlOOH, during TEM analysis.

In the present work we applied a focused electron beam to study the nanocrystallization of indium oxide, In₂O₃, from indium hydroxide, In(OH)₃. For the first time, the unusual and not previously observed instability of indium hydroxide crystals in a focused high-energy electron beam could be followed by in-situ observation. In₂O₃ is a transparent n-type semiconductor used in a variety of applications, the most important is Sn-doped In₂O₃ (ITO; indium-tin-oxide), the key technological material for solar energy utilization or TFT-displays.

High interest in size- and shape-controlled In₂O₃ nanoparticles resulted in a continuously increasing number of new synthesis and assembly methodologies to produce either a bixbyite- (c-In₂O₃, space group \( la\bar{3} \), No. 206, \( a=10.126\text{Å}, Z = 16 \)) or a corundum-type (rh-In₂O₃, space group \( \bar{R}\bar{3}c \), No. 167, \( a=5.491 \text{Å}, c = 14.526 \text{Å}, Z=6 \)). The corresponding hydroxylated phases, i.e. indium hydroxide, In(OH)₃ (c-In(OH)₃, space group \( Im\bar{3} \), No. 204, \( a=7.979 \text{Å}, Z = 8 \)) and indium oxohydroxide, InOOH (o-InOOH, space group \( P2_1nm \), No. 31, \( a=5.26 \text{Å}, b=4.56 \text{Å}, a=3.27 \text{Å}, Z = 2 \)) were synthesized by using sol-gel or precipitation routes or solvothermally and dehydroxylated to obtain In₂O₃.

The transformation mechanism involved in the dehydroxylation reactions in the In-O-H system is discussed controversial with or without involving intermediate or amorphous phases. Several experiments pointed out that the c-In₂O₃, as a product of the c-In(OH)₃ dehydroxylation, inherited not only the parents’ “cubic” \{100\} morphology of In(OH)₃ but also remains single-crystalline. Other works indicated that c-In₂O₃ cubes obtained in this way are smaller in size, when compared to those of the parent c-In(OH)₃ structure and revealed cracks on the surface and micropores inside the crystal.

Ex-situ X-ray powder diffraction characterization indicates that the c-In(OH)₃ transforms irreversible to c-In₂O₃ on heating. The morphology of the crystals remains unchanged after the phase transition. The phase transition from c-In(OH)₃ to c-In₂O₃ leads to broadening of the reflections, which can indicate a decrease in the mean crystallite size upon transformation from c-In(OH)₃ to c-In₂O₃. To clarify this discrepancy, high-resolution TEM was applied in quasi in-situ conditions to characterize the decomposition of one single c-In(OH)₃ nanocrystal. The fresh prepared In(OH)₃ crystals show cubic to orthorhombic shapes with homogenous contrast indicating a perfect crystal lattice as depicted in Figure 1a. To induce the phase transition in c-In(OH)₃, the electron beam was focused on these crystals. After irradiation (approximately 50 sec), the crystal was reduced in size and a grainy contrast inside the particle was observed (Figure 1b), which is seen as an indication for the transition from c-In(OH)₃ to c-In₂O₃.
A number of subgrains were induced inside the particle as a result of irradiation damage. The structural rearrangement within the crystal could clearly be seen in the diffraction patterns. The spotted pattern of the single c-In(OH)$_3$ crystal given as an inset in Figure 1a was transformed to a diffuse ring-like pattern of c-In$_2$O$_3$ (cf. inset in Figure 1b), which indicates the phase transition of c-In(OH)$_3$ to c-In$_2$O$_3$, accompanied by the fragmentation of the initial c-In(OH)$_3$ single crystal. No secondary phase formation was observed during the hydroxide/oxide transition. The persistent cube-like shape is due to a pseudomorphosis. The former single c-In(OH)$_3$ crystal has disintegrated into c-In$_2$O$_3$ nanocrystallites with dimension of typically 5 nm to 10 nm.

The results of the high-resolution TEM observation applied to one individual c-In(OH)$_3$ crystal showed unambiguously that upon decomposition of c-In(OH)$_3\rightarrow$c-In$_2$O$_3$ (i) no intermediate phases appear; with this it confirms our recent in-situ synchrotron radiation study and (ii) the single c-In(OH)$_3$ nanocrystal breaks into fragments resulting in a pseudomorphose, i.e. a polycrystalline cubic-shaped polycrystal composed of c-In$_2$O$_3$ domains (~5-10 nm) with different orientation within the cube-shaped matrix. These findings allowed us to clarify the morphological relationship between c-In(OH)$_3$ and c-In$_2$O$_3$ as well as the mechanism of the decomposition c-In(OH)$_3\rightarrow$c-In$_2$O$_3$. It is concluded that

(i) the dehydroxylation of c-In(OH)$_3$ occurs as displacive decomposition with a considerable volume change and atomic rearrangements; the latter are so considerable that a fragmentation of even small c-In(OH)$_3$ crystals is induced;

(ii) this displacive decomposition involves heterogeneous nucleation of c-In$_2$O$_3$ crystals which starts at different planes/directions of the nascent c-In(OH)$_3$ crystal, accordingly; the resulting domains of the new phase are not orientated identically.

Fig. 1: a) TEM bright field image of an unaltered crystal of In(OH)$_3$ before radiation with the electron beam and b) the same crystal after radiation. The insets show the FFT calculated from the HRTEM figures. Please note the perfect symmetry of the diffraction pattern for the unaltered in a) crystal versus the broadened reflections for the irradiated crystal representing domains of In$_2$O$_3$ in b).
Technical Petrology with Emphasis in Low Temperature Petrology

Petrology is devoted to study the genesis and the mineralogicalevolution of a rock with a specific bulk composition at various physical and chemical conditions. The scientific and educational fields of this branch within the applied geosciences are based on crucial knowledge in magmatic-, metamorphic-, hydrothermal petrology, mineralogy, structural geology, tectonophysics, geothermal geology, sediment petrography, thermodynamics/kinetics and geochemistry.

Technical Petrology aims to assess the physical and chemical properties of natural or synthetic rocks for applied purposes at various physical and chemical conditions (e.g. pressure, temperature, chemical composition). The Technical Petrology group is in particular devoted to study the low temperature domain. These low temperature studies serve as an aid to qualify and quantify processes occurring in hydrocarbon prospecting, geothermal system, and geodynamic study.

The principal motivation of our Low-Temperature Petrology research group is to understand and to quantify low temperature petrologic processes. For this purpose, an effort is addressed to innovate new tools to calibrate and to model the metamorphic P-T-X-d-t conditions in low-grade rocks. A multidisciplinary approach is necessary because crystallization and recrystallization are not obvious at low temperature. Hence, our work links field petrology, experiments, analytical methods, and thermodynamic and kinetic modeling.

Moreover, the Low-Temperature Technical Petrology group interdisciplinary cooperates to other research fields present in our institute such as environmental mineralogy, applied sedimentology and geothermal science. Consequently, low temperature petrology embraces a broad field of studies:

- diagenesis concerning hydrocarbon, hydrothermal and geothermal exploration;
- applied organic and clay petrology studies:
  - maceral analysis of carbonaceous matter;
  - sorption properties of carbonaceous and clay materials;
  - recognizing of soot and carbon black in filtering installations;
- determination of graphitization nano- and microstructures (refractory quality);
- improvement of forward numerical geothermal, maturity, and basin-analysis models;
- studies of hydrocarbon and fluid migration;
- synthesis of graphite structures and maturation of organic matter.

Another facet of our research is dedicated to study geodynamics through tectono-metamorphic studies that combine metamorphic petrology and structural geology (from the kilometer to nanometer scale). This aims to determine the pressure–temperature–
deformation history of natural rocks, and thus to aid understanding of orogenic belts. Due to the scale our petrologic work is strongly field-oriented.

A broad analytical spectrum must be applied in low-temperature petrology due to very small grain-size. In the Technical Petrology group, general microscopy (MPV coal reflection microscopy, fluorescence microscopy, transmitted light microscopy) and basically XRD powder and texture studies (Clay and XRD Laboratory and a research XRD Laboratory recently installed with thankful help by Merck KGaA) can be combined with ICP-AES, TOC, AOX and gas chromatography (GC-ECD, GC-MS) in the Organic Geochemical Laboratory (installed with thankful help by the Hessische Industriemüll GmbH). A XRF laboratory (Wave-dispersive BRUKER S8-Tiger) was installed in 2008 and is maintened together with the research groups of Chemical Analytics and Environmental Mineralogy.

The main research interests of the study group of R. Ferreiro Mählmann (head of the group since August 2002) are concentrated on the petrologic and petrographic study of tectono-metamorphic orogenic terranes. The major aim is to discriminate specifically between pre-, syn- and post-kinematic metamorphic events to get a better understanding of the orogenic processes that were active during subduction, collision, stacking and exhumation in several parts of mountain belts. More specific research is concentrated on diageneis and low-temperature metamorphism, dealing primarily with pelites and organic matter rich rocks. Here the principal interest is devoted to study vitrinite, bituminite and secondary macerals that are important constituents of source rocks (oil + gas + coal).

R. Le Bayon (assistant since December 2004) focuses his research in metamorphic petrology on the maturation of carbonaceous organic matter and silicate bearing-rocks. To understand and to quantify metamorphic processes and in particular to model kinetics of the maturation of organic matter, R. Le Bayon (associated with G. Brey – University of Frankfurt am Main, D; L. Nasdala – University of Vienna, A; W.G. Ernst – University of Stanford, USA) bases his research on pressure-temperature-time experiments at the Institute of Geosciences of Frankfurt am Main University.

B. Šegvic joined the group in May 2010. His research interests are set on ophiolite and ophiolite-related metamorphic rocks and their role in the development of Jurassic oceanic domains within the present eastern Mediterranean Alpine orogens. Besides, he is actively involved in research on ancient ceramic materials and its technological properties. His special interest is put on clays, as raw material, and clay related provenance studies. This work is performed in close collaboration with archaeologists from several institutions (e.g. L. Šešelj, University of Zadar; M. Ugarković, Institute of Archaeology Zagreb).
**Staff Members**

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Erika Doerner, Rebecca Kämmerling, Robert Priebs

**Technical Personnel**
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**Secretary**
Inge Schmitt (to 31.05.2010)
Natali Vakalopoulou Buffet

**Research Projects**

Petrology of the Phyllite-Diabas-Zone at the KaschanaPass in the Stara Planina of central Bulgaria, DAAD, ERASMUS (cooperation with University of Sofia, Bg).

Structural, stratigraphic and diagenetic analysis of the Jurassic-Early Cretaceous forland Trojan-basin in central North Bulgaria, DAAD, ERASMUS (cooperation with University of Sofia, BG).

Origin of the ophiolite-related Al-(Mg) metamorphites – case study of sapphire and corundum amphibolites from the Central Dinaridic Ophiolite Zone (CDOB, NE Bosnia and Herzegovina), DFG and DAAD (cooperation with University of Heidelberg).

Geochronology and tectono-thermal history of the Penninic-Austroalpine boundary (Arosa Zone) in Eastern Switzerland; a multi-methodical comparison of methods, SNF and Willkomm Fond (cooperation with University of Bern, CH and Departement für Zivilschutz, Bern, CH).

Composition, manufacture technology, and circulation of Hellenistic pottery from Eastern Adriatic: a case study of three archaeological sites in Dalmatia (Croatia), (MZOŠ, cooperation with University of Zadar and University of Zagreb, HR).

Very low to low-temperature coal and clay-mineral indicators, comparative application from diagenesis to green- and blueschist facies (cooperation with University of Basel, CH).

Organic matter studies on graptolite-schist, their hydrocarbon potential and maturation level to determine the palaeo-geothermal history and to elucidate geodynamic processes (Bulgaria and Turkey). – (Different national science founds and DAAD (cooperation with University of Sofia, BG and University of Sivas, TR).

Experimental kinetic study of organic matter maturation: an appraisal of pressure, temperature and time effects on reflectance properties of vitrinite, DFG (cooperation with University of Frankfurt a. M., D; University of Vienna, A and Stanford University, USA).
Bituminite parameters to determine thermal metamorphism - field data and experimental studies., different science founds and DAAD, ERASMUS (cooperation with University of Chile, Santiago de Chile, Cl; Institutul Geologic al Romaniei, Bucharest, Ro; University Complutense, Madrid, E; Stanford University, USA; Peking University, China and ETH Zürich, CH, University of Sofia, BG and University of Sivas, TR).

**Publications**

The Arosa Zone in Eastern Switzerland, the Diagenetic to Metamorphic Pattern of a Tectono-Metamorphic Mélange

Ferreiro Mählmann, R.1,3,4 & Giger, M.2,3

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2 Dammweg 27, CH-3604 Thun (Switzerland)
3 Abteilung für Isotopengeologie, University of Bern, CH-3012 Bern (Switzerland)
4 Lehrstuhl für Geologie, Geochemie und Lagerstätten der Kohle und des Erdöls, RWTH Aachen (Germany)

In the area of Arosa-Davos-Klosters (Eastern Switzerland) the different tectonic elements of the Arosa zone mélange e.g. the Austroalpine fragments, the mafic and ultramafic basement rocks as well as the matrix (oceanic sediments and flysch rocks) show a distinctively different metamorphic history and also a different climax ("peak") of alpine metamorphism. This is proofed by a wealth of Kübler Index (KI) - vitrinite reflectance (VR) measurements and kinetic numerical modelling, bituminite reflectance, illitization indices (related to the smectite-illite reaction progress), K-white mica b-cell dimension determinations, index minerals, microprobe data as well as geo-chronological results.

Whereas the matrix sediments of the Arosa zone mélange are overprinted by a low anchizonal to high anchizonal metamorphism, Lower Austroalpine fragments in the mélange and the adjacent Lower Austroalpine units (e.g. Tschirpen-Dorfberg nappe) were overprinted by a widespread syn-sedimentary burial and orogenic epizonal metamorphism. High anchizonal rocks are found in the Lower Austroalpine locally. Flysches at the hanging wall of a disconformity in the mélange zone show lower diagenetic thermal conditions.

At least six main metamorphic events can be recognized in the area of Arosa-Davos-Klosters:

i) A pre-orogenic event is recognized in the sediments at the base of the Silvretta nappe, typical for the Upper Austroalpine.
ii) The epizonal oceanic metamorphism observed in the close vicinity of oceanic basement rocks (e.g. pillow-basalts, peridotites of the South Penninic units) of the Arosa zone is another pre-orogenic process.
iii) Based on stratigraphic, tectonic and geo-chronologic considerations the overprint of lower structural Austroalpine fragments in the Arosa zone and the adjacent Lower Austroalpine nappes is attributed to the orogenic metamorphic processes during the Late Cretaceous.
iv) The thermal climax observed in the sediments of the Arosa zone can be bracketed into the time span between the Austroalpine Late Cretaceous (iii) event and the middle Tertiary event in the Middle Penninic (v) as well as the Oligocene "Turba phase". North of Klosters, in the northern part of our study area, the entire tectonic pile from the North Penninic flyschs to the Upper Austroalpine is strongly influenced by a late Tertiary event.

In the Arosa zone mélange an individual orogenic metamorphic event is evidenced and gives a new chance to resolve still not understood diagenetic-metamorphic versus deformation relations. By different KI-VR correlations we can distinguish 6 heating episodes in sedimentary rocks and 7 deformation cycles. This is well explained by the propagation of the Alpine deformation front onto the foreland units.
Comparative archaeometric characteristics of ceramic sherds recovered from the excavation site of Roman villa situated on the island of St. Klement (Pakleni otoci, Croatia)

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\textsuperscript{2}Institute of Archaeology, Ulica grada Vukovara 68, HR-10000 Zagreb,
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Key words: archaeometry, ceramic sherds, amphorae, dolia, firing conditions, comparative analyses, Adriatic, Pakleni otoci, Soline

Introduction with archaeological background
In this abstract, we deliver first preliminary results on the petrographic and mineralogical characteristics of selected archaeological materials from the Soline bay locality. The bay presents a safe anchorage place of the island of St. Klement, the largest in the Pakleni Otoci archipelago (~ 5.3 km\textsuperscript{2}), lying 3 km westwards from the city of Hvar. Along the bay, architectural remains of the Roman maritime villa are still visible in the landscape. From 2007 to 2009, the Hvar Heritage Museum, in collaboration with the Institute of Archaeology, Zagreb and St. Thomas University, Minneapolis, USA, has conducted a small-scaled archaeological investigation of the area. A great number of finds of various materials have been recovered, with ceramics constituting the majority. Preliminary typological and fabric analyses of ceramic sherds suggest that 98\% of them can be dated from 2\textsuperscript{nd} century BC to 5\textsuperscript{th} century AD, and propose several different provenances from around the Mediterranean. Five ceramic sherds of different technological levels have been chosen to represent the most common coarse pottery finds. They were subjected to comparative archaeometric analyses.

Analytical methods
Petrographic properties of ceramic sherds were examined optically by Leica DM-LSP polarizing microscope. Conventional point-counting procedures were used for rough estimation of relative abundances of temper materials (VAN DER PLAS & TOBI, 1965). XRD was used to reveal the ceramics mineral composition. The powdered samples were scanned at a rate of 1°/min over a range of 2-70° 2\theta, using Phillips diffractometer 1820 and CuK\textsubscript{α} radiation, graphitic monochromator (U = 40 kV, I = 20 mA). The diffraction patterns were identified through published files from the International Centre for Diffraction Data (JCPDS-1996). The petrographic and XRD analyses were done at the University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering.

Results
Prehistoric potsherd (sample 1, Table I.) contains about 5 to 7 mm thick walls. It possesses coarse red-brownish fabric, darker on the outside, along with visible small to medium-sized inclusions. Petrographic inspection defined it as relatively massive, non-plastic calcite mineralization, accompanied with minor ceramoclasts and organic particles. Distribution of non-plastic inclusions is bimodal and coarser grains show preferential orientation parallel to the vessel walls. The matrix is anisotropic and microcrystalline with medium optical activity. Voids of undefined shape are rare, being randomly distributed in the ceramic body. XRD analysis confirms presence of calcite and a high amount of amorphous matter. Furthermore,
occurrence of zircon is indicated along with 10Å mica (illite/muscovite), marked by diminishing 00l diffraction lines.

Sample 2 (Table I.) is defined as an extensively worn fragment of a square plate of medium fine buff fabric. The matrix is characterized as anisotropic and partly microcrystalline. Its microtexture is uniform, having evenly distributed non-plastic inclusions composed mostly of quartz, mica, micritic calcite and plagioclase. Distinguishing characteristics of the sample are coarser fragments of fossils, mostly bryozoans and foraminifera. Their skeletons are made of thermally untouched micritic calcite. Voids are irregular, occurring sporadically, due to shrinkage of host clay material. XRD mineralogy is consistent with the petrographic phase determination. As in the previous sample, it points to the diminishing mica signatures, remnants of partial collapse of clay minerals structure induced by the firing process (e.g. RICCARDI et al. 1999).

Tab 1. Petrographic features of studied ceramics obtained by polarizing microscope and XRD mineral composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Matrix</th>
<th>Voids (vol%)</th>
<th>Temper material (vol%)</th>
<th>Temper dimens. (mm)</th>
<th>XRD mineral composition</th>
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<td>anisotropic</td>
<td>5-10</td>
<td>30-35</td>
<td>0.10-2.50</td>
<td>Cc, Zrn, 10Å-mica</td>
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<tr>
<td>2 plate</td>
<td>anisotropic</td>
<td>&lt;5</td>
<td>5-10</td>
<td>0.03-0.40</td>
<td>Q, Cc, 10Å-mica, Pl</td>
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<tr>
<td>3 dolia</td>
<td>anisotropic</td>
<td>15-20</td>
<td>20-25</td>
<td>0.05-1.00</td>
<td>Q, Pl, Cc</td>
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<tr>
<td>4 amphora</td>
<td>isotr. to anis.</td>
<td>&lt;5</td>
<td>30-35</td>
<td>0.005-0.2</td>
<td>Q, Pl, Cpx</td>
<td></td>
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<tr>
<td>5 amphora</td>
<td>isotropic</td>
<td>10-15</td>
<td>20-25</td>
<td>0.01-1.10</td>
<td>Q, Pl, Cc, Kfs (?)</td>
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</table>

Temper material and voids proportions are approximations determined by point counting analyses. Mineral abbreviations: Cc=calcite; Q=quartz; Zrn=zircon; Cpx=clinopyroxene; Pl=plagioclase; Kfs=K-feldspar.

The Roman dolia (sample 3, Table I.) is characterized by coarse texture along with inclusions visible to the naked eye and colour gradation from core to the rims of the vessels. It is featured by coarse microcrystalline matrix with low optical activity. Matrix microtexture is dominated by a large number of coarse ceramoclasts. The rest of temper is constrained to quartz with minor amounts of plagioclase, K-feldspar, and biotite. Their distribution is typically bimodal. A highly abundant number of spherical voids (<0.55 mm) is connected with pore water and related gas migrations. They are filled by the late, sea-induced, calcite and minor prehnite mineralizations. According to XRD analyses, quartz and plagioclase mineralizations have been reported. The half-widths of calcite diffraction lines indicate relatively small-sized crystallite mineralization.

Sample 4 (Table I.) presents a fragment of the Roman amphora, here marked by red fabric, with external surface having dark-grey skin. Traces of a wheel are likely to be observed on the vessel’s inner surface. Microtextural characteristics comprise optically low active, almost isotropic matrix, featured by an elevated proportion of non-plastic material of silt dimensions. Dominantly, it is quartz, with minor K-feldspar and plagioclase. Along the edges of the vessel, one can observe coarser inclusions of ceramoclasts as well as many acicular void forms. The X-ray analysis of this sample shows presence of quartz and plagioclase. Moreover, several diagnostic diffraction reflexes indicate clinopyroxene formation.

Last analysed shard (sample 5, Table I.) introduces a typical Late Roman/Byzantine amphora of orange coarse inner fabric and bleached surface area. Matrix is isotropic, having low optical activity. Non-plastic material is ubiquitous, distributed bimodally and unevenly.
It comprises quartz and minor quartzite/chert as well as muscovite. Cracks and voids are numerous, being slightly spherical and filled by the late calcite mineralization. XRD mineralogy includes quartz, plagioclase, calcite and indications of K-feldspar presence.

Discussion
Presented petrographical and mineralogical characteristics of analysed ceramic fragments (Table I.) depict a variety of production techniques. In case of the prehistoric pot, presence of thermally untouched calcite, 10Å-mica, and organic matter call for relatively low firing conditions, not exceeding 600-700°C. Zircon occurrence could be beneficial for a further provenance study. The plate fragment would also fit a given temperature range, having much better and complete working of the clay. Microtexture of Roman dolia is indicative for coarse ware with poorly prepared paste. Due to lack of sintering phases, firing temperatures are set under 800°C. Characteristics of fabrics in Roman amphora imply technically well-prepared clay. Furthermore, partially isotropic matrix, sintering processes and presence of newly formed Ca-silicate (clinopyroxene) suggest firing over the temperature of 900°C. Late Roman/Byzantine amphora is featured by comparatively poorer clay working, but firing temperatures are inferred to be elevated (800-900°C), taking into account a highly isotropic matrix and indication of K-feldspar formation.

References

Environmental Mineralogy

Environmental mineralogy focuses its research on the characterization of individual aerosol particles by electron beam techniques (high-resolution scanning electron microscopy, transmission electron microscopy, environmental scanning electron microscopy).

We study individual aerosol particles in order to derive the physical and chemical properties (e.g., complex refractive index, deliquescence behavior, ice nucleation) of the atmospheric aerosol. These data are of great importance for modeling the global radiation balance and its change due to human activities.

We are also interested in studying the particulate matter exposure in urban environments and at working places. As aerosol particles may have adverse effects on human health, the knowledge of the particle size distribution and the chemical and mineralogical composition of the particles is of prime importance in order to derive the exact mechanisms of the adverse health effects.

Our research is carried out in cooperation with the following national and international partners: Max Planck Institute for Chemistry in Mainz, Institute for Atmospheric Physics (University of Mainz), Forschungszentrum Karlsruhe (Institut für Meteorologie und Klimaforschung), Institute for Tropospheric Research in Leipzig, Paul Scherrer Institut (Laboratory of Atmospheric Chemistry) in Villigen (Switzerland), National Institute of Occupational Health in Oslo (Norway), and the National Institute for Air Research (NILU) in Kjeller (Norway).

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Institute of Applied Geosciences – Environmental Mineralogy
Research Projects

Environmental scanning electron microscopical studies of ice-forming nuclei (SFB 641; “Die troposphärische Eisphase”).

Electron microscopy of Saharan mineral dust (DFG Forschergruppe SAMUM).

Source apportionment of rural and urban aerosols.

Characterization of working place aerosols (National Institute of Occupational Health, Oslo, Norway)

Environmental scanning electron microscopical studies of the hygroscopic behaviour of individual aerosol particles.

Publications


Book contributions


The effects of aerosol particles on heterogeneous ice formation are currently insufficiently understood. Modelling studies have shown that the type and quantity of atmospheric aerosol particles acting as ice nuclei (IN) can influence ice cloud microphysical and radiative properties as well as their precipitation efficiency. Therefore, the physicochemical identification of IN and a quantitative description of the ice nucleation processes are crucial for a better understanding of formation, life cycles, and the optical properties of clouds as well as for numerical precipitation forecast.

During the CLACE 5 campaign in 2006 at the high alpine research station Jungfraujoch (3580 m above sea level), Switzerland, the physicochemical parameters of IN within mixed-phase clouds were studied. By the use of special Ice-Counterflow Virtual Impactor, residual particles of small ice nuclei (IN) and the interstitial aerosol fraction were sampled separately within mixed-phase clouds.

**Fig. 1:** Secondary electron image of a) C-O-S particle, b) Al-rich particle; c) Pb-bearing particle (bright inclusions) and d) complex internal mixture (silicate/sulfate).
The size, morphology, elemental composition and mixing state of more than 7000 particles of selected IN- and interstitial-samples were analyzed by scanning electron microscopy (SEM) combined with energy-dispersive X-ray analysis (EDX). For selected particles, the mineralogical phase composition was determined by transmission electron microscopy. In order to receive detailed information about the mixing state (coatings, agglomerates, heterogeneous inclusions) of the IN- and interstitial-samples, the complete individual particle analysis was performed operator controlled.

Four different particle types were identified to act as IN (Figure 1).

1) Carbonaceous particles, which were identified to be a complex mixture of organics, sulphate, nitrate and soot.
2) Complex mixtures of two or more diverse particle groups. In almost 75% of these particles silicates or metal oxides are the main-components.
3) Aluminium oxide particles, which were internally mixed with calcium and sulphate rich material and
4) Pb bearing particles.

The high abundance of Pb-bearing particles in the IN-samples (up to 24% by number) was an unexpected finding. Besides a smaller content of larger PbO and PbCl2-particles the main component of the particles within this type are predominantly sea salt, soot or silicates, while Pb in these particles is only present as small (50 – 500 nm) heterogeneous PbS inclusions (Figure 2).

Fig. 2: Mixed secondary/backscatter electron images of Pb-bearing particles.

In all 4 particle types identified as IN, the mixing state seems to play an essential role. The mixing state seems to be a key parameter for the ice nucleation behaviour that cannot be predicted from the separate components. Consequently, future laboratory experiments should expand their scope from pure external mixtures or pure components with coatings to the more complex internal mixing observed in natural aerosols.

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