Leibniz
Gemeinschaft

INM
Leibniz-Institut für
Neue Materialien

# Jahresbericht 2009

# Jahresbericht / Annual Report

## 2009

INM – Leibniz-Institut für Neue Materialien
Ein Institut der Leibniz-Gemeinschaft

INM – Leibniz Institute for New Materials
An Institute of the Leibniz Association

Saarbrücken

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# Vorwort / Preface

**Liebe Freunde des INM,**

die Neuorientierung des INM kommt planmäßig weiter voran. Im Jahr 2009 hat sich das „neue“ INM erstmals einer kritischen Evaluierung durch seinen Wissenschaftlichen Beirat gestellt. Der Beirat hat den Kurs des INM sehr begrüßt; die Themen wurden als „hochaktuell mit internationaler Beachtung“ begrüßt. Dieses Audit hat uns die ersten Erfolge vor Augen geführt, etwa in der interdisziplinären Verbreiterung der Forschungsbasis, der starken Vernetzung mit der Universität des Saarlandes und dem Umfeld, der stark gestiegenen Anzahl und Qualität der Publikationen sowie der internationalen Sichtbarkeit des INM. Gleichzeitig haben wir gelernt, wo noch Optimierungsbedarf besteht – ein Ansporn für die Evaluierung des INM durch die Leibniz-Gemeinschaft, die im Jahr 2010 ansteht.

„Das Ganze ist mehr als die Summe seiner Teile“ – in diesem Sinne bestand ein wichtiges Ziel im Jahr 2009 in der Integration der verschiedenen Programmbereiche und Juniorforschungsgruppen – sowohl fachlich als auch personell. So wurden die Bereiche in drei Forschungsfelder – Chemische Nanotechnologie, Grenzflächenmaterialien und Materialien in der Biologie – sowie einen Querschnittsbereich thematisch gruppiert. Ein weiteres Element in der Zusammenführung war die Bündelung von Aktivitäten zu einer Reihe von übergreifenden Themen. Diese reichen von der Erforschung der Tribologie über Haftmaterialien (Gecko-Strukturen) bis zur Nanosicherheit. Diese und weitere aktuelle Fragestellungen werden das INM in Zukunft prägen. Damit wird das Institut weiterhin seine Bedeutung in der deutschen und internationalen Wissenschaftsszene verstärken.

Wir danken allen, die zu der erfolgreichen Arbeit des INM im Jahr 2009 beigetragen haben, und hoffen, dass der vorliegende Bericht Ihr Interesse findet.

E. Arzt

Prof. Dr. Eduard Arzt
(Wissenschaftlicher Geschäftsführer und Vorsitzender der Geschäftsführung)

M. Veith

Prof. Dr. Dr. h. c. Michael Veith
(Wissenschaftlicher Geschäftsführer)

Prof. Dr. Eduard Arzt

Prof. Dr. Dr. h.c. Michael Veith

**Dear friends of INM,**

The reorientation of INM is progressing as planned. In 2009, the “new” INM faced up to an evaluation by its Scientific Board for the first time. The Board appreciated the new direction of INM: the topics were appreciated as “highly topical with international attention”. This Audit visualized our first successes, like the interdisciplinary broadening of our research base, the cross linking with Saarland University and the scientific environment, the strongly increased number and quality of publications and international visibility of INM. At the same time, we became aware of the need for further optimization – a challenge for the evaluation of INM by the Leibniz Association in 2010.

“The whole is more than the sum of its parts“ – in this spirit, an important goal of 2009 was the integration of the different Program Divisions and Junior Research Groups, in terms of contents and people. The Divisions were grouped thematically into three research areas – Chemical Nanotechnology, Interface Materials and Materials in Biology – and one cross linking area. Bundling activities in a number of general topics was another element of integration. These activities range from the investigation of tribology to adhesive materials (gecko surfaces) and nano safety. Together, we will approach these and further relevant topics in the future. With this, INM will continue to strengthen its role in the German and international scientific community.

We would like to thank all who contributed to the successful work of INM in 2009 and we hope that this report will meet your expectations.

E. Arzt

Prof. Dr. Eduard Arzt
(Scientific Director and Chairman)

M. Veith

Prof. Dr. Dr. h. c. Michael Veith
(Scientific Director)

# Wissenschaftliche Artikel / Scientific Articles

# Kinetic investigations on $TiO_2$ nanoparticles as photo initiators for UV-polymerization in acrylic matrices

Sabine Schmitz-Stöwe, Carsten Becker-Willinger,
Dirk Bentz, Britta Abt and Michael Veith

## Abstract

$TiO_2$ nanoparticles of anatase, useful as photosensitive initiators to induce free radical polymerization in acrylic monomers have been prepared by chemical synthesis. Appropriate surface modification of $TiO_2$ has been achieved in order to compatibilize the particles with the acrylic monomers to obtain an almost homogeneous distribution down to the primary particle size. The surface modification has been additionally fine tuned in such a way, that an efficient transfer of the electrons generated on $TiO_2$ during UV-exposure could be achieved towards the monomer mixture in order to start the polymerization reaction. The formation of the anatase modification could be confirmed by XRD. Particle sizes were determined by UPA, which showed a distribution between 1-10 nm depending on the preparation method used. Transmission electron microscopy carried out with the UV-polymerized coating layers proved the homogeneous distribution of the anatase nanoparticles. Kinetic investigations on the photo-polymerization behavior have been accomplished by photo-DSC and Raman spectroscopy. Curing time was determined in dependence of the materials composition.

## Introduction

Two effects of $TiO_2$ are commonly known; first the high refracting index and the associated effect of light scattering [1] and second the degradation effect on polymer matrices [2; 3].

Besides the two mentioned effects of $TiO_2$ in polymer mixtures a third effect can be taken into account. Several authors describe the possibility that $TiO_2$ may catalyze the photo polymerization of acrylic monomers. But they come to different results concerning the accelerating or non-accelerating properties of $TiO_2$ for the polymerization process of acrylate monomers. Damm et al. describe acrylate polymerization with pure $TiO_2$ [4]. Samples of $TiO_2$ having different BET surface areas and different numbers of primary crystallites per secondary particle were prepared by annealing amorphous $TiO_2$ at different temperatures. Amorphous $TiO_2$ was not able to initiate the polymerization of the trisacrylate used. The maximum polymerization rate as well as the monomer conversion after an illumination time of 120 s increased with increasing number of primary crystallites per agglomerate. Damm et al. as well applied doped $TiO_2$ [5; 6]. The polymerization rate slightly increased with increasing $Fe^{3+}$ content of the $TiO_2$ in the concentration range from 0.1 to 1 mol % $Fe^{3+}$. Maximum polymerization rate was observed for 1 mol % $Fe^{3+}$ followed by decreasing rates at even higher $Fe^{3+}$ contents. A $TiO_2$ sample containing 10 mol% $Fe^{3+}$ did not show any photocatalytic activity [5]. Also nitrogen and carbon doped titania powders initiated acrylate polymerization upon UV excitation. The polymerization rate constants were similar for titania or N-doped titania but about two times larger for the

C-doped materials [6]. Ni et al. pointed out the pH-dependence of the photo catalytic effect of $TiO_2$ [7]. The results from ESR spin-trapping analysis at various pH conditions suggested that trapping holes by $OH^-$ act as competitive ways towards OH radicals. With the aid of these results, pH-dependence of the initiation quantum efficiency was correlated to the influence of pH on the initiating species. Assuming that the photogenerated holes have higher initiation efficiency than OH radicals, the observed pH dependence of polymerization rate was reasonably interpreted. Li et al. examined different monomers with $TiO_2$ and found accelerating and decelerating properties depending on the used monomers [8]. $TiO_2$ nanoparticles were first milled into butyl acetate or trimethylolpropane triacrylate (TMPTA) to obtain TSB (Nano $TiO_2$-slurry in butyl-acetate) and TST (Nano $TiO_2$-slurry in trimethylolpropanetriacrylate) slurries, then embedded into epoxy acrylate to obtain UV-curable coatings. It was found that TST-based coatings had a decreasing but TSB-based coatings had an increasing UV curing rate in comparison to the pristine epoxy acrylate. They also made kinetic investigations using IR-spectroscopy [9]. Here epoxy acrylate/$TiO_2$ nanocomposites showed decreasing photopolymerization rates in comparison with pure epoxy acrylate. The photopolymerization rate of the nanocomposite could also be influenced by initiator types, oxygen content, film thickness, irradiation intensity, dispersing media of $TiO_2$ slurry, and of course by the properties of the used monomers.

Semiconducting $TiO_2$ is a potential candidate for the UV-curing of monomers [10; 11; 12], as it is well known that by UV-excitation a valence hole and a conduction electron can be created in the solid. Such a transition only takes place if the energy of the irradiated wavelength is equal or higher than the band gap of the used photo catalyst. $TiO_2$, in its modification anatase, has a band gap of 3.289 e V. With respect to nanoparticles acting as polymerization initiators there is already a patent which describes this feature for the thermal and/or photochemical polymerization of species which have at least one polymerisable carbon-carbon multiple bond and/or at least one ring which contains carbon and which is accessible to ring-opening polymerization [13].

In the present investigation it was of interest to use the anatase modification because of its better performance in quantum efficiency and stabilization of charge carriers [14]. In addition a particle size range of about 10 nm has been chosen for the investigations. In this size range for $TiO_2$ a quantum size effect leading to a blue shift of absorption is expected [15].

The special advantage of using a solid state catalyst for UV-polymerization is that the catalytic function of the particles is sustained when particular conditions are fulfilled. It has to be assured that redox reactions $Ti^{4+} \rightarrow Ti^{3+} \rightarrow Ti^{4+}$ are possible. In contrast to this organic molecular initiators are destroyed during the UV irradiation to form radicals that initiate the polymerization process. Molecular fragments are able to migrate through the polymer matrix which might lead to some contamination problems e. g. if the food package sector is focused. Nanoparticles are assumed to be linked to the polymer matrix thus avoiding migration problems.

## Results and discussion

For the basic investigations of free radical photo-polymerization behavior of reactive monomer mixtures in presence of inorganic nanoparticulate photo-initiators a combination of acrylate monomers and titania nanoparticles in the anatase modification have been chosen. Acrylates offer the possibility to provide a wide variability of different monomers having different polarity and polymerization speed which might be important to select a suitable test system. Anatase type titania has been preferred because sufficient quantum yield could be expected. Before starting the formation of nano-dispersions consisting of liquid acrylates and titania nanoparticles, suitable and reproducible synthesis conditions have been worked out concerning the fabrication of anatase nanoparticles with controlled particle size in the lower nano-size range and appropriate surface modification providing compatibility to the acrylate matrix selected.

*Ex situ* synthesized $TiO_2$-nanoparticles coated with 1-propanol crystallize in the favored anatase modification (Figure 1).

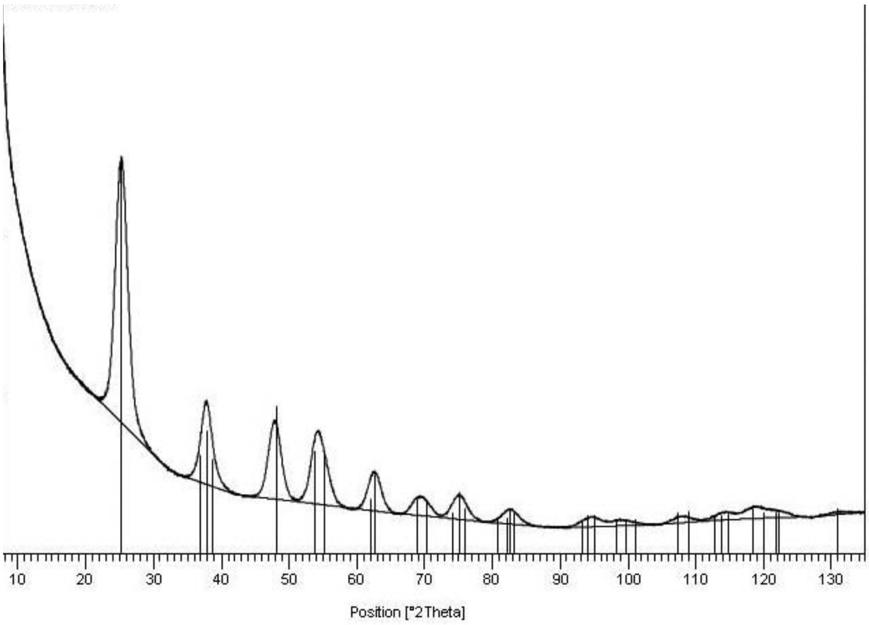

Figure 1: XRD-spectrum of $TiO_2$-nano-particles coated with 1-propanol (= $TiO_2$-1P); vertical lines show the theoretically calculated intensities of the anatase modification. The calculated particle size from the halfwidth of the signals was 4.9 nm.

The diffraction pattern proves the formation of the anatase modification of titania. Particle size was calculated by the Debye-Scherrer equation to be about 5 nm. This should correspond to the primary particle size.

The particle size of $TiO_2$-1P particles was also investigated by TEM (s. Figure 2) and dynamic light scattering measurements (s. Figure 3) in order to compare it with the particle size from XRD. TEM gave similar values of 5 nm, corresponding to the primary particle size calculated from XRD. In the TEM also agglomerates of about 8 nm can be observed. UPA gave values between about 6 to 11 nm.

The slightly higher value of UPA is caused by the different measuring methods. TEM and XRD usually show a number average of the particle size radius whereas UPA results correspond more to a volume average because the first measure is the coefficient of diffusion which is calculated according to Stokes' equation which contains the hydrodynamic radius (Stokes radius) that includes the solvent-covering of the particles. The particle size $d_{10}$ means that 10 % of the volume of all the particles have a size of 5.8(3) nm and less. This value corresponds well to the primary particle size calculated from XRD. The $d_{90}$-value shows that 90 % of the volume consist of very small agglomerates having a size of about 10.8 nm.

Kinetic investigations were done by photo-DSC measurements in combination with IR- and Raman-spectroscopy. In order to obtain comparable results all UV-curings were done with the Hg-Xe-lamp of the photo-DSC device. It provides an UV intensity of 3500 mW/cm² at a distance of 10 mm to the sample. Photo-DSC data obtained during UV-curing of DTMPTA (di(trimethylolpropane) tetraacrylate) with different amounts of $TiO_2$-1P are shown in Figure 4.

DTMPTA without any nanoparticles (full line) already shows a curing behavior. The maximum conversion takes place 80 s after the start of UV-irradiation, but even after 1200 s there is still a remaining heat flow indicating a slow reaction. DTMPTA with 1 % of $TiO_2$-1P (dashed line) shows a faster reaction time. The maximum of conversion appears 23 s after the irradiation starts and the total conversion is finished after about 300 s which is indicated by the horizontal baseline. With 2.5 % of $TiO_2$-1P (dotted line) the main conversion time after 23 s is still observed but a second heat flow peak appears after about 200 s, pointing to a second reaction. Also the reaction is finished after about 300 s. In the case of 5.0 % $TiO_2$-1P (dash-dotted line) no reaction at all is observed, indicating that the UV absorbents properties of the titania become dominant over the electron transfer which could start polymerization.

For the investigation of the double-bonding conversion Raman-spectroscopy has been applied. The C=C double bond conversation is followed in spectra normalized on the C=O carbonyl signal as internal standard in acrylate systems.

Figure 5 shows Raman spectra of DTMPTA with 0 and 5 % $TiO_2$-1P uncured and DTMPTA with 5 % $TiO_2$-1P after curing in the photo-DSC-device. The spectra are scaled on the C=O band at 1723 cm$^{-1}$, which is not changing during polymerization reaction.

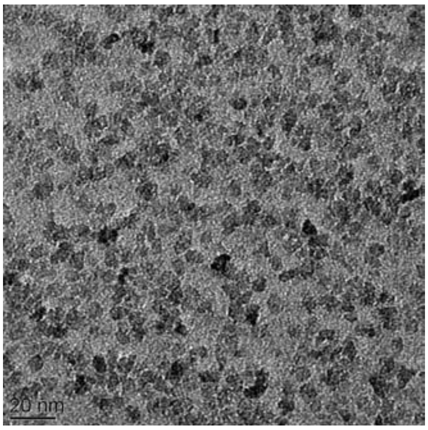

Figure 2: TEM-micrograph of $TiO_2$-nano-particles coated with 1-propanol (= $TiO_2$-1P); measured average particle size = 4-8 nm.

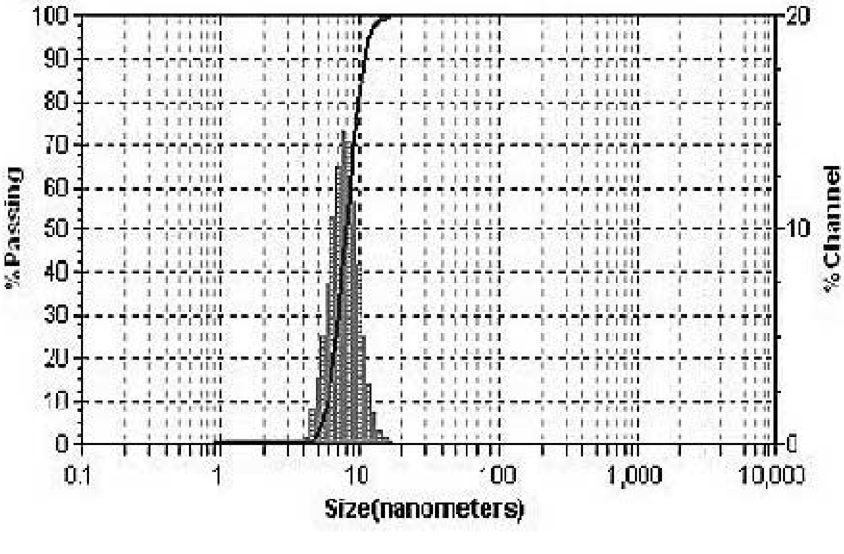

Figure 3: UPA-measurement of $TiO_2$-nano-particles coated with 1-propanole (= $TiO_2$-1P) in toluene; volume distribution; loading index 0.048; $d_{10}$ = 5.84 nm; $d_{50}$ = 8.00 nm; $d_{90}$ = 10.80 nm; $M_{Volume}$ = 8.21 nm; $M_{Nummber}$ = 6.96 nm; $M_{Average}$ = 7.76 nm.

In the spectra there are three different vibrational absorptions proving a bidental chelating $TiO_2$-COO complex: 1600 $cm^{-1}$, 1499 $cm^{-1}$ and 1161 $cm^{-1}$. They only occur in samples with $TiO_2$-1P being present, no matter whether the samples are cured or not. The diagram also shows that C=C double-bondings decrease whereas $CH_2$ bondings are formed. This is a hint proposing a polymerization process.

To take a closer look to the polymerization process, mixtures of DTMPTA with various amounts of $TiO_2$-1P have been compared. In Figure 6 the Raman spectra clearly show that there is a dependence between the amount of $TiO_2$-nanoparticles and the conversion rate of the C=C double bonds of acrylate DTMPTA.

Increasing $TiO_2$-1P content in the mixture leads to a decrease of C=C double bonds. Combining the results of DSC-measurement and Raman-spectroscopy a complex relationship has to be taken into account. Obviously, the total reaction conversion passes through a maximum of speed when using 1 % $TiO_2$-1P in the mixture. Responsible for that could be three different effects: First, $TiO_2$-nanoparticles catalyze the polymerization of double-bondings like those in acrylates; second, $TiO_2$ is known to work as a UV-absorber which inhibits photo chemical reactions.

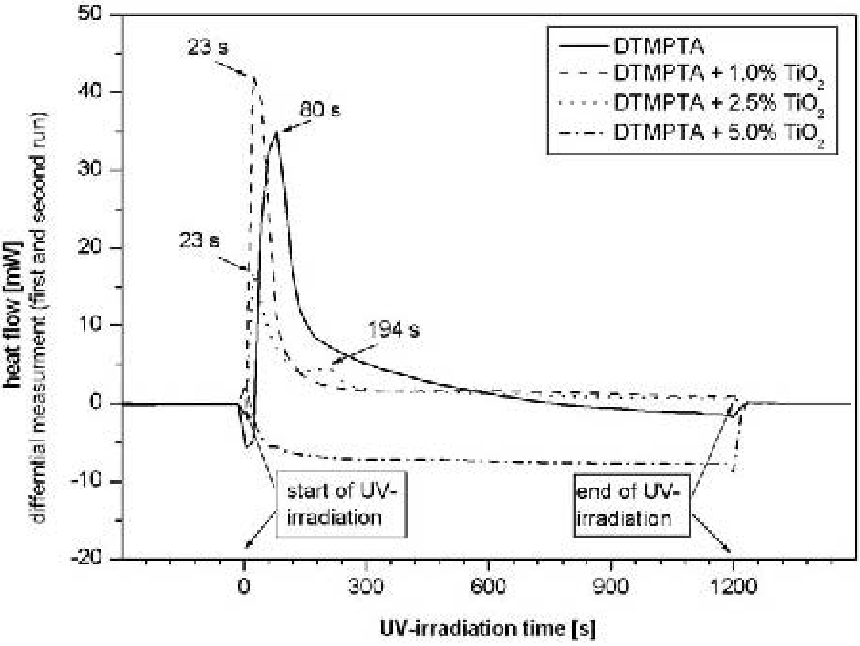

Figure 4: Photo-DSC-measurement of di(trimethylolpropane) tetraacrylate (=DTMPTA) with different amounts (0, 1, 2.5, 5 %) of $TiO_2$-nano-particles coated with 1-propanole (= $TiO_2$-1P). Diagram shows spectra after subtraction of the heat flow baseline of the UV-lamp. UV-irradiation initiates 5 min after the start of the run (point 0); it ends 25 min after the start of the run (point 1200) => irradiation time 20 min. Measurement under $N_2$-flow at a constant temperature of 25 °C. UV intensity of 3500 mW/cm² at a distance of 10 mm to the sample.

A third reaction possibility is the degradation of the monomer and / or polymer in form of an ester cleavage that had to lead to carbonic acid fragments. These fragments could not be verified, neither by NMR nor by IR. The second effect of inhibiting C=C double bonding conversion may be seen in Figure 6. The first effect of catalyzing the reaction, e. g. to speed up the polymerization process can be pointed out with photo DSC measurement as we see in Figure 4. With 1 % and 2.5 % of $TiO_2$-1P in DTMPTA the process starts earlier than without a catalyst, but in total the conversion rate decreased as the UV absorbing properties prevailed over the catalytic ones.

All samples showed a change in color during irradiation. The samples switched from transparent yellow ($Ti^{4+}$ from $TiO_2$-COO complex) to dark blue which is due to the formation of $Ti^{3+}$. By UV-irradiation an electron–hole–pair formation takes place. The hole can be filled by an electron coming from the acrylate matrix. This transfer produces a $Ti^{3+}$ and an acrylate radical, which now may polymerize. In order to get the catalyst ($Ti^{4+}$) back, the $Ti^{3+}$ must formally be oxidized either by diffusing oxygen from the top of the surface or by another oxidizing agent. By storing the samples under normal atmosphere, the blue color again turned transparent, which supports the idea of reversible change between $Ti^{4+}$ and $Ti^{3+}$ and of oxygen-diffusion. If the amount of $TiO_2$-1P rises to an amount of 5 % in the mixture the color turned to a very dark blue but the complete polymerization process is hindered by absorption due to the general UV-protecting properties of $TiO_2$.

For this reason the finding that the mechanism of photo-catalytic polymerization only works satisfactorily in thin layers could be supported, where the oxygen might diffuse through the coating layer or in mixtures with a low amount of particles where enough UV-light might be transmitted through the monomer matrix. Curing of acrylate mixtures containing more than 2.5 % $TiO_2$ might be possible by using a UV source with higher radiation output.

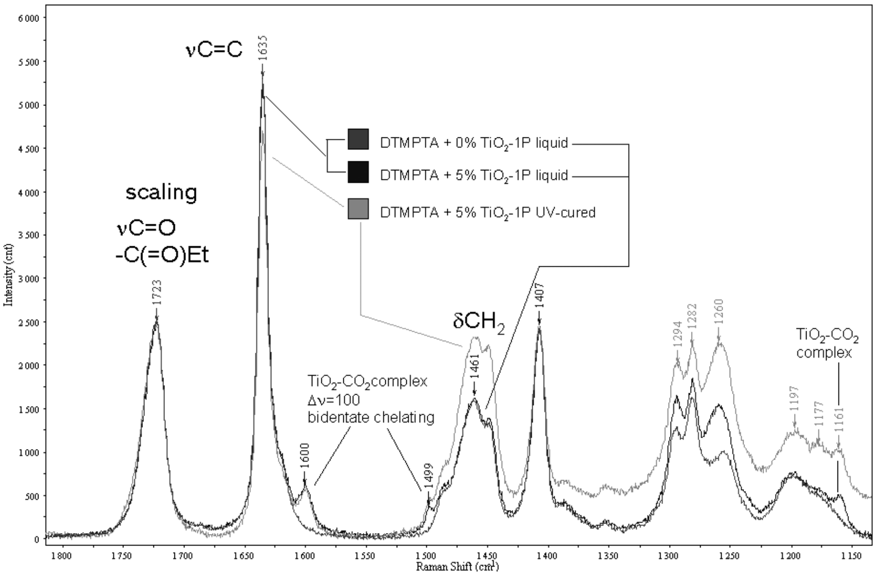

Figure 5: Raman-spectra of di(trimethylolpropane) tetraacrylate (=DTMPTA) with different amounts of $TiO_2$-nanoparticles coated with 1-propanole (= $TiO_2$-1P) (0 %, 5 %) before and after UV-curing. The spectra are normalized on the C=O band at 1723 $cm^{-1}$. UV-source for curing: Hg-Xe-lamp LC 5 L8222-01 without filter from DSC-device. UV intensity of 3500 mW/cm² at a distance of 10 mm to the sample. Curing time : 20 min.

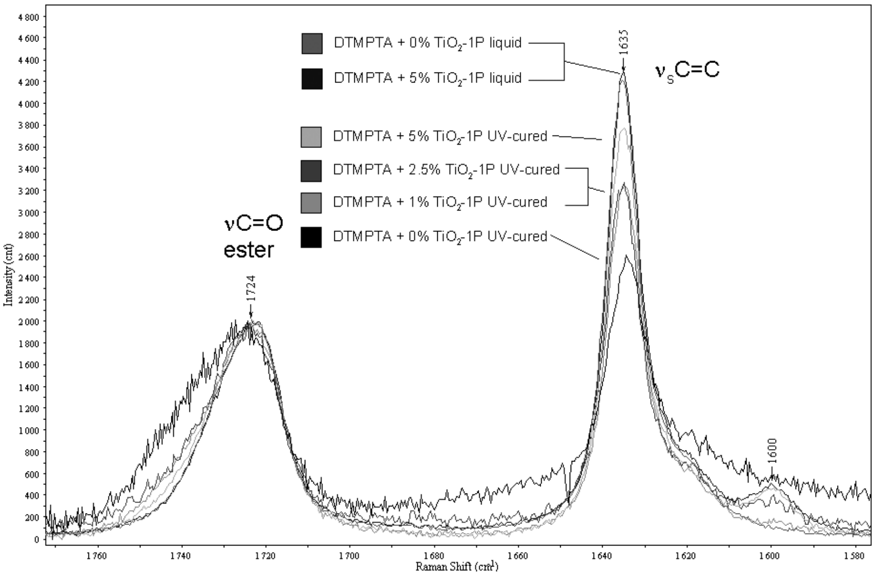

Figure 6: Raman spectra of di(trimethylolpropane) tetraacrylate (= DTMPTA) with various amounts of $TiO_2$-nanoparticles coated with 1-propanole (= $TiO_2$-1P) (0, 1, 2.5 and 5 %) before curing (liquid) and after UV-curing in the photo-DSC device. UV-source for curing: Hg-Xe-lamp LC 5 L8222-01 without filter from DSC-device. UV intensity of 3500 mW/cm² at a distance of 10 mm to the sample. Curing time : 20 min.

## Conclusion

$TiO_2$-nanoparticles can be synthesized *ex situ* using common precursors like titanium tetraisopropoxide in the solvent 1-pentanol that simultaneously works as a surface modifier. Homogeneous distribution of the particles in acrylates can be achieved. This leads to particles in the low nano-size range (1-11 nm). Raman measurements showed that $TiO_2$ is linked to the acrylic matrix by complexation of Ti by the carboxylic groups of the acrylates. It can be assumed that there is no unwanted migration process in the final polymer. This statement has to be an object of further investigations.

Looking at the polymerization process different effects during the UV-irradiation of the mixtures of acrylate with $TiO_2$-nano-particles have been observed. It could be shown that three influences may have to be taken into account in order to judge the catalytic performance of $TiO_2$. The accelerating catalytic effect of $TiO_2$-1P is superposed by the UV-absorbing effect of $TiO_2$ that leads to a decrease of the total conversion rate for filler contents higher than 2.5 %. This was shown by comparing measurements in photo-DSC and Raman-spectrometry. In the present case the degradation of monomer and/or polymer, a third possible effect, could be ruled out neither by Raman nor by photo-DSC. The implication of these findings is that $TiO_2$ can only be used in low concentrations and for thin films.

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# A new approach for a slurry based coating system for the prevention of high-temperature oxidation

Mesut Aslan, Matthias Wittmar, Henning Bolz and Michael Veith

## Introduction

Surface coatings to protect against oxidation extend the service temperature and the service life of basic metals. The commercially used coating systems can be divided into three main groups: first diffusion layers based on Al, Cr or Si which will be converted to corresponding protective oxide phases during the service, second M-Cr-Al-X based overlay coatings where M refers to Ni or Co and X refers to oxygen-active elements such as Y and Hf, third thermal barrier coatings consisting of an overlay coating and a zirconia coating. These coatings are produced mainly by methods like PVD, CVD and plasma spraying [1]. Compared to highly sophisticated commercial coating methods, slurry based oxidation protection coatings for metals are very interesting because of their simple applicability even to complex shaped parts. Pandey et al. report the efficiency of different slurry based coating systems including different phosphate bonded oxides and oxide mixtures with respect to their oxidation protection for carbon steels [2]. Slurries containing a mixture of zirconia and metallic components such as W, Co, Cr and organic binder applied by dipping, painting or spraying were also used for the preparation of oxidation protecting coatings [3]. The reaction bonding of alumina with metallic aluminum to produce near-net-shape bulk ceramics by reaction sintering at moderate temperatures (RBAO) was developed by Claussen et al. [4]. In this method, the metal phase oxidizes to alumina and the volume expansion ocurring during the oxidation partly compensates for the overall shrinkage. The advantage of this RBAO (**R**eaction **B**onded **A**luminum **O**xide) technique concerning the reduced shrinkage is also necessary for the preparation of crack-free/crack-reduced ceramic coatings on rigid substrates. Some work can be found in the literature concerning the use of RBAO technique for oxidation protection and surface sealing [5-7]. Wang et al. describe a coating method by modified electrophoretic deposition with Al containing slurries on Fe-Cr-Al steel substrates, giving no detail about the performance of such coatings. Mechnich et al. use slurries of $Al/Al_2O_3$ mixtures to coat highly porous ceramic matrix composites with a dense layer to reduce their permeability [6, 7]. However, publications concerning the oxidation protection of carbon steels (which are widely-used and easily oxidized under high-temperature) with RBAO-based coatings could not be found.

Therefore, the aim of the present work was to test a RBAO-based coating system for its ability to prevent high-temperature oxidation of carbon steels. The system consisted of a mixture of alumina and aluminum powders in ethanolic suspensions. To increase the initial packing density powder mixtures of two different particle size ranges were used as alumina source. It is expected that green coatings with higher green densities should result in fired coatings with improved performance.

## Experimental

For the preparation of ethanol-based coating slurries the following starting powders were used: alumina (corundum) in two different particle size ranges with specific surface areas of 7.5 m²/g and 1.5 m²/g and metallic aluminum powder with a particle size range of 0-50 µm (Al-Sprühgrieb, 0-50 µm, Possehl Erzkontor, Lübeck). The ratio of fine grained alumina/coarse grained alumina was 38/72 by volume. The aluminum/alumina volume ratio varied between 0.2 and 1.0. Ethanolic slurries with a total solid content of 50 wt.% were prepared by attritor milling with alumina balls for 3 h. As a dispersing aid for the slurries an organic acid (trioxadecanoic acid) was used. The all-side coatings on plates from carbon steel (Nr. 1.0330) of different thicknesses were prepared by spraying. The oxidation kinetics of coated and non coated steel samples were characterized by thermogravimetric measurements on samples of dimensions 5 x 5 x 1.5 mm³ (Netzsch, STA 449C). Large size samples of dimensions of 100 x 100 x 1.5 mm³ were annealed at 950 °C in air atmosphere (heating rate 10 K/min, cooling rate 15 K/min). The degree of oxidation was determined quantitatively by light/electron microscopic examination of polished cross sections of the oxidized samples.

## Results and discussion

The aluminum powder used for the coating formulations consists of nearly spherical particles ranging from few µm to 20-30 µm (Figure 1a). The morphological changes of this powder as a result of ball milling in ethanol for 3 h are shown in Figure 1b. Obviously a significant plastic deformation of the single aluminum particles took place during this treatment resulting in a plate-like structure (aspect ratio > 3). This plate-like structure was expected to be more adequate for coatings with smooth surfaces, even for systems containing large particles as in the present case. This assumption was proved correct by the observation of the surface morphology of a sprayed coating prepared from slurries with Al:$Al_2O_3$ ratio of 50:50 by volume as shown in Figure 1c. The coating shows good coverage of the steel substrate and relatively smooth with some rises and dimples. The alumina fraction of the coating seemed to fill the voids between the Al-platelets, as expected.

Oxidation tests of steel samples coated with formulations containing different amounts of metallic aluminum revealed that an aluminum content of around 50 vol.-% was needed to achieve an optimal oxidation protection (Figure 2a). Apparently, formulations with these compositions also result in coatings with optimal density. This can be verified by considering the volume expansion of metallic aluminum during the oxidation reaction. Volume expansion during the oxidation of metallic aluminum amounts to 27.6 % with respect to the initial volume of aluminum. By assuming an initial coating density of 80 % (determined indirectly on slip casted samples from slurries with a Al:$Al_2O_3$ ratio of 50:50 by

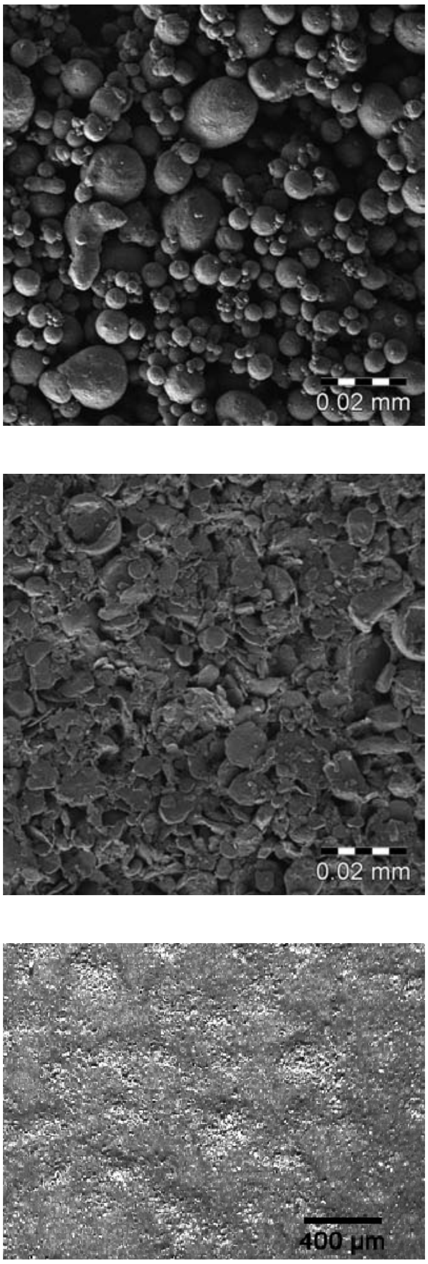

Figure 1: Effect of ball milling on the morphology of aluminum powder and a representative top view of a green coating on steel prepared by spraying. a) (top) SEM picture of as received aluminum powder, b) (middle) the same powder after ball milling for 3 h, c) (bottom) top view of a green coating.

volume) a green coating would densify up to closed density (> 92 vol.-% space filled) by the reaction $2\ Al + 3/2\ O_2 \rightarrow Al_2O_3$. Coatings with higher aluminum content would tend to crack thereby reducing their performance with respect to oxidation protection as was seen experimentally (Figure 2a).

Results of experiments with coatings with equal amounts of Al and $Al_2O_3$ (50:50 composition), but different thicknesses show that the optimal coating thickness seems to be approximately 40 µm (Figure 2b), which relates to the upper limit of the particle size range of the deformed metallic aluminum powder used for the coating formulations.

Following the optimization of the composition and coating thickness the influence of the coatings with these optimized parameters ($Al:Al_2O_3$ ratio 50:50, coating thickness around 40 µm) on the oxidation kinetics of steel substrates was investigated. The related experiments were carried out on small samples by thermogravimetric (TG) measurements as well as by furnace annealing of large sized samples on which cross sections were observed with respect to oxidation propagation (Figure 3). The plot in Figure 3a shows the TG curves obtained on samples of non-coated steel, steel coated with $Al:Al_2O_3$ and steel coated only with alumina (to demonstrate the exhibit of metallic aluminum addition), respectively. Non-coated samples and samples coated with alumina mixtures show similar oxidation character, indicating a strong weight gain at the beginning of isothermal holding at 950 °C which decreases with time

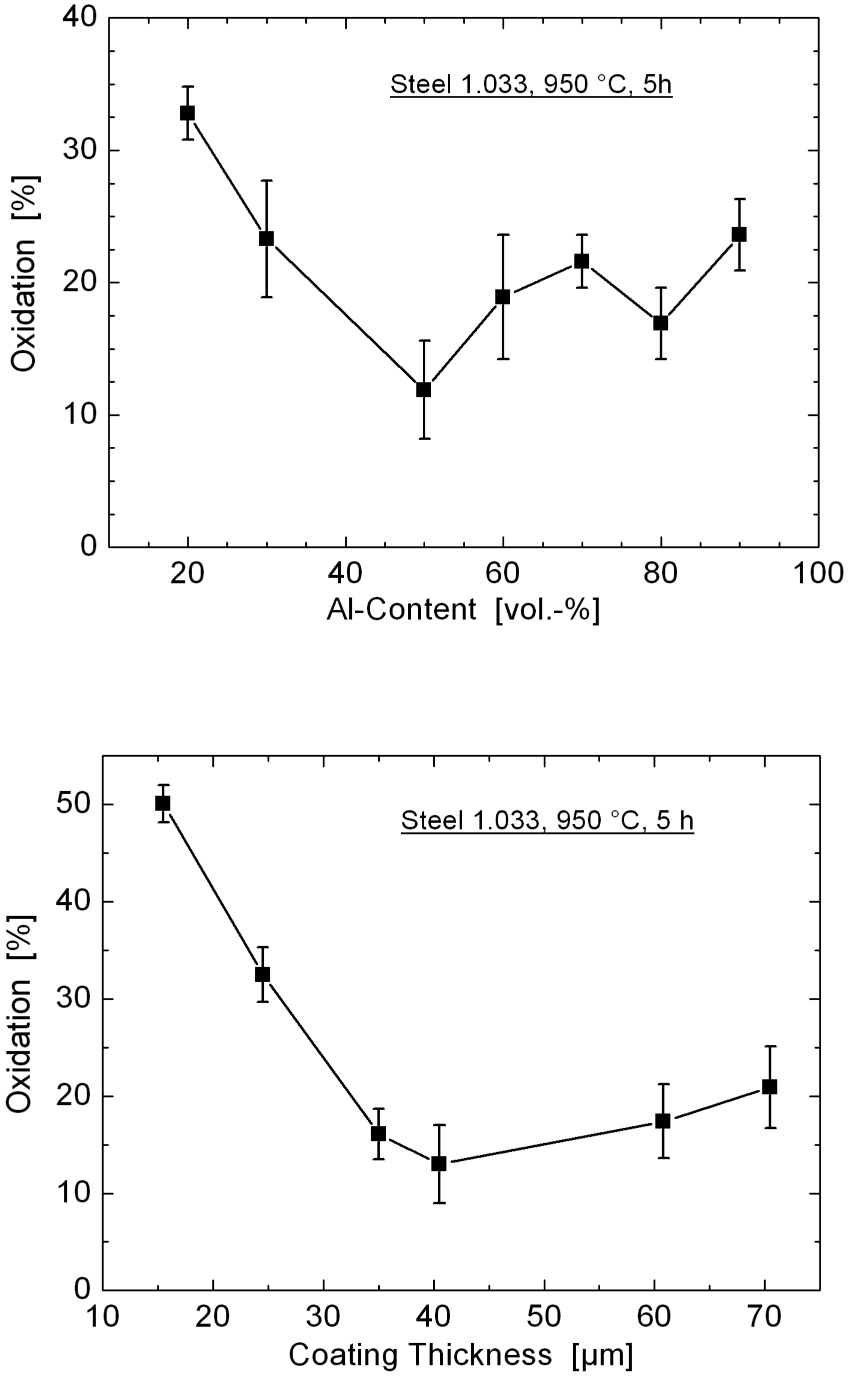

Figure 2: Optimization of the coating formulation with respect to aluminum content and coating thickness. a) (top) Oxidation vs. aluminum content, b) (bottom) oxidation vs. coating thickness.

and becomes almost linear after 60 min. The coatings with an alumina mixture effect only a minor decrease of weight gain compared to the non-coated samples and thus, seem to be not effective for oxidation protection. The reason is that alumina and even alumina mixtures can not form a dense protecting layer at temperatures of 950 °C due to low sintering activities. In contrast, samples coated with $Al:Al_2O_3$ show from the beginning of the isothermal holding a nearly continuously decreasing weight gain which indicates diffusion controlled oxidation through dense protecting layers (total weight gain after 120 min isothermal holding, 110 µg/mm$^2$ for $Al:Al_2O_3$ coated samples, 350 µg/mm$^2$ for non-coated samples, respectively). The effect of long term air annealing on the oxidation propagation of coated and non-coated steel samples is shown in Figure 3b. It can be clearly seen that $Al:Al_2O_3$ coatings are very effective for oxidation protection. After 10 h holding at 950 °C in air only 20 % of the initial thickness of the steel samples is lost if they are coated. In case of non coating almost 85 % will be lost. In contrast, coatings from phosphate bonded oxide mixtures allow under similar conditions only an oxidation protection of around 50 % as reported by Pandey et al. [2].

Quantitative and qualitative microstructural analysis were carried out on polished cross sections of the samples by SEM and EDX analysis, respectively (Figure 4). Figure 4a shows a SEM picture of a coated sample which was heated to 950 °C and cooled down to room temperature after 1 min holding time. The coating seems to be dense (closed porosity) with some large pores inside the coating. The cross section clearly shows crack formation along the phase boundary between metal and coating. Therefore, the scales formed is easily removable. The coating seems to consist of different phases. A closer look by EDX reveals that aluminum, iron and oxygen are detectable over the coating indicating alumina and iron oxide phases might be present. No metallic aluminum cluster could be found by EDX. But, in samples which were annealed at 950 °C for 1 min metallic aluminum could be detected by XRD measurements. The results of EDX analysis on locations labeled as 1-8 on the SEM picture in Figure 4a are shown in Table 1.

| Location | Intensity [counts] | | |
|---|---|---|---|
| | **Fe** | **Al** | **O** |
| 1 | 3423 | 0 | 0 |
| 2 | 3258 | 0 | 0 |
| 3 | 2212 | 0 | 0 |
| 4 | 333 | 4188 | 1972 |
| 5 | 120 | 4284 | 1798 |
| 6 | 0 | 4805 | 1705 |
| 7 | 403 | 2591 | 1597 |
| 8 | 901 | 386 | 1269 |

Table 1: Results of EDX analyses on sample in Figure 4a.

After a long time exposure to air at 950 °C for 5 h a formation of $FeO_x$ scale takes place, not only between the $Al:Al_2O_3$ coating and metal substrate, but also above this coating as outer layer. This behavior indicates that the $Al:Al_2O_3$ coating must be partly permeable for Fe and

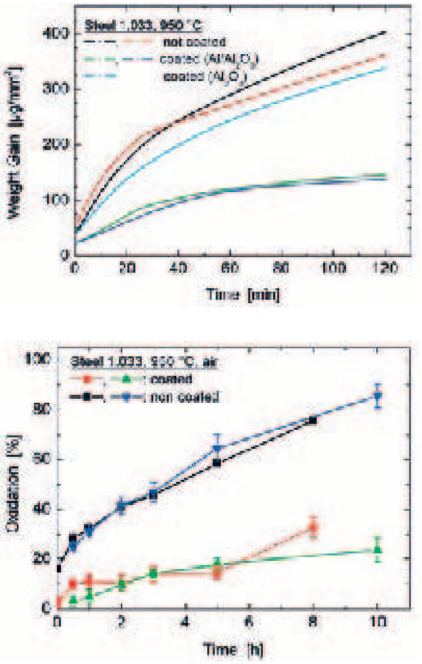

Figure 3: Oxidation behavior of samples during isothermal holding at 950 °C in air. a) (top) TG plot, b) (bottom) furnace annealing.

also for O with local permeability differences (Figure 4b).

## Summary and conclusions

Coatings containing Al and $Al_2O_3$ binary mixtures with an Al content of 50 vol.-% and a thickness of 40 µm result in a significant reduction of the oxidation of steel at high temperatures. The scale formed can be easily removed due to crack formation along the phase boundaries of metal and coating. Thus, this coating system can be used as temporary coating to reduce scaling loss. There is an additional potential for the further improvement of the coating properties to be used as permanent protective coatings by reducing/preventing the crack formation through optimization of the processing and the starting powders, especially metallic aluminum.

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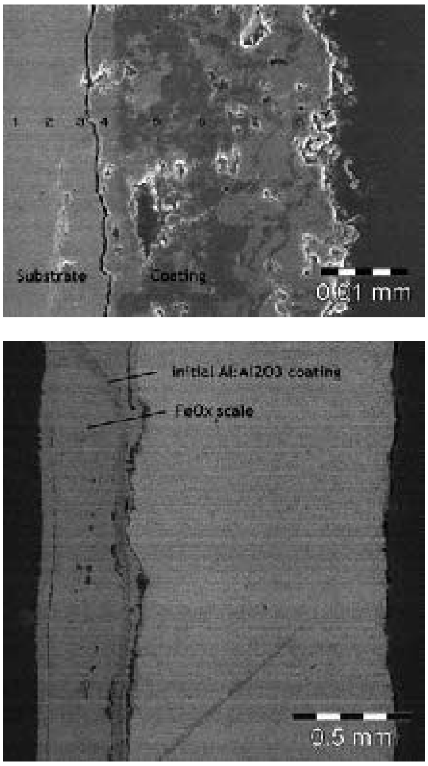

Figure 4: SEM pictures of $Al:Al_2O_3$ coatings after annealing at 950 °C in air. a) (top) SE picture, 950 °C, 1 min, b) (bottom) BSE picture 950 °C, 5 h.

# Size dependent strength of bcc metal micropillars: towards high strength surfaces by micropatterning

Andreas Schneider and Eduard Arzt

## Abstract

The size effect in body-centered cubic (bcc) metals was comprehensively investigated through microcompression tests performed on focused ion beam machined tungsten (W), molybdenum (Mo) and niobium (Nb) pillars, with single slip [235] and multiple slip [001] orientations. The relationship between yield strength and pillar diameter as well as the deformation morphologies were found to correlate with a parameter specific for bcc metals, i. e. the critical temperature $T_c$. This finding sheds new light on the phenomenon of small-scale plasticity in largely unexplored non-fcc metals. This effect may be used in the patterning of surfaces to achieve higher strengths.

## Introduction

The mechanical behavior of metals exhibits a size dependence, in which the flow stress is usually inversely proportional to some power of the smallest geometrical dimension [1]. This effect has been convincingly demonstrated for a variety of metals in the micron and nanometer scale. Several mechanical testing techniques measured at e. g. whiskers, nanowires, thin films, etc. have confirmed this effect. Recently several studies have also demonstrated a size effect in single crystal metals via compression testing of focused ion beam (FIB) manufactured micro- and nano-pillars [2-3]. Unlike whiskers, FIB machined small-scale compression pillars are not initially dislocation free. Consequently, near theoretical strengths are not observed in FIB manufactured pillars, even though the strength is significantly higher than in the bulk. These yield stress values, $\sigma_y$, have been shown to correlate with pillar diameter, *d*, according to $\sigma_y \mu d^{-0.6}$ to $d^{-1.0}$ for all face-center cubic (fcc) metals tested to date [2-3].

While many efforts have been made to understand the mechanisms responsible for this effect in fcc metals, both through experimentation and theoretical and simulation-based models, little work has been done on alternative crystal structures, such as body-centered cubic (bcc). The plastic deformation in bcc metals differs fundamentally from that of fcc metals [4]. In bcc metals, the deformation is largely controlled by screw dislocations which, due to the geometry of the glide planes, have non-planar dislocation cores and high Peierls potentials. This intrinsic resistance to their motion can be overcome through thermally activated processes, leading to a strong temperature and strain rate dependence of the flow stress. Although these fundamental differences between the deformation behavior of fcc and bcc metals have been characterized in bulk, it is not well known how the size effect in bcc metals may deviate from that observed in previous fcc studies.

The aim of this work is to study the mechanical properties of bcc metals at the micron and submicron scale and to investigate the effect of the screw dislocation mobility in small dimensions. For this purpose, microcompression tests were conducted at room temperature (RT) on bcc metals with different critical temperatures (Table 1). The critical temperature ($T_c$) is defined as the temperature at which the flow stress becomes insensitive to the test temperature, i. e. screw and edge dislocations have equal mobility due to thermal activation of the screw dislocations [5]. Below $T_c$, screw dislocations are less mobile than edge dislocations and their mobility is a function of test temperature $T_{test}$ relative to $T_c$.

| Material | Nb | Ta | Mo | W |
|---|---|---|---|---|
| Critical temperature $T_c$ [K] | 350 | 450 | 480 | 800 |
| Temperature Ratio $T_{test}/T_c$ | 0.851 | 0.662 | 0.621 | 0.373 |

Table 1: Critical temperatures of the bcc metals used in this study; $T_{test}$ = 25 °C in our experiments.

## Experimental

Tungsten (W), molybdenum (Mo) and niobium (Nb) samples with multiple slip [001] and single slip [235] orientation were prepared from single crystals by means of electron discharge machining after the orientations of the crystals were determined by Laue diffraction. The sample surfaces perpendicular to either the [235] or [001] direction were mechanically and electrochemically polished. Pillars ranging in diameter from approximately 200 nm to 6 µm were machined with a focused ion beam (FIB) on the surface of both the [001] and [235] single crystal pieces using a DualBeam™ FIB. In general, pillars were cut with a diameter to length aspect ratio of approximately 3:1, and then compressed in load-control with a nanoindenter fitted with a 10 µm flat sapphire punch. Further description of the testing and the data analysis can be found in [6].

## Results

Representative compressive stress-strain curves for [001] oriented W, Mo, and Nb pillars for various diameters are shown in Figure 1. The overall shapes of the stress-strain curves are typical for load-controlled single crystal pillar compression and display the stochastic nature of slip in small dimensions. Strength increases markedly with decreasing diameter. Pillars larger than roughly 2 µm exhibit bulk-like flow with a gradual transition from elastic to plastic deformation and relatively little strain hardening. Pillars with smaller diameters exhibit a staircase-like deformation due to strain bursts associated with individual dislocation events. Although the nominal stress values for the materials tested are different, the qualitative features of the stress-strain response are consistent with one another and are similar to observations in fcc single crystalline pillars [2-3].

Figure 2 shows representative scanning electron microscope (SEM) images of deformed W and Nb pillars with diameters close to 200 nm (2a and b) and 5 µm (2c and d). The deformation morphology of Mo is similar to that of W. Regardless of size, the [001] oriented pillars exhibited slip along multiple systems, as evidenced by the geometry of slip traces in Figure

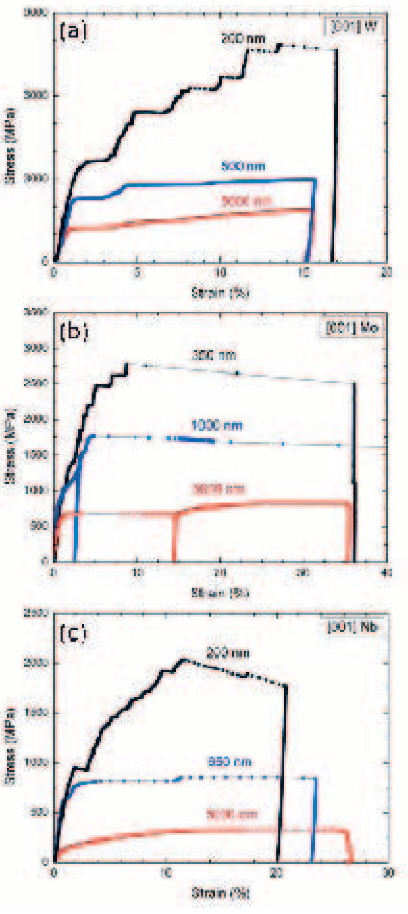

Figure 1: Representative stress-strain curves for [001] (a) W, (b) Mo and (c) Nb pillars over a range of diameters from 200 nm to 6 µm.

2, while the [235] oriented pillars exhibited primarily single slip along a preferred slip system [7]. As seen in Figures 2c and d, the larger pillars had a tendency to display slip traces on the pillar surface throughout their length, while pillars with diameters less than approximately 500 nm were more likely to exhibit observable slip deformation closer to the pillar top. For pillars with larger diameters, two different deformation morphologies were identified. In large W and Mo pillars, there are no continuous slip steps on the pillar surfaces. The slip steps appear wavy throughout the sample, as is typically found for bulk bcc metals. Wavy slip planes are consistently more difficult to observe in the Nb pillars, which primarily exhibit localized slip on preferred glide planes with clear slip traces ranging across the pillar surface.

The mechanical size effect of the [001] oriented bcc pillars is shown in Figure 3a, which illustrates the stress at 5 % strain as a function of diameter. For comparison, data from fcc Au [8] and bcc Ta [9] pillars is also shown. The strengths of the bcc metals are higher than those of Au and the relative differences in strength between the different materials decrease with decreasing pillar size. Using a power law fit, slopes of -0.21, -0.38, -0.41 and -0.48 are obtained for W, Mo, Ta and Nb pillars, respectively. By comparing these slopes with the critical temperatures given in Table 1, it can be seen that the higher the critical temperature, the weaker the size dependence. In Figure 3b the power law exponent determined for the [001] and [235] oriented bcc pillars is plotted as a function of test temperature divided by $T_c$, to examine the role of screw dislocation mobility on the size dependence. The ratio of $T_{test}$ to $T_c$ is a measure for the thermal activation of the screw dislocations: a larger ratio means higher thermal activation and therefore higher mobility of the screw dislocations. The data points in Figure 3b follow roughly a linear relationship. The extrapolation of the line of best fit to lower critical temperatures yields an exponent of about -0.6 (represented by the horizontal line in Figure 3b) for $T_c = T_{test}$, which corresponds to the condition where screw and edge dislocations have equal mobility. This value is in agreement with exponents found for fcc metal pillars where screw and edge dislocations have the same mobility at room temperature.

## Discussion

The results presented here show that deformation mechanisms in small-scale bcc metals depend on size as well as on critical temperature. All materials tested show an increase in strength with decreasing pillar diameter, indicating that confinement of dislocation processes starts to dominate the deformation; this leads to a transition from continuous, bulk-like to jerky, staircase-like stress-strain behavior and a significant change in the deformation morphology between small and large pillars. The critical temperature of the bcc metals was found to have a strong influence on the deformation morphology of the large pillars. In general, the deformation of bcc metals is controlled by the

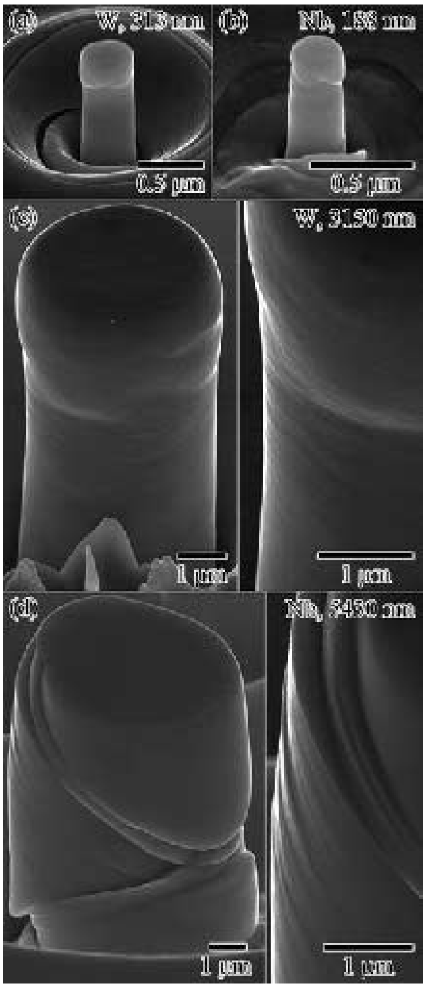

Figure 2: Post-compression SEM images of representative [001] oriented Nb and W pillars: (a) 313 nm W, (b) 188 nm Nb, (c) 4870 nm W, and (d) 5430 nm Nb pillars. Slip traces on the pillar surfaces indicate multiple slip.

motion of long and straight screw dislocations [4; 5]. Their ability to cross-slip between crystallographic planes which intersect along the <111> direction leads to wavy slip steps. The cross-slip of screw dislocations may account for the deformation morphology of the large W and Mo pillars. The well-resolved slip steps of Nb indicate that less cross slip occurred during deformation. For metals with low $T_c$ (Nb) the dislocations may bow out and deviate from pure screw character over considerable length in the pillar. As dislocations of mixed character are confined to specific glide planes, this may lead to localized slip.

Besides the deformation morphologies, the strength values and their size dependence were also found to correlate with $T_c$ (Figure 3). A general correlation of the strength values with $T_c$ is not surprising as the strength of bcc bulk metals at temperatures below $T_c$ is related to the low mobility of screw dislocations. As $T_c$ increases from Nb to W, the mobility of screw dislocations decreases because thermal energy becomes small relative to the height of the Peierls potential, resulting in high stresses for materials with a high $T_c$. The correlation between size dependence and $T_c$ suggests that the mobility of screw dislocations affects the size scaling. It seems that for temperatures close to $T_c$, where the influence of the low mobility of screw dislocations becomes negligible, the behavior of bcc also approaches that of fcc metals. The similar behavior of fcc and bcc pillars for test temperatures near $T_c$ indicates that under conditions where

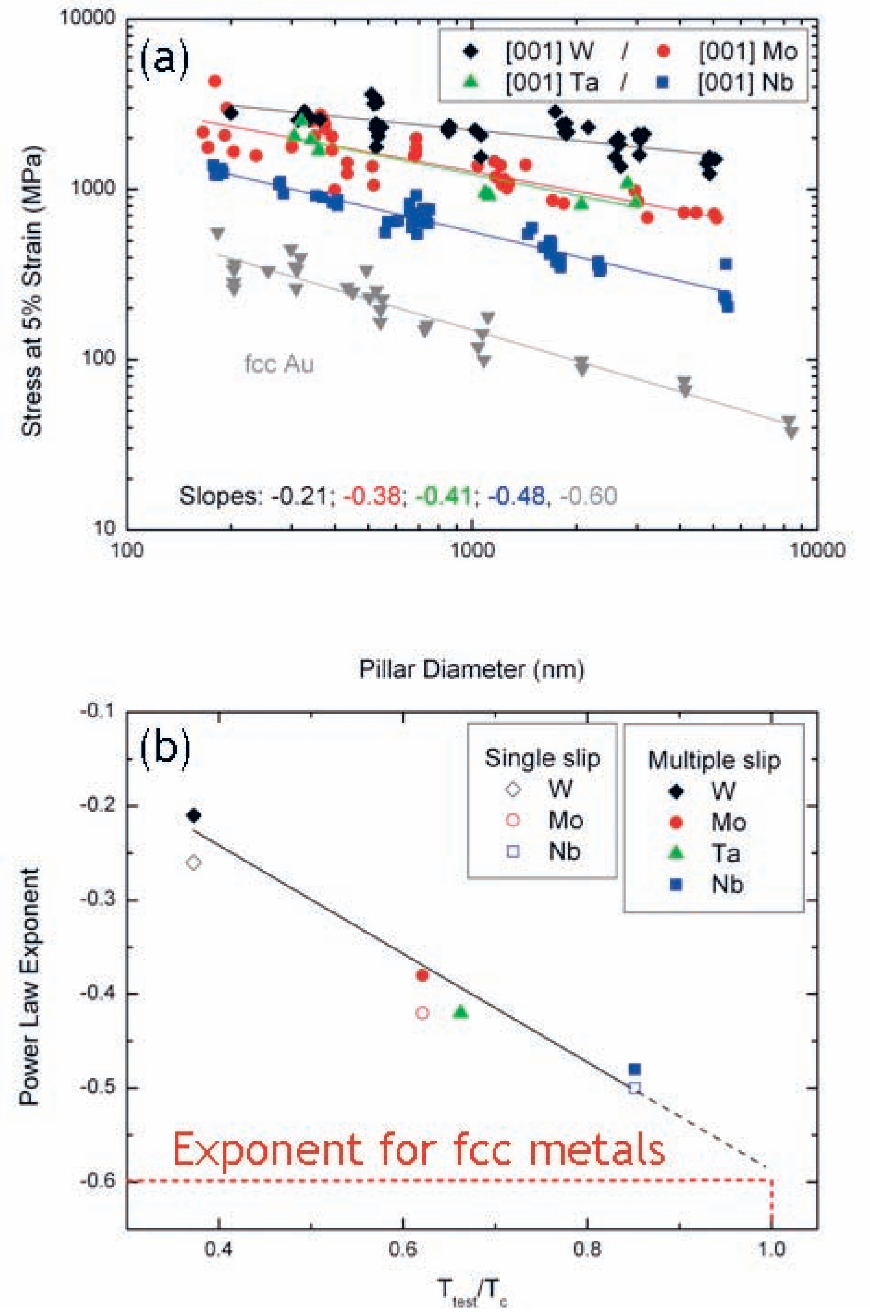

Figure 3: Comparison plots: (a) of stress measured at 5 % strain versus pillar top diameter for all [001] bcc pillars tested (i. e. W, Mo and Nb) as well as Au [8] and Ta [9] pillar data, (b) slope of the line of best fit (exponent) for the size dependence of the [001] and [235] oriented bcc pillars versus normalized test temperature $T_{test}/T_c$ (see text and Table 1).

screw dislocation motion is not the limiting mechanism, the strength of bcc and fcc pillars may be controlled by the same dislocation processes. With increasing critical temperature an increasing effect of screw dislocation mobility becomes apparent, leading to a deviation from fcc behavior that scales with $T_{test}/T_c$.

## Summary and outlook

We have demonstrated that the size dependence of the yield stress differs fundamentally between fcc and bcc metals. In contrast to fcc metals, bcc metals were found to have a weak size dependence, which scales with the critical temperature of the tested material. This difference was attributed to the special role of screw dislocations inherent to the bcc crystal structure.

To obtain a better understanding of the associated mechanisms responsible for the size effect, we are currently investigating the influence of internal size parameters on the mechanical properties of small-scale single crystals. For this purpose, microcompression tests have been performed on oxide-dispersion-strengthened (ODS) alloys with an oxide particle spacing smaller than the sample size. Future experiments will be conducted on age hardenable alloys giving the opportunity to change the internal size parameter with respect to the sample size by an appropriate heat treatment. This will enable us to explore the transition from obstacle- to size-controlled deformation in more detail and will give new insights into the microstructure evolution in small dimensions.

Another goal of our group is to transfer these fundamental studies into potential applications. Since small-scale metal structures have superior mechanical properties compared to their bulk counterparts, large-scale micro- or nano-structuring of metal surfaces may offer radical improvements of tribological properties and new functions. Current approaches to make patterned surfaces are expensive because they require multiple steps, in clean and highly controlled environments, on expensive equipment. Therefore, we also investigate new ways for macroscopical micropatterning of metal surfaces.

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# The role of the backing layer in the mechanical properties of micrometer-scale fibrillar structures

**Griselda Guidoni[1], Dominik Schillo[1], Ude Hangen[2], Graciela Castellanos[1], Eduard Arzt[1], Robert McMeeking[1,3] and Roland Bennewitz[1]**

1: INM – Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany.

2: Hysitron, Inc., 10025 Valley View Road, Minneapolis, MN 55344, USA.

3: Department of Mechanical Engineering, University of California, Santa Barbara, California 93106, USA.

## Abstract

The contact mechanics of a micro-fabricated fibrillar surface structure made of poly(dimethylsiloxane) (PDMS) was studied in this work. The attachment and detachment of individual fibrils to and from a spherical indenter upon approach and retraction are detected as jumps in force and stiffness. A quantitative model describes the jumps in stiffness values by taking into account the deformation of the backing layer. The results emphasize the importance of long-range interactions in the contact mechanics of elastic materials and confirm the concepts underlying the development of fibrillar adhesive materials.

## Introduction

Fibrillar microstructures of elastic materials interacting with substrates by short-range molecular forces, such as Van der Waals attraction, have recently attracted attention as dry adhesives [1-8]. Their development is motivated by the study of adhesion in biological systems such as the feet of some insects and geckos [5; 6; 9-12]. These fibrillar architectures exhibit high adhesive strengths for a variety of reasons, previously summarized by Majumdar, Sharma and Ghatak [13] and subsequently by Kamperman et al. [14]. For example, fibrillar surfaces resist peeling more effectively than those without textured patterning because the detachment of one fibril does not lead automatically to the detachment of its neighbors, whereas a smooth surface can peel continuously and relatively easily due to the strain concentration at the detachment front. In addition, surfaces with compliant fibrils can conform to rough surfaces more easily than monolithic pads, and so can adhere more strongly. Other benefits arise because fibrillar surfaces can be made with small dimensions (µm to nm scale), so that in some architectures the penalty due to elastic stresses that tend to drive the separation of surfaces is reduced compared to the adhesive tractions holding them together [5], a phenomenon known as strengthening due to contact splitting. Another benefit of small dimensions is that the pull-off force achieved can rise to levels comparable with the maximum Van der Waals adhesive strength times the area in contact [15], with advantages to adhesive strength realized for dense packing of such fibrils in comparison to undivided surfaces. Structures from µm to nm dimensions also limit the size of detached regions that can be present on the surfaces in contact, so that the extent to which large defects of this nature can undermine strong adhesion is limited [16-18].

Many of the systems presented thus far are produced by a molding process with elastomers. In these systems, fibrils and backing layer are made of the same elastic material. In this study, we quantify the combined elastic response of fibrils and backing layer and show that the measured stiffness of the fibrillar system is strongly influenced by elastic deformations of the backing layer. Such long-range deformation of the substrate is an essential ingredient in the recent modeling of the mechanical response of elastic materials [19].

In our experimental work, we focus on the approach of a stiff sphere into contact with the fibrillar system. The high sensitivity of a nanoindenter allows us to register the sequence of attachment of individual fibrils. Analyzing attachment rather than detachment avoids the nonlinear effects of large strain and viscoelastic response which often hamper the quantitative analysis of adhesion experiments with elastomers. In our modeling we describe the combined deformation of fibrils and backing layer in a linear model at small strains. The combination of experiment and model allows us to understand the measured stiffness as a function of the number of fibrils in contact and to determine the elastic modulus of our material by an *in situ* measurement of individual fibrils on the backing layer.

## Experimental

The PDMS (Sylgard 184) samples were prepared using a soft-molding process. The tested area consisted of an arrangement of 7 fibrils of radius 5 µm each and of height 18.7 µm. They were packed in a hexagonal pattern; separated by a distance 20 µm between the centre of neighboring fibrils (see Figure 1 for an image of a larger-scale model of the structure). Nanoindentation tests were carried out using a TI 900 instrument with a Performech controller (Hysitron TriboIndenter, Hysitron Inc., Minneapolis, MN, USA). A spherical sapphire indenter (radius R = 348 µm) was used. By means of an optical microscope, the indenter was located above the middle of the centre fibril. The approach was done from a height where there was no contact and where no attractive or repulsive forces were registered.

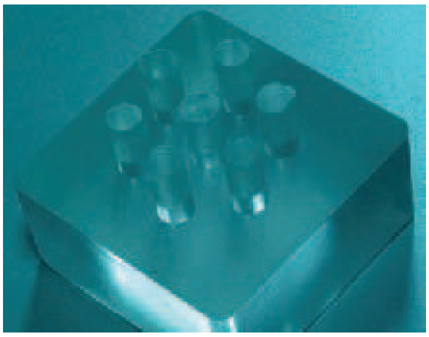

Figure 1: Model of the hexagonal arrangement of fibrils tested in this study.

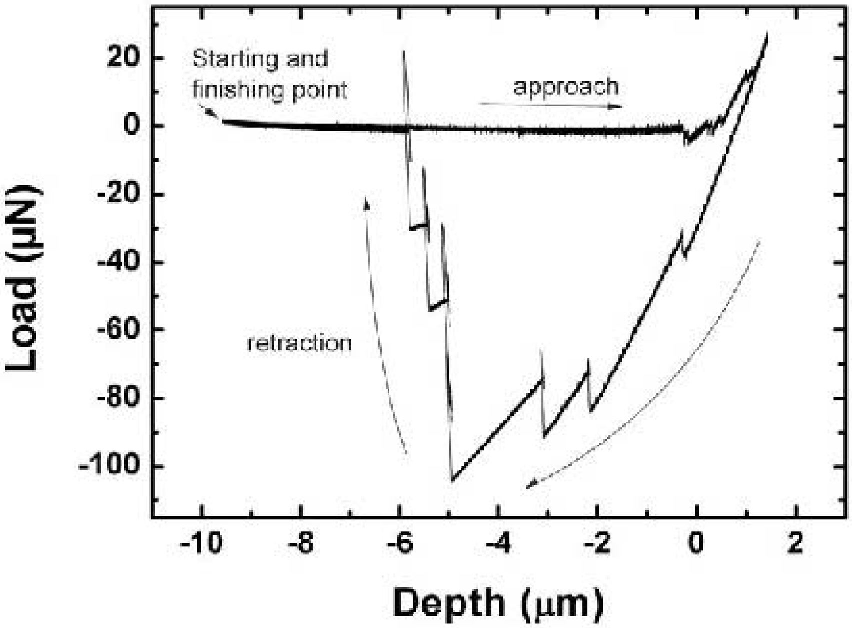

Figure 2: Force vs. depth curve during approach and retraction to and from the seven micrometer-sized PDMS fibrils on the backing layer of same material. Attachment and detachment can be recognized for each individual fibril.

All measurements were done under displacement control, at an approach and retraction rate of 200 nm/s using a close-loop feedback control.

## Results

Figure 2 shows a typical load-displacement curve for approach and retraction. The individual attachment and detachment of the seven fibrils can be recognized through sudden jumps in the force. The attachment of the first fibril upon approach always generated a force drop into tension. The general shape of the approach-retract curve resembles the non-linear characteristics and the large hysteresis expected for indentation into an elastomer (see for example Figure 1 in [20]). However, the curve is composed of linear sections with different slopes separated by the force jumps. This observation reflects a step-wise increase in contact area, as we will discuss later in detail.

Figure 3 is a detailed view of the force data recorded upon approach. Each drop in force corresponds to the consecutive contact formation with single fibrils. The increasing slope of the linear sections quantifies the increase in overall stiffness with an increasing number of fibrils in contact. Correspondingly, a decrease in slope is observed in the unloading data (see Figure 2) as the number of fibrils in contact decreases.

The stiffness values ($k_i$), where $i$ is the number of fibrils in contact, were determined for each section of the curve by linear fitting. Figure 4 summarizes the average stiffness values. While the stiffness does increase monotonically, it does not scale linearly with the number of fibrils in contact as it would be expected if the fibrils would act as independent identical springs in parallel. The stiffness of the nanoindenter is 1400 N/m, 35 times larger than the highest stiffness values measured in our experiments. Therefore, the deformation of the force sensor was neglected in the calculations.

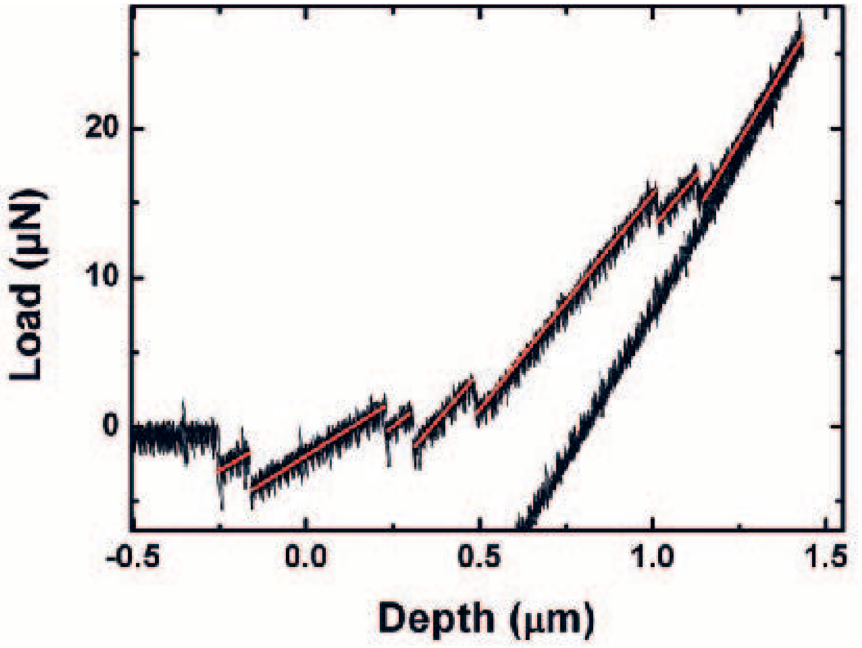

Figure 3: Detail of Figure 2, where the linear sections of the force curve between the attachment events are highlighted. The linear fitting yields the combined normal stiffness of the group of fibrils already in contact with the indenting sphere.

## Discussion

For the calculation of the stiffness values $k_i$ for $i$ fibrils in contact a model has been developed which takes into account either the elongation or the compression

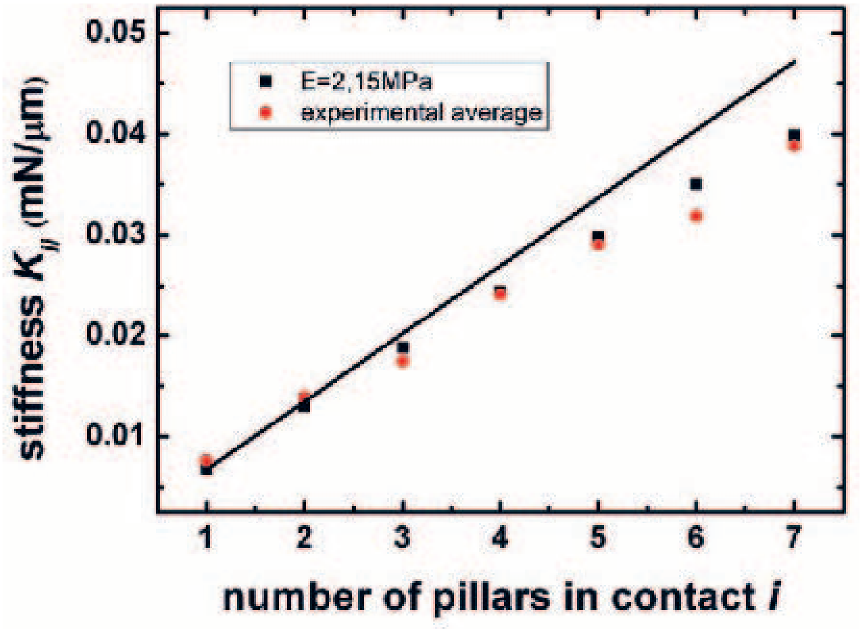

Figure 4: Stiffness $k_i$ as function of the number of fibrils in contact with the indenter. Circles provide the average values for several experimental series, squares the results of our model. The straight line indicates the expected relation if no deformation of the backing layer was taken into account.

of each fibril and the deformation of the backing layer. Details of the model will be published elsewhere. In short, the homogeneous stress in each fibril is assumed to act on a patch of the surface with the area of the fibril's cross section. This stress deforms the surface in a way predicted by Johnson through the methods of contact mechanics [21]. The surface deformation lifts or lowers the base of neighboring fibrils, thereby changing the stress in these fibrils. The balance between stresses in all fibrils in contact with the indenting sphere and the surface deformation defines the total stiffness of the system.

In this section we discuss the experimental results in tandem with the modeling result. We proceed chronologically with the observed events when approaching and retracting the indenter to the structured surface.

The indenter approaches the sample surface from a distance where interactions between sample and indenter cannot be detected. The first significant deviation from zero force is a sudden drop in load when the first fibril makes contact with the indenter (see Figure 2). The first contact always results in a tensile force, resulting from attractive forces between indenter and fibril. The linear increase of the force after the drop yields a value for the combined stiffness of the sample and the force sensor. The average value is $k_1$ = 7.7 N/m, almost two orders of magnitude lower than the stiffness of the force sensor. We conclude that the jump into contact of the first fibril occurs through a sudden stretching of the fibril and deformation of the backing. The stretching distance can be calculated as the force drop divided by the stiffness $k_1$. The values vary between 300 and 450 nm, i. e. typical strain in the fibril after jump into contact is of the order of 2 %.

We estimate maximum distances for the jump-into-contact instability based on Van der Waals forces to be only 11 nm. The contribution of Van der Waals [10; 22] and capillary forces [6] to long range attractive forces has not been fully understood. Our results strongly indicate that long-range interactions like electrostatic forces have to be considered for the case of PDMS and sapphire.

The jump-into-contact events recur as the indenter moves toward the sample and the number of fibrils in contact with the indenting tip/sphere increases. At a certain indenter position, the force measured by the indenter will change from tension to compression since the stretching of the latest fibrils into contact is compensated by the compression of the earlier attached fibrils. The force vs. depth curve becomes steeper with each additional fibril in contact, reflecting the expected increase in stiffness. The linearity of the section between force drops indicates that each fibril immediately makes complete contact. Such increases in contact area in well-defined steps are very helpful for the quantitative evaluation of elasticity parameters. It has been shown that the dynamics of the stress singularities at the edge of the contact are a challenge in quantitative indentation studies in PDMS [20]. In our system, the gain in adhesion energy is large enough to elastically stretch and deform the fibrils such that full contact is established once the fibrils come close to the indenter. This observation is a clear demonstration of the optimization of contact formation by micro-structuring surfaces, a core concept of fibrillar biomimetic adhesive materials.

The stiffness increases sublinearly with the number of fibrils in contact. Our model explains this trend taking into account the deformation of the backing layer. Figure 4 compares the experimental $k_i$ values with the model data. The straight line represents the stiffness assuming a rigid substrate. The model correctly predicts the stiffness relations. The only adjustable parameter is the elastic modulus E. It was found by minimizing the sum of square differences to the averaged experimental $k_i$ data to be E = 2.15 ± 0.10 MPa. Note that the combination of our experimental method and our model allows for the unique *in situ* determination of the elastic modulus of PDMS fibrils within a given micro-structure. The elastic moduli of PDMS polymers similar to our material have been determined by a variety of methods and values are between 1.3 and 4 MPa [23-27]. Our method avoids the contact size problems usually encountered in indentation of flat elastomer samples [20; 24] and takes into account possible variations of the elastic modulus for a material which is cured in a confined geometry.

Upon retraction of the indenter, a significant adhesion hysteresis is observed in Figure 2. The seven fibrils are detached one after the other. However, detachment of the first of seven fibrils occurs far into the tensile regime. The shape of the adhesion hysteresis resembles the curves measured with similar indenters on flat PDMS surfaces [20]. However, for the micro-structured PDMS surface the adhesion hysteresis is far larger, emphasizing once more the function of the microstructured surface in the adhesive properties. While the maximum adhesion force on the flat PDMS surface is determined by the radius of the indenter, the adhesion force in the fibrillar system is determined by the sum of the adhesive forces of the fibrils, which is larger due to the effects discussed in the introduction. Additionally, the strength of adhesion compared to the softness of the fibrils at the micrometer scale yields perfectly flat contacts. Flat punch contacts however show a strong resistance against peeling as there is no stress singularity at the edge as in sphere-on-flat situations for frictionless contacts or a much reduced one for frictional contacts [18; 20].

## Conclusion

In conclusion, we have performed contact mechanics experiments on a fibrillar micro-structured PDMS surface. Attachment and detachment of individual fibrils have been detected in force and stiffness measurements. Small deformations during approach of an indenter have been quantitatively modeled taking into account deformation of both the fibrils and the backing layer. The results emphasize the importance of long-range interactions via the substrate for the contact mechanics of elastic materials. The discrete growth of the contact area with increasing number of fibrils in contact allows an accurate *in situ* determination of the elastic modulus of the PDMS to be 2.15 MPa.

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# Organosilicate nanoparticles - a familiar material in new shape

## Eoin Murray and Tobias Kraus

### Introduction

Silica nanoparticles have been commonly used as nanoscale components in hybrid systems for many years. For example, polydispersed nanoscale silica is used as a transparent filler in polymers, modifies the flow properties of emulsions and improves the properties of construction materials. Since Stöber et al developed a low-cost, facile synthetic route to highly monodispersed silica nanospheres, they have become the cornerstone of many facets of nanoparticulate research. When produced with a narrow size distribution, silica nanoparticles can introduce nanoscale regularity on surfaces or in bulk materials either as a component of the final material or as an etch mask in further processing steps. As such, assembly of monodispersed silica nanoparticles into regular superstructures is a promising route to materials with rationally designed microstructures. However, in all cases, the particle-matrix compatibility and composite behavior depend on the surface chemistry of the particles.

A commonly-used method to change and improve the properties of existing hybrid materials and to broaden the range of possible composite materials is to alter the surface chemistry of silica particles. Functionalization of the particle surface using organic modifiers can reduce aggregation, improve matrix compatibility or change the physical properties of a composite material. Functionalized silica nanoparticles have found application in many areas including paints and coatings [1; 2], sensors [3], catalysis [4; 5] and drug delivery methodologies [6; 7]. For example, in previous projects at INM, silica nanoparticles have been coated with methylalkoxysilanes which resulted in weak bonding between the particles forming a soft network of binder molecules in a flexible gel, which prevented cracking of the otherwise brittle systems [23; 24].

Modification of particle surfaces using organic moieties can also produce hydrophobic particles. Hydrophobic silica nanoparticles interact strongly with the constituent molecules of apolar polymer matrices and have been shown to enhance their physical and mechanical properties in polymeric nano-composites [8; 13]. Stable suspensions of hydrophobic silica nanoparticles in apolar solvents are also good model systems for studying the equilibrium and transport properties of colloidal dispersions; their refractive index matches that of some apolar solvents, minimizing multiple scattering in light scattering experiments [9-11].

Two methods are presented here to produce two very different types of hydrophobic silica nanoparticles. The first approach is based on the commonly applied hydrolysis and condensation of tetraalkyl orthosilicates by a strong base as originally developed by Stöber [12]. The resulting hydrophilic particles were then modified by the grafting of organosilicate compounds onto their surfaces or by the co-hydrolysis of a tetraorthosilicate with the required functional organosilane. Using these techniques, silica nanoparticles were previously

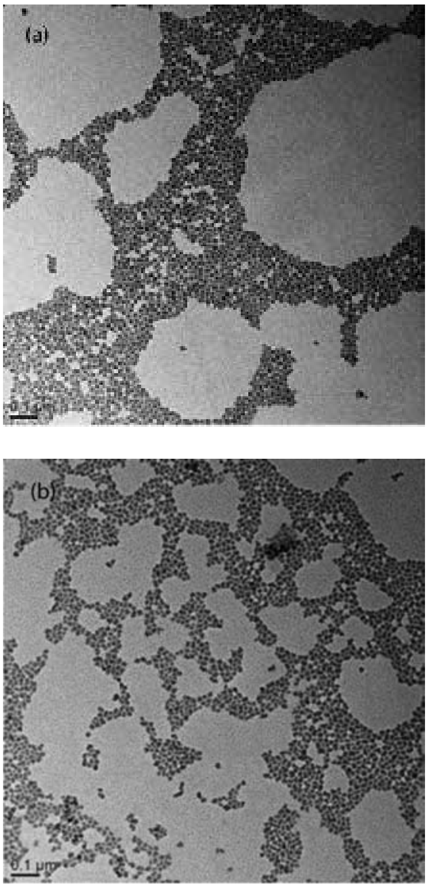

Figure 1: Transmission electron microscopy images of octadecyl coated silica nanoparticles synthesized using the modified Stöber route at ambient temperature, (a) with silane addition after the reaction and (b) during the reaction. Scale bars are 100 nm.

coated with a number of functional groups including vinyl, carboxylate, thiol, mercaptopropyl and amine [14; 15; 19; 20] and a variety of biomolecules [3; 21]. The surface of particles from the Stöber synthesis were also made hydrophobic by the esterification of the surface hydroxyl groups using octadecanol [9; 10; 14]. The resulting so-called octadecylsilica is a popular model system for hard-sphere colloids. In this work monodispersed colloidal $SiO_2$ particles with diameters of 15 to 25 nm were prepared via the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) by aqueous ammonia in ethanol. The surfaces of these particles were rendered hydrophobic with octadecyltrimethoxysilane (ODTMS) after the reaction or, more conveniently, by addition towards the end of the growth phase.

The second route departs from the core-shell structure to produce uniformly hydrophobic particles. Instead of using two different silanes, only one of which carries the desired surface functionality, synthesis is done starting solely from the alkylsilane. The resulting organosilica particles are inherently hydrophobic and carry organic moieties not only on their surface, but also throughout their core, which can thus host suitable dyes or other apolar agents [18]. In this case pure octadecyltrimethoxy silane (ODTMS) was hydrolyzed with ammonia to directly yield hydrophobic organosilicate particles.

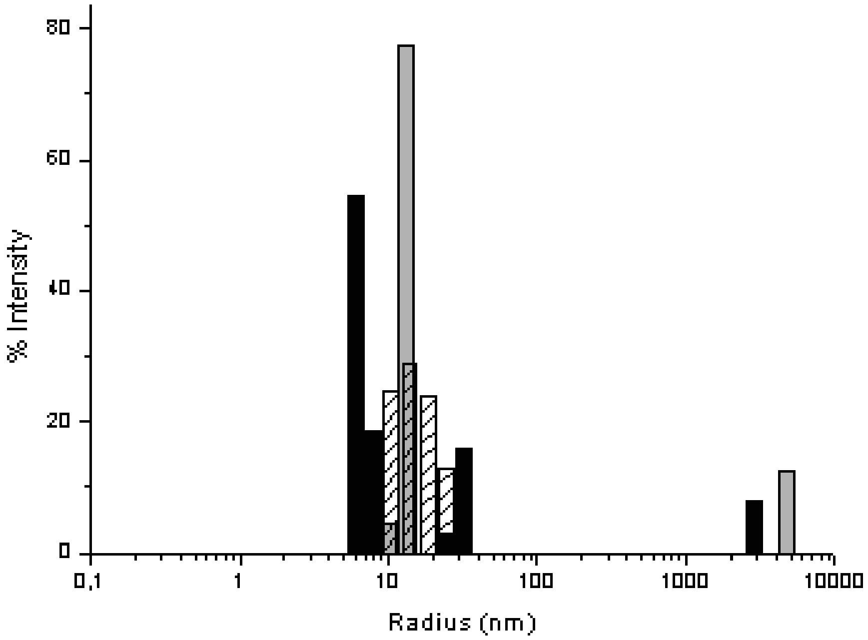

Figure 2: Particle size distribution from dynamic light scattering (DLS) of silane modified hydrophobic silica in heptane, produced using the Stöber synthesis with addition of octadecylsilane after the reaction (light) and during the reaction (dark) compared to the size distribution of the uncoated particles in ethanol from a similar Stöber synthesis (striped). The unmodified particles exhibit a slightly broadened size distribution while the modified particles contain a small fraction of large agglomerates. Note that the agglomerates scatter light strongly, but their fraction of the total particle mass is below 0.1 %.

## Results and discussion

The hydrophilic particles obtained by Stöber's synthetic route were found, by both transmission electron microscopy (TEM) and dynamic light scattering (DLS) size distribution measurements, to have diameters in the range of 15 to 25 nm with a polydispersity (by DLS) of approximately 10 to 15 % (Figure 1). These particles were subsequently modified and made hydrophobic by the addition of ODTMS without significant increase in either the size of the particles or their polydisperity. Similarly modified particles were produced by *in situ* coating with ODTMS added during the hydrolysis reaction. These particles showed a slight increase in DLS polydispersity over both the bare silica in ethanol and post-reaction modified silica in heptane (Figure 2).

While the synthetic route detailed above yields hydrophobic silica nanoparticles with acceptable quality, they are not useful in the preparation of very small (< 15 nm), spherical particles. There are limitations to the silica nanoparticles attainable using variations of the Stöber process. While narrow size distributions can be achieved for larger particles (> 200 nm), smaller particles generally exhibit more irregular shapes and sizes. Indeed, to our knowledge, the smallest useable particles that have been produced using the Stöber process are approximately 15 to 20 nm and have a polydispersity of 10-20 % [16; 17]. To obtain smaller, monodispersed particles, we resorted to a route that was again similar to the Stöber synthesis, but used ODTMS as the single silica source in an ethanol/ammonia solution. In this synthesis, the size of the organosilica nanoparticles could be controlled by varying the concentration of the reactants.

At low reactant concentrations and ambient temperatures, from DLS results the resulting particles were smaller than 10 nm and exhibited below 10 % polydispersity but at high reactant concentrations the particles were 20 to 40 nm in diameter, with polydispersities above 25 % (Figure 3). This reaction appears to be a quick and facile route to hydrophobic silica nanoparticles with size and shape dispersity comparable to or better than those produced by the Stöber routes. However, the TEM images revealed a fundamental difference with the particles produced using this method: The particles produced are of extremely low density due to the fact that, unlike those produced from method one, they do not have a surface modified $SiO_2$ core, but a -Si-O-Si- framework supporting an amorphous network of organic chains. These chains are a 15-20 Å long when stretched so that a sub-10 nm particle can only contain a small number of $C_{18}$-Si-O molecules. In stark contrast to those produced using conventional Stöber routes using TEOS, the resulting particles are porous and the core is inherently hydrophobic resulting in particles that can possibly be used as hosts for hydrophobic agents such as dyes.

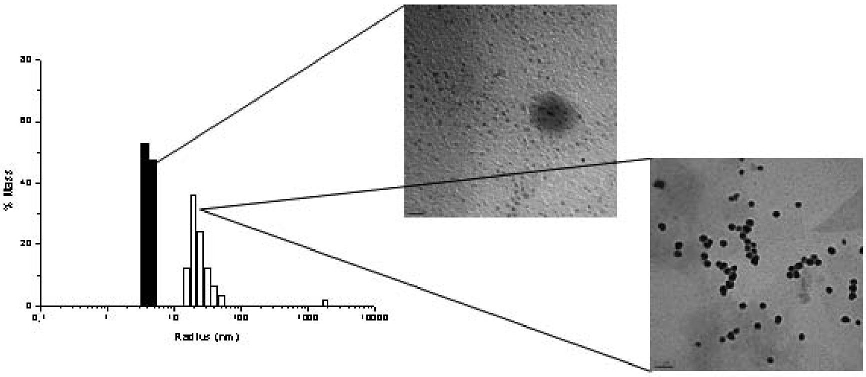

Figure 3: Particle size distribution from DLS of organosilica in heptane produced with low reactant concentrations (light) shows a very narrow particle size distribution with a minimum of large aggregates while the particles produced using higher concentrations show a broader distribution (dark). The corresponding transmission electron microscopy images are also presented showing the very low-density of the smaller particles.

Thermal analyses were performed to assess the fraction of the organic component in the organisilica particles and the degree of surface coverage of the Stöber particles with ODTMS modifier (Figure 4). Differential scanning calorimetry (DSC) showed an endothermal peak at ~ 495 °C, which was identified via mass spectrometry (MS) as alkyl chain fragments formed during the desorption of the alkyl chains from the surface of the particles. The associated weight loss from thermal gravimetry analysis (TGA) was ~ 20 %, indicating the removal of organic modifiers from the silica particle surface. The DSC of the organosilica particles showed a double alkyl peak at ~ 495 °C, again identified by MS as alkyl chain fragments, likely from the decomposition of the particle's organic components. However, in this case the associated weight loss was close to 70 %, indicating that the decomposition affected both alkyl chains from the surface and from the organosilica core network that forms the bulk.

## Conclusion

In summary a synthetic route to a novel type of hydrophobic silica nanoparticles has been developed and compared to conventional particles produced using a proven route based on the Stöber synthesis. In the standard synthetic route, nanoparticles in the diameter range of 15 to 25 nm with polydispersity below 15 % were prepared via hydrolysis of TEOS by ammonia under sonication and then modified with ODTMS to yield high coverage hydrophobic surfaces. We also developed a synthetic route, parting with the dual precursor concept, that led to the production of silica particles whose surface chemistry is similar to those produced using standard methods but which exhibit very different physical characteristics. The synthesis of hydrophobic organosilica particles from ODTMS as the single silica source in a mixture of ethanol and ammonia yielded very small nanoparticles from 5 to 50 nm with polydispersities between 8 and 25 %. These particles contain 70 % by weight organic moities in an organosilica network that make up a low density, porous hydrophobic core. As such, the surface chemistry of these particles is similar to those produced by regular synthetic routes but they are likely to exhibit disparate physical properties, such as the bulk absorption of molecules, different mechanical and optical properties and, possibly, weaker interparticulate attraction. The particles are promising candidates as host systems for hydrophobic moieties, such as dyes or additives or as low-k component in hybrid materials.

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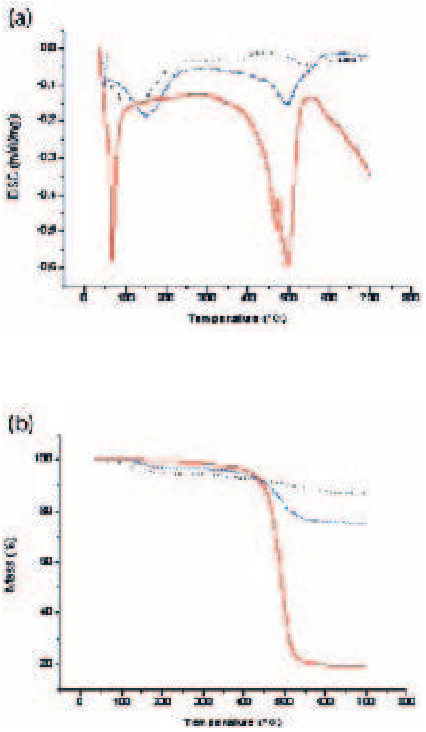

Figure 4. (a) Differential scanning calorimetry and (b) thermal gravimetry analysis results from hydrophilic unmodified Stöber particles (black ···), hydrophobic Stöber particles modified with ODTMS (blue ---) and hydrophobic organosilica particles (red —). The DSC peaks between 70 °C and 100 °C in all three samples are due to residual solvents (ethanol in the case of the hydrophilic particles and heptane for the hydrophobic particles – the associated weight loss is less than 3 % in all cases). The weight-loss associated with the endothermic peaks at 495 °C was less than 3 % for unmodified Stöber particles (residual unreacted TEOS), 20 % for modified Stöber particles and over 70 % for the organosilica particles.

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# Single source precursors for piezoelectric and optical coatings

## Michael Veith, Michael Bender, Carsten Bubel and Cenk Aktas

The field of chemical vapor deposition (CVD) has grown very rapidly in the last thirty years and applications of this versatile fabrication process are now used in many industrial products, such as semiconductors, optoelectronics and optics [1]. In comparison to thermal evaporation, sputtering and other physical vapor deposition (PVD) approaches, CVD offers excellent conformity to cover deep recesses, holes, and other difficult three-dimensional geometries [2]. In addition to thin film applications, where an ultra thin deposit is desired, CVD is also applicable for thick coatings due to its high deposition rate [3]. Another advantage is that CVD does not normally require ultrahigh vacuum unlike to state of the art PVD methods [4].

Beside these unique process advantages however, CVD has also some disadvantages, such as the need of high deposition temperatures, generally above 600 °C [5]. Development of metal-organic molecular precursors partially solved this problem and opened up new possibilities to deposit crystalline thin films at much lower temperatures [6]. As the material of interest becomes increasingly complex, the choice of the precursor also becomes more difficult. In the deposition of such multi-component complex materials, the common approach is to use several different precursors simultaneously [7]. On the other hand, the different volatilities of the precursors and undesired side reactions between decomposed chemical species affect the purity, composition, homogeneity and microstructure of the resulting materials [8]. In order to overcome these difficulties, the *single source precursor (SSP)* approach has been developed [9]. This is based on a molecular design which, instead of using several precursors, contains all desired elements in one molecule.

In the last years we have researched a number of SSPs for the synthesis of different nanocrystalline and composite materials. Recently, we have shown the synthesis of $Al/Al_2O_3$ and $Ga/Ga_2O_3$ nanocomposite structures with precisely controlled composition and microstructure [10]. The control of the composition, purity and homogeneity is especially critical for synthesis of electronic and optical materials. Thus, we present the use of the SSP concept for the synthesis of ferroelectric and optical coatings. First the synthesis of PZT coatings with a precise stoichiometry (between lead, zirconate and titanate) is presented. Dielectric properties of deposited PZT coatings (dielectric constant $\varepsilon_r$ and dielectric loss $\delta$) were measured with a precision LCR Meter. The remnant polarization ($P_r$) was also determined. The effectiveness of the SSP method is also shown by presenting transparent ITO layers with controlled dopant concentration. The ITO layers were characterized with the X-ray diffraction method. Electrical resistivity of the deposited layers is also presented.

## Experimental

*Synthesis and characterization of PZT coatings*

The combination of two bimetallic alkoxide compounds, $(C_2H_5)_3Pb[O\text{-}C(CH_3)_3]_5Ti$ and $(C_2H_5)_3Pb[O\text{-}C(CH_3)_3]_5Zr$ a lead titanate and a lead zirconate source with identical properties and complete miscibility resulted in a new mixed single source PZT precursor which evaporates at a temperature of 25 °C and a pressure of 0.13 mbar. The composition of the precursor is adjusted to Pb:Zr:Ti = 2:1:1.

The precursor was deposited at temperatures around 400 °C on (100) Pt/Ti/$SiO_2$/Si substrates using a vertical cold-wall CVD chamber. Following the deposition, the coatings were annealed at 650 °C. After sputtering the top electrode with diameters from 100 µm to 400 µm, the planar PZT-films were structured by wet chemical etching using lithographical techniques.

The crystallization behaviour of the PZT films was analyzed by X-Ray diffraction (XRD, Bruker (AXS D8 Advance)). Surface microstructures of the films were observed using a FEI (Quanta 400 ESEM FEG) field emission scanning electron microscope (SEM).

The dielectric properties of the films (dielectric constant $\varepsilon_r$ and dielectric loss δ) were measured with a precision LCR Meter (Agilent 4284A). To display the ferroelectric hysteresis loop, a classical Sawyer-Tower circuit [11] was used (A modified PUND setup, as described by Veith et al. [12] was employed for the determination of the remnant polarization $P_r$.).

*Synthesis and characterization of ITO coatings*

For the synthesis of the precursor, an organometallic indium compound $[(CH_3)_2In\text{-}O\text{-}C(CH_3)_3]$ is chemically bonded to an organometallic tin-compound $Sn[OC(CH_3)_3]_2$. Through intra- and intermolecular interactions, a quasi-SSP system can be formed, the source material for ITO-coatings. The ratio of In to Sn was adjusted to 9 to 1 to give a doping concentration of 10 % of tin in ITO.

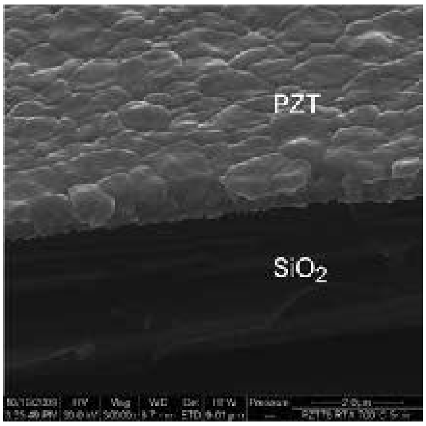

Figure 1: SEM-Image of the deposited PZT-film on a Pt/Ti/$SiO_2$/Si-substrate.

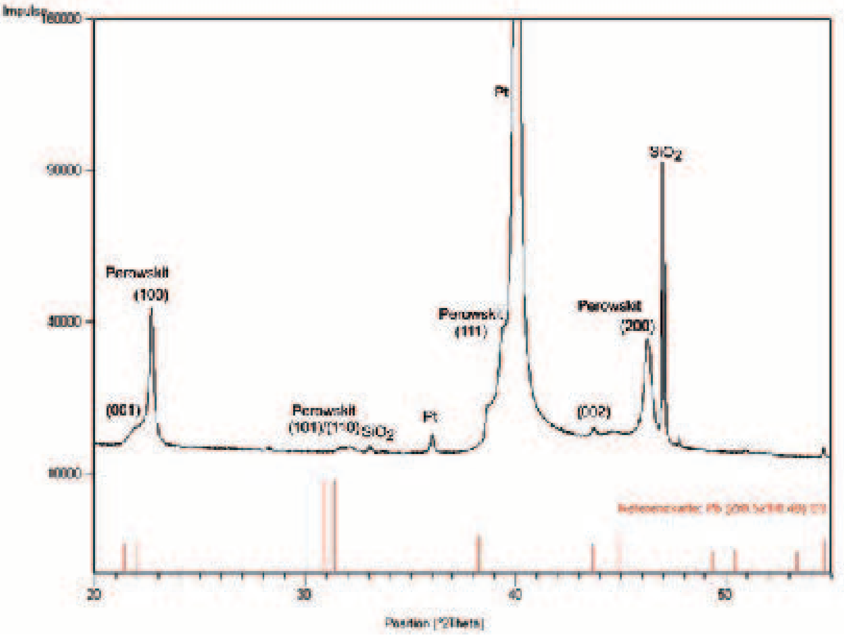

Figure 2: XRD-pattern of a deposited PZT film. The film shows a (100)-orientation.

A cold-wall-CVD-apparatus was used to deposit the ITO-films. 1g of the precursor was placed in a reservoir-container and connected to the CVD-reaction chamber. Glass substrates (borosilicate, 2 mm thick) of 15x15 mm in size were cut and placed onto the graphite substrate holder. Both the wall of the reaction chamber and the precursor reservoir were heated to 80 °C. The substrate was heated to 500 °C by a HF-generator. After reaching the desired temperature, the precursor-valve was opened for five minutes to enable deposition of the film from gaseous materials.

The composition and morphology were analysed by X-ray diffraction, using Cu $K_\alpha$ radiation. Layer thickness was measured by ellipsometry. Post-treatment in reducing atmosphere was performed for 30 minutes at 300 °C in forming gas (95 $\%N_2$, 5 $\%H_2$). Measurements of electrical resistivity have been performed with a four point probe technique (Hewlett-Packard 34401-A). SEM-images were taken by a JEOL JSM-7000 F scanning electron microscope.

## Results

### *PZT coatings*

After the CVD-process, the deposited films were thermally annealed at 650 °C to obtain the desired perovskite-phase. The SEM-images show a smooth 1 µm thick film-surface with a grain-size of about 500 nm (Figure 1). In XRD-measurements, a pure (100)-oriented perovskite-phase on the $Pt/Ti/SiO_2/Si$-substrate is observed (Figure 2).

The dielectric constant $\varepsilon_r$ and dielectric loss $\delta$ of the PZT-films were measured to be 412 and 0.025. The hysteresis loop (Figure 3) shows a remnant polarization of 25 µC/cm² and a coercive field of 30 V/µm.

### *ITO Coatings*

The deposited films appear transparent and show a crystalline cubic tin-doped indiumoxide phase in the SEM-image (Figure 4) and in the diffractogram (Figure 5) with a crystallite size of approx. 100 nm. No other crystalline phases could be observed.

The thickness of the ITO-layer is 23 nm. The as-prepared transparent samples show a sheet resistance of 1640 kΩ/sq. After post-treatment in reducing atmosphere, the value has slightly decreased to 1542 kΩ/sq, corresponding to a specific electrical resistivity of $3.55 \times 10^{-3}$ Ωcm. This increase in electrical conductivity can be explained by the creation of oxygen vacancies in the oxide lattice during reduction treatment.

## Discussion

The synthesis of a quasi-SSP is a key issue in the simplification of state-of-the-art CVD processes. PZT-films with the desired perovskite phase were deposited using only one source instead of three (lead, zirconate and titanate). The film properties ($E_c$ = 30 V/µm, $P_r$ = 25 µC/cm²) exceed those of sol-gel-PZT-coatings [13]. The properties are comparable with PZT-films, produced by sputtering-techniques [14]. In comparison to sputtered films

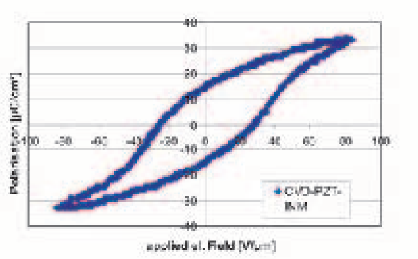

Figure 3: Hysteresis-loop of the deposited PZT-film.

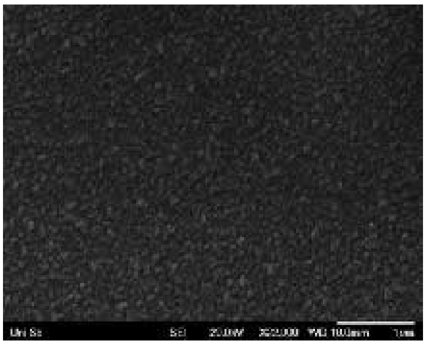

Figure 4: SEM image of the transparent ITO coating.

our layers show a better coverage on complex geometries.

CVD of a new SSP was shown for synthesis of ultra thin films of ITO. After five minutes deposition, a 23 nm thick, crystalline layer of tin-doped indiumoxide has grown on the glass substrate. The electrical resistivity after post-annealing in reducing atmosphere is 3.55 x $10^{-3}$ Ωcm. Further enhancement of the layer growth might be achieved when oxygen is added to a carrier gas.

## Conclusion

Single-Source-Precursors have been used to produce high performance coatings of PZT and ITO using the CVD-process. PZT-coatings from a single source combining Pb, Zr and Ti in one metal-organic precursor system show excellent properties. ITO-CVD-coatings from a SSP-system exhibit high transmission in visible range and good electrical conductivity. The ITO-layer consists of densely packed, cubic ITO-crystals.

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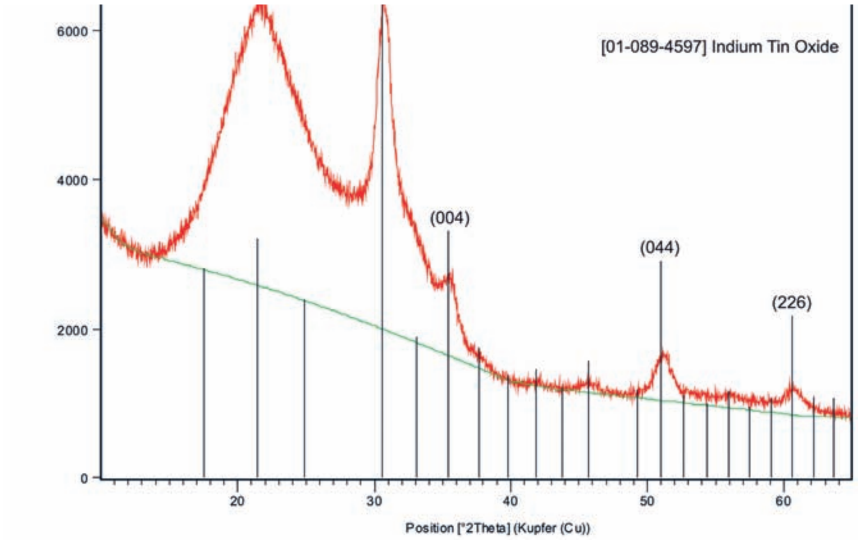

Figure 5: XRD-Pattern of the ITO-coating on glass substrate. Reference lines according to Indium Tin Oxide (PDF-Nr. 01-089-4597).

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# Stimulated emission depletion microscopy for imaging of engineered and biological nanostructures

Christian Schumann, Christian Cavelius, Sabrina Schübbe and Annette Kraegeloh

## Abstract

The investigation of interactions between engineered nanostructures and biological systems is a key component in the assessment of potential environmental and health implications due to the increasing application of nanotechnology. Combining the high specificity of bioconjugate fluorescence labeling techniques with the sub-diffraction resolution of Stimulated Emission Depletion (STED) microscopy and state-of-the-art nonlinear image restoration allows the imaging of these interactions on the length scales demanded by the interaction partners. In this article, we give an overview of the experimental approach and discuss its implications on the biological interpretation of the resulting fluorescence micrographs.

## Introduction

The ongoing development of new nanoscale materials raises the important question about their effects on human health and environmental implications [1]. The properties and technological applications of nanomaterials are intimately interwoven with dimensions on a nanometer and thus sub-cellular length scale. Their interaction with biological systems is dominated by their physicochemical properties, which strongly depend not only on their chemical composition, but also on a multitude of parameters including surface chemistry, morphology, etc. [2]. It has been shown that nanoparticles are in principle able to penetrate biological membranes and enter biological cells, but the nature of this cellular uptake, as

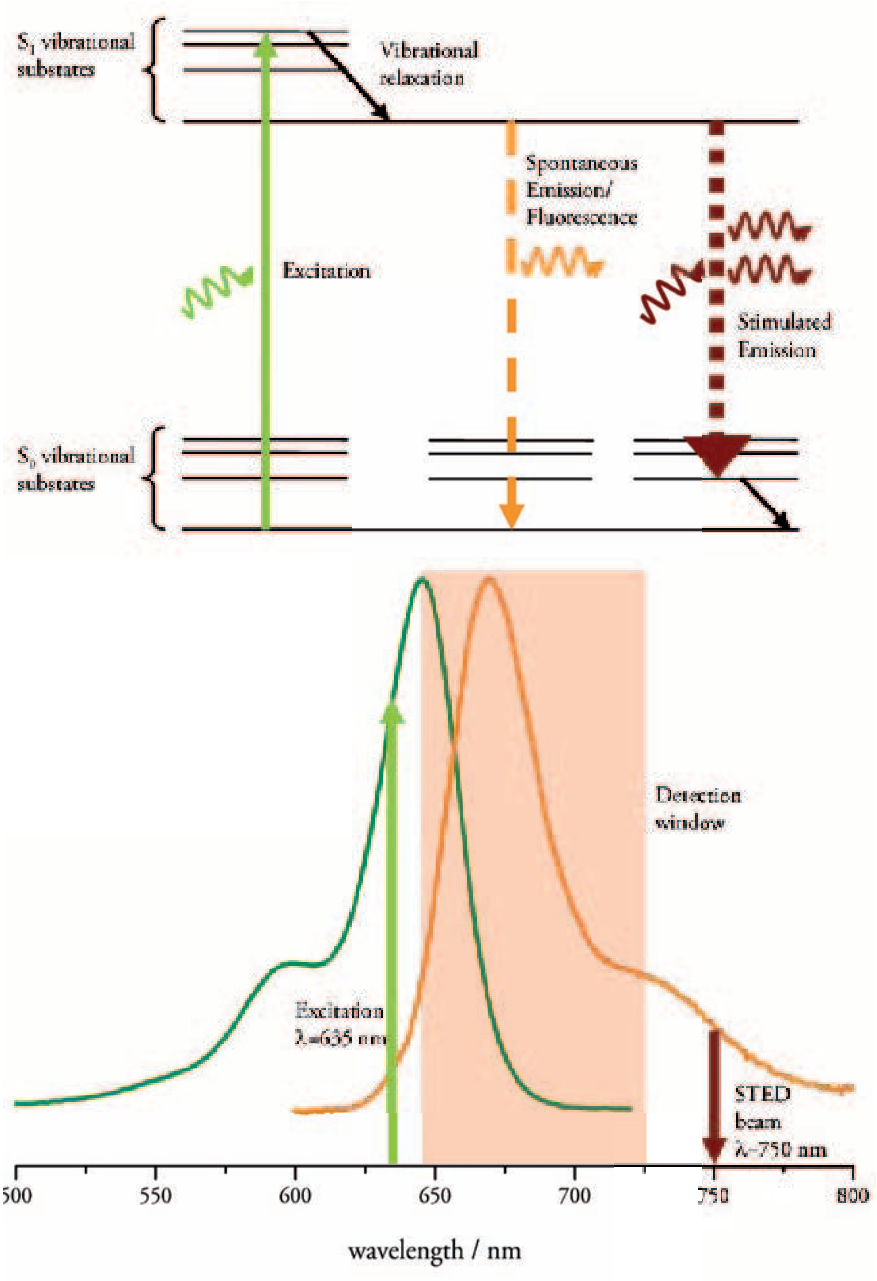

Figure 1: Top: molecular scheme of the STED process: After excitation to the S1 state and vibrational relaxation, fluorescence is suppressed by depopulation of the S1 state using stimulated emission in a pattern confining the center of the excitation spot. Bottom: Spectral realization for the STED-compatible dye Atto647N. The detection window is located between excitation and STED laser lines.

well as the mechanisms that determine the subcellular localization, the interaction with cellular components and finally the cellular response, are still unclear and subject to widespread research.

In our research, we seek to elucidate the transmembrane and intracellular transport processes of nanoparticles in human cells and to identify their biological interaction partners on a molecular level. In order to achieve this goal, we apply an imaging approach based on stimulated emission depletion (STED) microscopy, which enables us to visualize the interactions between engineered and biological structures with a spatial resolution beyond the optical diffraction limit.

## Experimental

*Imaging:* All fluorescence imaging was performed on a Leica TCS SP5-STED (Leica Microsystems, Mannheim, Germany) using a Leica HCX PL APO 100x/1.4 oil objective. Excitation for STED imaging is accomplished by a picosecond diode laser (Picoquant, Berlin) with a wavelength of 635 nm. For point spread function (PSF) determination, confocal stacks with a pinhole size of 0.5 Airy units were recorded from samples of appropriate sub-resolution sized fluorescent beads (Invitrogen, Karlsruhe, Germany). PSFs were reconstructed by deconvolution of the image stacks with spherical object models. Biological specimens and PSF reference samples were mounted in FluorSave (CalBioChem, Merck, Darmstadt, Germany).

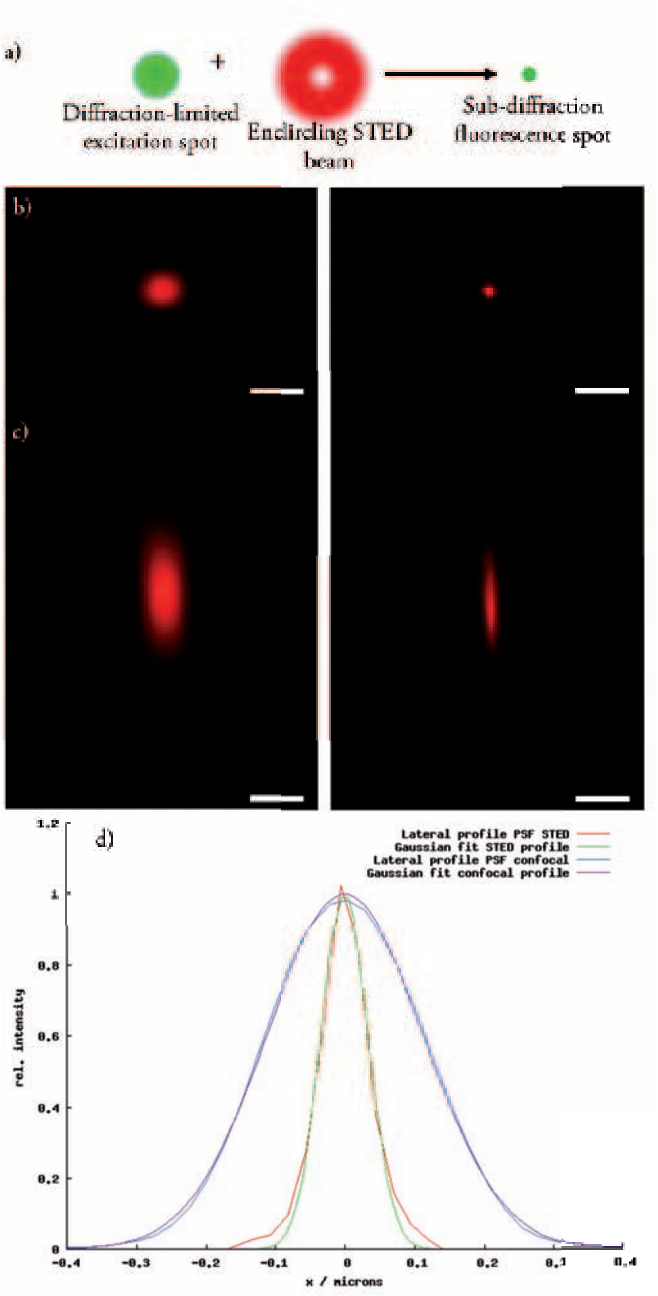

Figure 2: a) Lateral beam alignment of excitation and STED laser. Depopulation of the $S_1$ state by a STED laser spot with a node at the center of the excitation spot effectively reduces the size of the fluorescence spot scanned across the specimen. b) Lateral sections of the confocal (left) and STED (right) PSF, scale bar 500 nm. c) Axial sections of the confocal and STED PSFs, scale bar 500 nm. d) Lateral section profiles and gaussian fits of the STED and confocal PSFs. FWHM is 80 ± 3 nm (STED) and 264 ± 2 nm (confocal).

*Image processing:* Deconvolution of fluorescence micrographs was carried out using Huygens Professional (SVI, Hilversum, Netherlands) and custom written code in MATLAB (Mathworks, Natick, MA, USA).

## STED confocal fluorescence microscopy

The idea of fluorescence microscopy is to excite a fluorescent dye by visible light (e. g. by a laser beam) to the $S_1$ state and detect the red-shifted fluorescence light that is emitted by its electronic relaxation back to the $S_0$ ground state [3]. The underlying physical process is spontaneous emission after vibrational relaxation in the $S_1$ state, causing the Stokes shift to longer emission wavelengths. This method not only enables background-free signal detection, but also enables molecular specificity of the fluorescent labels by conjugating them to particular molecules or structures. Fluorescence microscopy is realized by a vast array of concepts, among which conventional confocal microscopy achieves 3D optical sectioning by introduction of a confocal pinhole aperture in the fluorescence detection pathway and point-scanning of the specimen [4].

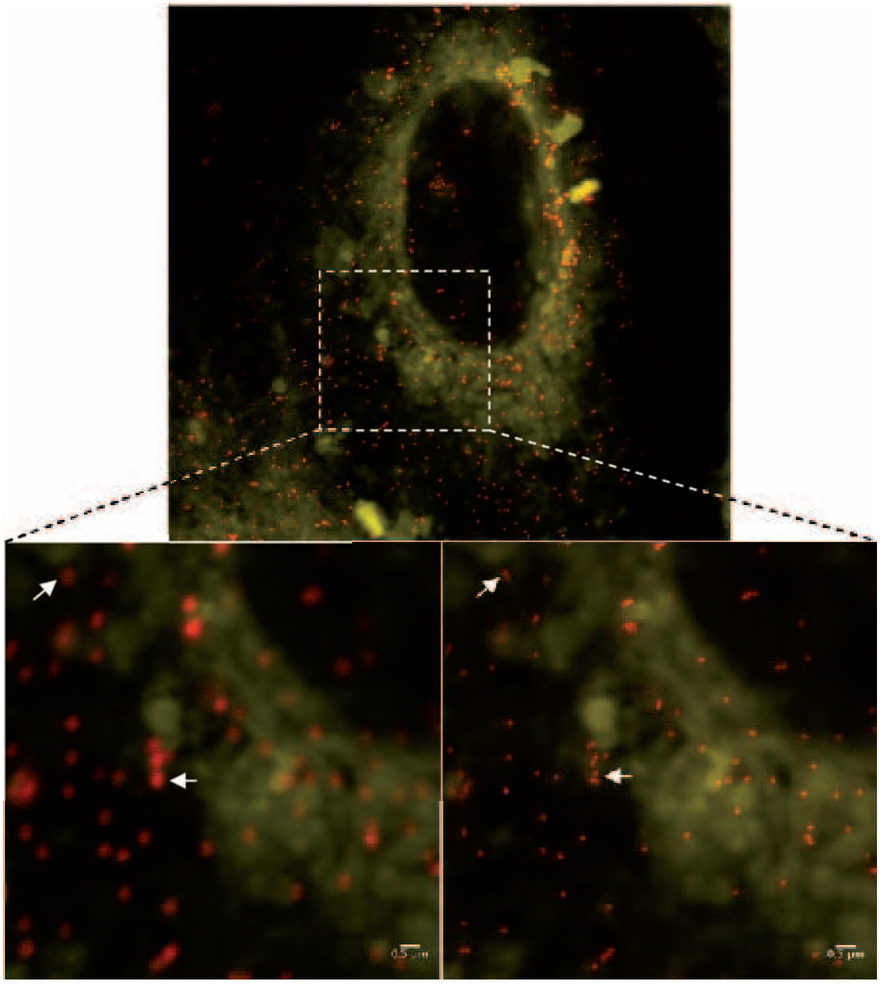

Figure 3: Top: A549 human lung epithelial cell (yellow: DiI membrane stain) after 24 h incubation with 130 nm diameter SiO2 nanoparticles (red). Bottom left: Zoom in using conventional confocal resolution. Bottom right: Same zoom area using STED. The arrows mark separation of sub-100 nm spaced particles not resolvable in standard confocal microscopy.

However, conventional confocal microscopy is limited by optical diffraction of the excitation laser spot and the resulting emission spot on the sample. This diffraction limiting case yields a lateral resolution of $\Delta s \approx \lambda / 2\ N\ A$, where $I$ is the emission wavelength of the fluorescent dye and NA the numerical aperture of the microscope objective. Even with high-performance immersion objectives, the numerical aperture is limited. Furthermore, the use of light with a smaller wavelength for imaging induces ionization and is not compatible with sensitive biological specimens, leaving the diffraction barrier as the central bottleneck for optical resolution in fluorescence microscopy.

The idea behind STED microscopy [5-7] is to confine the fluorescence emission spot on the specimen to a much smaller area than determined by diffraction by using the photophysical properties of the fluorescent marker. In the pulsed implementation used here, a short (picosecond) excitation laser pulse in the absorption spectrum of the dye is followed by an intense STED laser pulse in the red wing of the fluorescence spectrum that induces stimulated emission, and thus effectively depopulates the fluorescent $S_1$ state (Figure 1). In order for this scheme to induce a resolution enhancement, the depopulation is spatially located in a pattern encircling the center of the excitation spot (Figure 2a), and the photon flux of the STED laser is adjusted to saturate the transition from $S_1$ to $S_0$. The resulting optically induced, nonlinear deactivation of the fluorescence in the region covered by the STED laser yields a resolution enhancement which is theoretically only limited by the STED laser power applicable. The optical resolution in STED is given by $\Delta s \approx \lambda (2 N A \sqrt{1+I / I_S})$ where $I$ is the intensity of the depletion beam and $I_s$ is the intensity required to reduce the fluorescence by half. The performance of the STED technique was quantified by 3D imaging of sub-resolution sized fluorescent beads. Lateral and axial sections through the resulting point spread functions (PSFs) reconstructed from the experimental data are depicted in Figure 2b and 2c, respectively. The experimentally determined lateral resolutions are 80 ± 3 nm for STED imaging as compared to 264 ± 2 nm in conventional confocal mode (Figure 2d). However, it should be noted that the axial resolution is unaffected by the STED implementation used, and is rather still diffraction limited (Figure 2c), where the optical resolution is given by $\Delta s \approx \lambda / N A$. The central role of the fluorescent dye in the resolution enhancement puts spectral and kinetic compatibility requirements on its photophysical properties. Also, the combination of small pixel sizes and repetitive $S_0$-$S_1$ cycling of the dye by the laser pulse trains involved demands for excellent photostability. Furthermore, the reduced signal-to-noise ratio (SNR) of STED (see below) necessitates longer pixel dwell times and slightly higher excitation intensities. Finally, the desire for multidimensional recording (3D stacks, time series) requires extremely stable dyes compatible with the STED implementa-

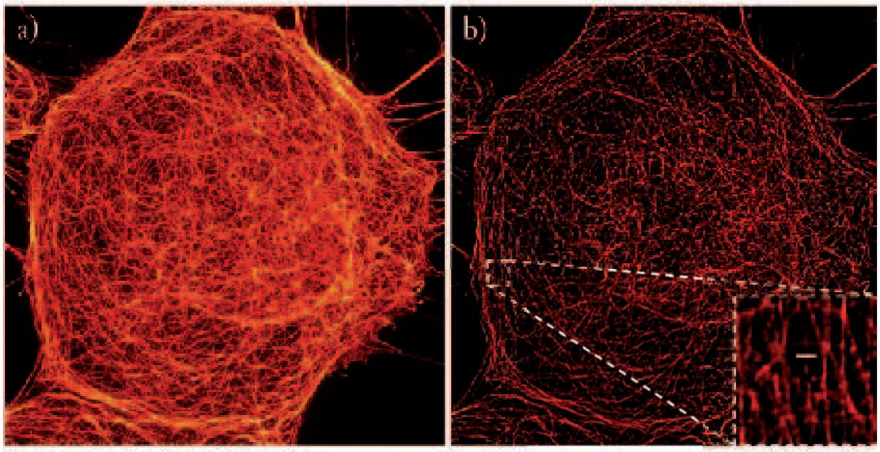

Figure 4: Nonlinear deconvolution of STED image data. a) Original data: Tubulin cytoskeleton of a Caco-2 colon epithelial cell, immunostained with Atto647N. b) Identical image after nonlinear deconvolution by wavelet-thresholded Landweber algorithm, regularization parameter 0.05. Inset: Zoom of indicated region, the FWHM (Gaussian fit) of the section profile of the marked filament is 55 ± 5 nm.

tion present, for example Atto647N and Atto655.

The direct point-to-point imaging property of STED substantially differentiates this super-resolution technique from statistical methods like PALM [8] or STORM [9] and gives access to sensible time-resolved (live cell) experiments [10]. Fixed-cell experiments, to demonstrate the applicability of STED microscopy on the investigation of nanoparticle-cell interactions, have already successfully shown the additional information gained by the increased resolution [11]. For example, the study of the agglomeration behavior of cell associated nanoparticles demands an experimental method that can resolve single particles while being able to precisely differentiate cellular components. As can be seen from Figure 3, STED microscopy is ideally suited to this range of applications, being able to separate single nanoparticles within agglomerates. Its compatibility with physiological sample conditions also opens the possibility of exploiting its superior resolution in live cell imaging [10; 12].

## Nonlinear image restoration

The resolution enhancement by STED microscopy is achieved solely by exploiting the photophysical properties of the fluorescent dyes, and thus STED microscopy still can be viewed as a purely physical image formation process with the ability of defining and measuring its PSF. The most common approach of modeling the physical image formation process assumes a linear relationship, in which the object is convolved with the PSF of the imaging system with additional poisson-distributed photon noise, $f = h \otimes g + n$ with the image $f$, the PSF $h$, the object $g$ and the unknown noise $n$. In order to recover the true object $g$ from the detected image $f$, the convolution operation is to be reversed [13]. In signal processing terms, the limited resolution of the imaging system is equivalent with a band limited spatial frequency response. Thus, spatial high-frequency noise is strongly amplified in the inverse operation of the convolution, and a successful determination of an estimate for $g$ requires additional constraints on the problem. This additional regularization differs among deconvolution methods.

Linear solutions to the regularized inverse problem apply least-square or smoothness constraints to the estimate for $g$ and are easy and computationally efficient to implement [14]. These additional constraints increase the SNR of the image; however, linear deconvolution techniques are unable to restore spatial frequencies lost in the band limited imaging process, and are thus unable to increase resolution.

Nonlinear image reconstruction methods are based on iterative deconvolution steps and application of the regularization operator. The most widespread class of methods relies on regularization by maximum entropy methods to enforce smoothness of the solution [15; 16]. Additionally, recent developments in mathematical image processing brought forth methods based on wavelet domain sparseness constraints [17-19], and hybrid methods have also been used [20]. In contrast to linear deconvolution, iterative nonlinear image reconstruction allows resolution enhancement. The increase in resolution is dominated by the regularization parameter balancing the data fitting and smoothness measures of the solution, the permissible range of which is determined by the signal-to-noise ratio (SNR) of the image.

Nonlinear deconvolution of fluorescence micrographs has been routinely applied to widefield fluorescence and confocal image stacks, but its application to STED images raises new challenges. It is especially important to choose an appropriate regularization parameter as a choice based on established methods [21], will result in smoothed solutions, effectively reducing the resolution gained by STED. Compared to conventional confocal microscopy, the resolution enhancement in STED is obtained at the expense of a reduced SNR, which is induced by the signal attenuation in the center of the fluorescent spot by residual STED beam light and the general increase of Poisson noise due to lower photon numbers per sampled Volume. Thus, special care has to be taken when manually adjusting the regularization parameter so that resolution is still increased while avoiding deconvolution artifacts. Examples of deconvolution results are depicted in Figure 4, which shows maximum projections of STED stacks of the immunostained tubulin cytoskeleton of Caco-2 human colon epithelial cells as original data and after deconvolution using a wavelet-thresholded Landweber algorithm [17; 18]. The noise reduction is clearly visible, and the resolution has been improved to approx. 60 nm (Figure 4b inset). Also, deconvolution can substantially increase the dynamic range of fluorescence micrographs, which leads to a visually darker appearance.

## Outlook

The combination of STED microscopy with nonlinear image restoration gives access to a substantial increase in optical resolution while still maintaining physiological conditions for the cell model. Together with the potential of selectively labeling cellular components involved in the nanoparticle-cell interaction, it constitutes a powerful tool for the exploration of the molecular and cell-biological mechanisms that underlie the effects of nanoparticle exposure. The application of these tools to the controlled experimental conditions of an *in vitro* cell model interacting with thoughtfully engineered and well-characterized nanoparticles in fixed-cell and live-cell experiments promises substantial insight into endocytotic pathways and intracellular transport, as well as intracellular interactions of nanoparticles.

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# Gruppenberichte /
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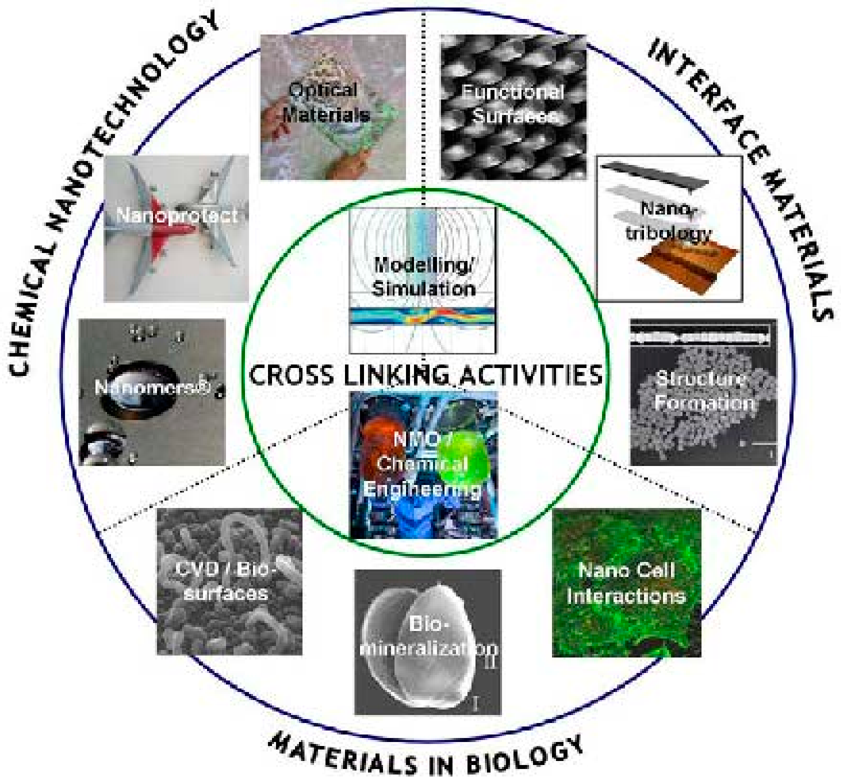


# Nanomere / Nanomers

### Dr. Carsten Becker-Willinger

Der Programmbereich *Nanomere* befasst sich mit Materialentwicklung im Bereich der Nanokomposite mit hybrider und polymerer Matrix zur Anwendung als funktionelle Beschichtungen sowie als kompakte Bulkmaterialien. Ein großer Anteil des Know-hows im Programmbereich betrifft die nasschemische Synthese und die spezifische, maßgeschneiderte Oberflächenmodifizierung von Nanoteilchen zur Kompatibilisierung mit überwiegend polymerartigen Matrizes um letztlich zu Nanokompositsystemen zu gelangen, in denen die Nanopartikel nahezu perfekt dispergiert vorliegen. Weiterhin werden neuartige polymerartige Matrizes entwickelt, die in Kombination mit den Nanopartikeln die Möglichkeit eröffnen, zu Materialien mit maßgeschneiderten Eigenschaften zu kommen. Der Programmbereich beschäftigt derzeit 14 Mitarbeiter mit überwiegend chemisch-synthetischem Hintergrund, die mit ihren Möglichkeiten das komplette Spektrum von grundlegender Materialentwicklung bis hin zur professionellen Abwicklung von Entwicklungsprojekten für industrielle Partner abdecken. Die Konzentration des Know-hows in der Gruppe ist ein unverzichtbares Werkzeug, um maßgeschneiderte Werkstoffe in kurzer Zeit zu entwickeln. Völlig neue Ansätze zur Erzeugung interessanter neuer Morphologien und Eigenschaften werden derzeit im Rahmen zweier Doktorarbeiten erarbeitet. Es konnte eine steigende Anzahl an Publikationen und Beiträgen in Proceedings bei unverändert hoher Akquisitionsleistung im Bereich von Industrieprojekten mit hochanspruchsvollen wissenschaftlich-technischen Fragestellungen erreicht werden. Dies ist das Ergebnis der erfolgreichen Kombination von langjährigem INM-Know-how durch erfahrene Mitarbeiter mit einer strategischen Quervernetzung des Programmbereiches mit den anderen Forschungsbereichen und den Ingenieursfachleuten innerhalb und in unmittelbarer Nachbarschaft des INM.

Schwerpunkte der Materialentwicklung bilden verschleißfeste Gleitbeschichtungen mit extrem niedrigem Gleitreibungskoeffizienten, multifunktionelle, flexible Hartbeschichtungen mit integrierter Barrierefunktion sowie smarte Kompaktwerkstoffe mit adaptiven mechanischen Eigenschaften. In den genannten Feldern besteht eine starke Nähe zur Anwendung, so dass nach erfolgter Optimierung der Werkstoffe eine problemangepasste Technologieentwicklung durchgeführt wird. Dabei ist eine enge Verzahnung mit der Applikationsabteilung und den Engineeringsbereichen notwendig, um die Basisentwicklungen auch erfolgreich in die Produktionsabläufe der entsprechenden Partner zu implementieren. Darüber hinaus werden auch Basisentwicklungen vorangetrieben, die beispielsweise das grundlegende Verständnis des Phänomens der Kratzfestigkeit von Oberflächen oder auch die Beeinflussbarkeit des Benetzungsverhaltens innerer Oberflächen poröser Körper verbessern sollen. Die so neu geöffneten Forschungsfelder sollen später in entsprechenden Anwendungsentwicklungen, beispielsweise in den Bereichen Energietechnik, Maschinenbau oder auch Elektrotechnik und Medizintechnik, umgesetzt werden. Zusätzlich wurden die Entwicklungen des Programmbereiches weltweit im Rahmen von Messen, Tagungen und Roadshows vorgestellt und über diesen Weg zahlreiche neue strategische Kooperationspartner gefunden. Aufgrund der guten Resonanz ist auch für zukünftige Entwicklungen von einem großen Potential der Nanomer-Technologie auszugehen.

The Program Division *Nanomers* is performing materials research in the field of hybrid and polymer matrix nanocomposites for the use as functional coatings and compact bulk materials. A big part of the know-how in the Program Division can be ascribed to the wet chemical synthesis, specific surface modification and compatibilisation of nanoparticles with polymer type matrices, which is crucial for obtaining nanocomposite systems with almost perfectly dispersed nanoparticles. Additionally, new polymer type matrices are developed, which in combination with the nanoparticles enable the development of materials with tailored properties. The Program Division consists of 14 persons with mainly chemical background and highly developed synthetic skills performing basic research, as well as applied research for industrial partners. The expertise concentration in the group is an important prerequisite for developing tailored materials within a short time. Completely new approaches on morphologies have been developed within the course of two doctoral theses. An increasing output of refereed papers and conference proceedings, while maintaining the successful acquisition of third-party financed projects from industry is a result of the combination of long term internal INM expertise and cross-linking activities of the Program Division *Nanomers* with other research groups and engineering people within INM.

One focus of the Nanomer materials is on wear resistant low friction coatings. Specific types of solid state lubricants and combinations thereof have been dispersed in Nanomer matrices which can be applied like paint. This approach enables the combination of a low friction coefficient with excellent adhesion and corrosion protection suitable for e.g. low alloyed steel and aluminum. Long term low friction properties over long sliding distance are of high interest as well as insight into stick-slip behavior. With respect to the latter point, a stick-slip testing device has been developed together with an industrial partner that enables the investigation of friction behavior at very short sliding distances with high lateral and time resolution. Figure 1 shows the experimental set-up of the new stick-slip testing device.

New material combinations and processing technologies enabled to achieve friction coefficients which are usually attainable by hydrodynamic lubrication only.

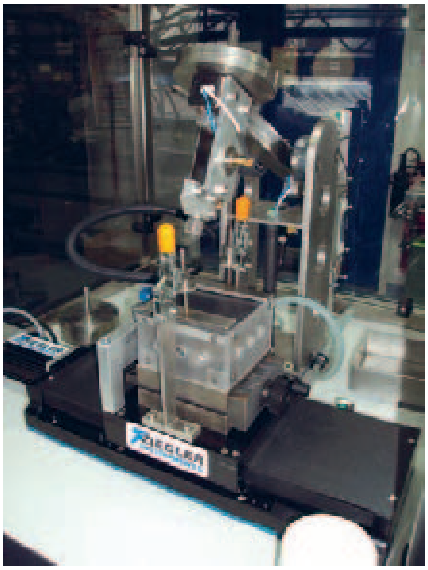


Figure 1: New stick-slip testing machine as excellent method to investigate the tribological properties of Nanomers at very short sliding distances with high lateral and time resolution.

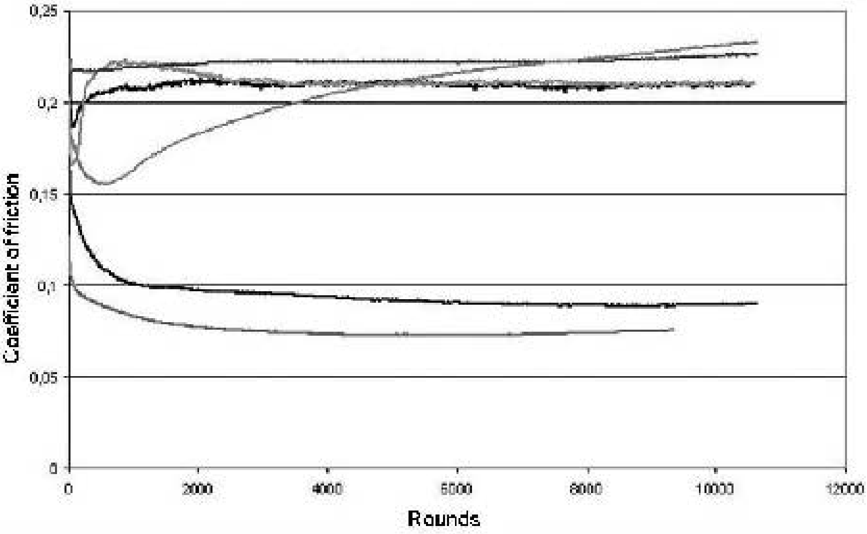


Figure 2: Friction coefficient for Nanomer low friction coatings with different composition in dependence on the number of cycles in the pin-on-disc tribometer.

Figure 2 shows examples of such Nanomer coating materials containing solid state lubricants, demonstrating extremely low friction coefficient without the use of oils (hydrodynamic friction mechanisms).

As can be seen in Figure 2, a friction coefficient below $\mu = 0.08$ can be achieved for one of the systems over a long sliding distance. This is an important milestone which shows the great potential of the Nanomer systems. Similar coating materials have been successfully applied on steel valves used in the oil industry, an application that will be followed up in 2010 by the *Application Center NMO*, with strong support by the Program Division *Nanomers* and in cooperation with a spin-off company already active in the oil business.

Another focus of Nanomer coating systems is on multifunctional flexible hard coatings. The development of a fast curing labeling paint has been performed for an industrial partner producing steel pipes for the oil industry. The paint provides highly visible contrast against the steel substrate, cures within seconds after spray coating using the remaining heat after pipe production, and shows extremely high abrasion and impact resistance. This material will be introduced in the near future into the running production at the customer site. For another area of application, abrasion resistance has been combined with barrier properties against gas diffusion. In this special application, a spray-coatable paint for the inside of steel pipes has been developed that controls the penetration of corrosive gases like hydrogen disulphide or carbon dioxide towards the substrate surface, thus preventing stress corrosion cracking. The concept has also been extended to the long term corrosion protection of gas cylinders. For both applications a technology transfer project is envisaged.

Much investigation effort has also been invested in the use of nanoparticulate additives for conventional coatings and paint systems with respect to polymerization catalyzing properties and tuning of optical properties. In a project supported by the BMBF, the investigations are focused on the effects of nanoparticles catalyzing especially UV photo-polymerization reactions in acrylic coating systems. Figure 3 shows nanoparticulate anatase synthesized *in situ* in an acrylic matrix.

By incorporation of these particles in a concentration of about 2 %, an increase of the polymerization rate by up to 75 % could be achieved compared to the unfilled acrylic systems. This intrinsic property of the nanoparticles has high industrial relevance and can be a useful alternative for conventional approaches using organic molecules as photo-initiators.

In addition to these ongoing projects, several postdocs are working on new topics such as fundamental investigations of the mechanisms involved in scratch formation and scratch prevention in collaboration with the Program Division *Nanotribology*, as well as the development of new materials with adjustable mechanical and thermal properties for gecko surfaces in collaboration with the Program Division *Functional Surfaces*. Another fundamental research activity has been started

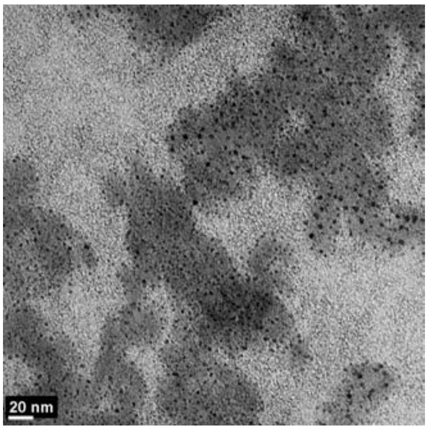


Figure 3: TEM micrograph of anatase nanoparticle photocatalysts after *in situ* synthesis in acrylate matrix.

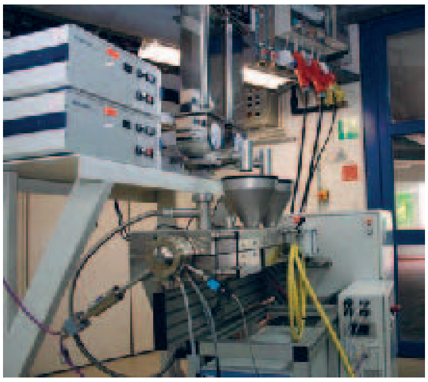


Figure 4: New two screw extruder for thermoplastic processing and compounding at the lab scale.

under the support of the BMBF concerning the development of new materials to provide enhanced oil recovery that can be applied directly in the bore hole. This activity has been started in order to meet future demands in the energy sector.

In the area of polymer matrix nanocomposites, nanoparticles have been used in polymer matrices to tailor optical, thermal and mechanical properties of compact bulk materials. In one project, high refractive index nanoparticles free of photocatalytic activity have been developed that can be incorporated as an additive in polymeric and hybrid matrices. Furthermore, an important development project is the creation of special morphologies in polymer based bulk materials, which allow the fabrication of smart composites with adaptive mechanical and thermo-mechanical properties. These types of materials are fabricated by compounding using a lab size two screw extruder as shown in Figure 4.

The analytical methods in the area of polymer matrix nanocomposites have been renewed and extended. Two dynamic methods have been established as important tools to monitor the visco-elastic and the dielectric behavior of the materials under investigation. Figure 5 and Figure 6 show the new dynamic mechanical thermal analysis (DMTA) equipment and the new dielectric spectroscopy (DE spectroscopy) respectively.

In 2009, many projects with industrial partners have been carried out in the Program Division, most of them subject to specific non-disclosure agreements.

Furthermore, it is important to note that for most of the cooperation projects, technology development in addition to the pure materials optimization was of high importance, to transfer the results from the lab scale to the practical application. This step has been performed together with the Application Center of INM (*NMO*). All technologies have been protected by appropriate patent applications to establish contact with prospective collaboration partners and to generate new opportunities for cooperational research projects.

In addition, the group has also participated in expositions on fairs and road shows worldwide. From these activities, the big potential of the Nanomer technology for a broad range of applications was obvious, especially for e. g. energy and power generation, engineering and printing industry. Consequently, it is expected that the chemical nanotechnology approach has not tapped its full potential yet and should be able to offer completely new solutions in the future. Such future applications require the development of new materials concepts e. g. for transparent conductive materials, high gas diffusion barrier properties and special morphological arrangements in composites, which will be performed in collaboration together with the Program Divisions *Optical Materials*, *Biomineralization*, *Nanoprotect* and *Structure Formation at Small Scale*, as well as research groups from the Saarland University.

Figure 5: Dynamic mechanical thermal analysis setup for polymer matrix nanocomposite films and bulks.

Figure 6: Dielectric spectroscopy for polymer matrix nanocomposite films and bulks.

# Nanoprotect / Nanoprotect

## Dr. Matthias Wittmar

Hauptaufgabe des Programmbereichs *Nanoprotect* ist die Entwicklung von neuen Schutzsystemen für Leichtmetalllegierungen und Stahl, die Synthese, Oberflächenmodifizierung und die Anpassung von unterschiedlichen, zumeist oxidischen Partikeln an unterschiedlichste Medien, die Verwendung derartig modifizierter Partikel in anorganisch-organischen Hybridmatrizes für z. B. den Korrosionsschutz von Metallen sowie die Entwicklung von Bindersystemen und Additiven auf Silanbasis. Eine weitere Kompetenz des Programmbereichs ist die Entwicklung von neuen Materialien mit kombinatorischen Methoden. Mittelfristiges Ziel des Programmbereichs ist die Entwicklung von selbstheilenden Materialien und funktionellen Partikeln z. B. für druckbare Schaltungen und keramische Beschichtungen. Hauptthemen im Jahr 2009 waren die Bearbeitung der folgenden Projekte sowie eines Industrieprojektes:

- Multiprotect
  Ziel des Projektes war die Entwicklung von chromfreien Korrosionsschutzschichten und Primern für Aluminium-, Magnesiumlegierungen und Stahl unter Verwendung von Inhibitoren in unterschiedlichen Matrices. Multiprotect wurde 2009 erfolgreich beendet.

- PriMeBits
  Das Projekt zielt auf die Herstellung von ferroelektrischen Partikeln zur Einarbeitung in Druckertinten und deren Verwendung zur Herstellung von druckbaren Speichern.

- Unacon
  Ziel ist die Entwicklung eines Betonadditivs, das abweisende Eigenschaften und damit einen Schutz vor Verschmutzung in den Stein einbringt.

- EcoRepair
  Im Projekt soll eine Reparaturmasse für die ökologisch und ökonomisch sinnvolle Ausbesserung von Glasurfehlern an Sanitärkeramiken entwickelt werden.

Die Projekte PriMeBits, UNACON und EcoRepair werden 2010 weiter fortgesetzt. PriMeBits und UNACON werden in diesem Jahr beendet werden. Die Entwicklung von Korrosionsschutzbeschichtungen, Inhibitoren, Bindern und Additiven sowie von funktionalen Partikeln und Partikelpackungen soll weiter fortgesetzt werden.

## Introduction

The main objectives of the Program Division *Nanoprotect* are the development of anticorrosive inorganic-organic hybrid coating systems for the protection of light metal alloys and steel, the synthesis, surface modification and adjustment of various, mainly oxidic, particles in organic solvents and water solutions, the use of these particles as functional elements, and the development of binder systems for a diversity of bindable materials. The use of combinatorial techniques to find novel materials is also a topic of the Program Division. The aim of the Program Division is the development of self-healing materials and special functional particles for printable electronics and ceramic coatings.

During 2009 the group was active in four publicly funded projects. The EU project MULTIPROTECT dealing with the development of Cr(VI) free corrosion protection coatings for light metal alloys and steel was successfully completed. The EU project PriMeBits on particles for printable electronics and the EraSME project UNACON on cement additives were continued. A new BMBF project EcoRepair was started; in this project *Nanoprotect* and the Program Division *Optical Materials* are working together on the development of energy saving repair techniques for ceramic products. An industrial project on corrosion protection coatings for steel was started.

## Anticorrosive coatings

In 2009 the Program Division continued the coordination of the European project MULTIPROTECT with 31 partners from 13 European countries. In May 2009 the final review meeting of MULTIPROTECT was held in Saarbrücken. The outcomes were presented in front of the representatives of the European commission, and approved by the reviewers. The final report of the project was subsequently submitted to Brussels. In the project, INM discovered synergistic effects of some rare earth components when used as corrosion inhibitors in coatings. Also, dense and easy to prepare corrosion protection systems for aluminum were investigated. Both investigations were presented on international conferences at Eurocorr 2009 and ASST 2009.

The year was mainly determined by the development of flexible corrosion protection coatings for steel surfaces. Here a bilateral industry project was started. The properties of corrosion protection coatings were further characterized. The resistance to outdoor weathering of aluminum and steel protection systems was investigated. Further, studies regarding the adhesion on and the corrosion protection of polished and non-polished steel substrate were stressed. It was found that polishing and primering of the substrates have a huge influence on the lifetime of the coating. Polishing without primer leads to an early failure of the coating by subsurface migration and by breakdown of the adhesion. Due to the higher roughness of non-polished steel

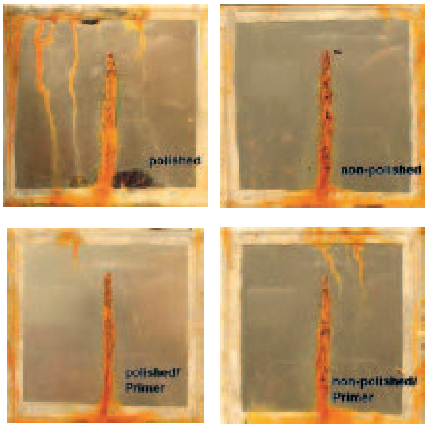


Figure 1: Polished and non-polished steel substrates with and without Zirconium-primer after 600 h in neutral salt spray test.

Figure 2: Logo of the EU project “PriMeBits“. For further information, please refer to the project website address www.primebits.eu.

substrates, coatings on these substrates survived the accelerated aging in neutral salt spray test (SST) ~1000h longer than polished ones. Using a Zr-primer a further increase of the lifetime of the coating was realized. Until the end of 2009, the coating had survived 1550 h in SST without significant degradation.

## Synthesis, processing and use of particles

Within PriMeBits, the Program Division is responsible for the development of synthesis routes for deagglomerated ferroelectric nanoparticles which are tailored with regard to the envisaged printing process and device. Further, the examination of the structure property relations of particulate FRAM (ferroelectric random access memory) cells arose as an interesting main topic of our work. In the reporting period, we presented first results on two conferences, and prepared two papers. The project cooperation was intensified for the FRAM part by an intense 'FRAM week' with colleagues from VTT, Evonik and EPFL at INM in November.

Also, the whole PriMeBits project (coordinator: VTT, Finland, Jan. 2008 - Dec. 2010) runs very successfully. The preparation of WORM (write-once-read-many-times) memory demonstrators as well as the development of application ideas for both memory types are exemplary highlights of the reporting period to be presented in public in 2010.

## Composites and ceramic coatings

Generally, the properties of composite materials are strongly influenced by the distribution uniformity of the dispersed phase within the matrix. This can be realized by a suitable surface modification of the dispersed phase particles.

Sol-gel based ceramic coatings containing surface modified inorganic particles of hard materials like SiC or $Al_2O_3$ were prepared. The coatings obtained were micro-porous, but suitable for several areas of application. Due to the inorganic bonding, the coatings are stable even above 1000 °C. The properties of the coatings could be tailored by the type of ceramic particles, their particle size distribution and by the way of binding. Figure 4 shows a steel test sample which is coated on one half with SiC (Taber abrader test CS 10F, 2000 cycles; total wear < 2 mg).

The hardness and wear strength of alumina ceramics can be improved significantly by the incorporation of nano scaled zirconia particles. A problem arising with the use of nano-scaled zirconia is the coarsening of the particles by sintering at temperatures below the onset of the matrix-phase sintering. That is the reason why the nano-effect cannot be utilized to full extent, but the agglomeration and coarsening of the nano scaled particles can be reduced by coating of the matrix phase particles with nano-scaled zirconia in wet conditions including a suitable surface modification of zirconia particles (Figure 5).

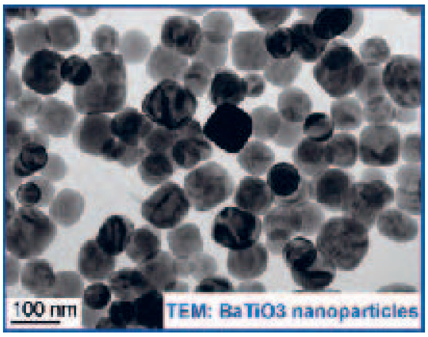


Figure 3: TEM image showing $BaTiO_3$ nanoparticles (average size 63 nm) synthesized at INM.

Figure 4: SiC coated steel sample after taber-abrader test.

## Combinatorial material development

In 2009, the fundamental research on materials within the ternary system CuO-$TiO_2$-CaO was continued. The doctoral student Shuhua Ren successfully finished her work on this topic. In her doctoral thesis she investigated the influence of sintering temperature and preparation conditions on the dielectric properties and the microstructure evolution of the resulting solids, with emphasis on the different phase regions in the ternary system. Depending on the sintering temperature in two regions of the system, giant dielectric constants over 10,000 were found.

## Binder and additive development

In 2009, the UNACON project (BMWi funded European project in the EraSME program) was continued. The overall idea was the development of a mass additive for earth moist concrete usable for the production of small-sized concrete goods showing enhanced hydrophobicity and resistance against environmental influences (Figure 6).

During the second year of the UNACON project, the main focus was the strongly retarding effect of additives on the concrete setting and hardening. It was assumed that the hardening process of the concrete samples can be influenced by higher condensation degrees and by reducing the alcohol content of the sol-gel based additives. Simultaneously investigations on the kinetics of the synthesis and the aging of the resulting product were performed. An assessment of shelf-life of the product, up-scaling of the synthesis or intensification of the hydrophobic effect was necessary. The only suitable method of characterization for the additives was $^{13}C/^{29}Si$-NMR, giving quantitative values for the degree of condensation and the amount of chemically bound masking agent.

As a second publicly funded project, the BMBF project EcoRepair was started together with the Program Division *Optical Materials* and three German SMEs. Our function in this project is the development of a low temperature sintering binding matrix based on the proven nanobinder concept (www.ecorepair.info).

## Outlook

For 2010, the continuation and finalization of the EU project PriMeBits and the EraSME project UNACON are planned. The technical management meeting of PriMeBits will be held in Saarbrücken in May. Also the BMBF project EcoRepair will be continued. The investigation of inhibitors for corrosion protection, the incorporation of inhibitors and/or nanoparticles in hybrid-coatings, the adjustment of particle surfaces and the synthesis of special, functional particles will be continued. New publicly and privately funded projects are planed.

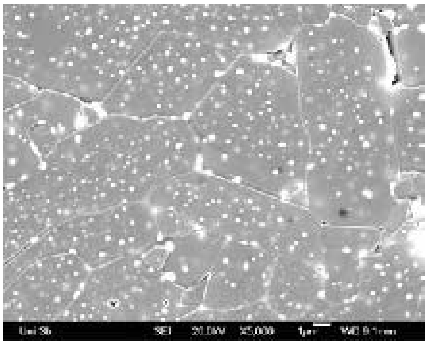


Figure 5: Sintered $Al_2O_3$-$ZrO_2$ composite ceramic.

Figure 6: Hydrophobic effect of a surface of a concrete with INM additive.

# Optische Materialien / Optical Materials

## Dr. Peter William de Oliveira

Der Programmbereich *Optische Materialien* ist ein technologisch orientierter Programmbereich, der sich vorwiegend mit der Entwicklung von Materialien und Methoden für optische und mikrostrukturierte Anwendungen beschäftigt. Mit Blick auf die im Folgenden genannten Anwendungsgebiete wurden zahlreiche Grundlagenarbeiten durchgeführt, aus denen sich elf referierte Publikationen ergaben. In den zahlreichen Projekten, die im Jahr 2009 durchgeführt wurden, stand die Entwicklung neuer Materialien und Technologien für die Fertigung optischer Komponenten und Beschichtungen für Solarenergietechnologie, sowie für Display- und gedruckte Elektronik-Anwendungen im Vordergrund.

Die Kooperationen mit anderen Programmbereichen konnten weiter ausgebaut werden, mit *Nanomere* auf dem Gebiet der Funktionalisierung von Nanopartikeln, mit *Nano Zell Interaktionen* zu DNA-basierten holographischen Materialien, und mit *Nanoprotect* auf dem Gebiet der photopolymerisierbaren Keramik. In Kooperation mit dem Programmbereich *Funktionelle Oberflächen* wurde das gemeinsame Up-scaling Programm für Geckostrukturen begonnen.

Folgende fünf Kernthemen standen im Mittelpunkt der Arbeiten:

*Antireflex (AR)-Beschichtungen*
Antireflexschichten auf Floatglas konnten die Transmission im Wellenlängenbereich zwischen 380 und 1200 nm um 8 % reduzieren. Sie sind durch den breiten Bereich des AR-Effektes besonders attraktiv für die Solarenergietechnik.

*Materialien für holographische optische Elemente*
In Kompositen konnte DNA erfolgreich als Biophotoinitiator zur Herstellung von Gradientenmaterialien und Hologrammen mit erhöhter Diffraktionseffizienz für optische Sicherheitsmerkmale bei Medikamenten und Lebensmitteln eingesetzt werden. Auch wurden neue ionische Flüssigkeiten in Verbindung mit neuen Mikrostrukturierungstechniken für die Anwendung z. B. in optischen Speichermedien entwickelt.

*Transparente, leitfähige Beschichtungen*
Bei den transparenten, leitfähigen Schichten lag ein Schwerpunkt der Arbeiten darin zu zeigen, dass sich die Gesamtleitfähigkeit eines Komposits aus ITO und Matrix durch Einsatz leitfähiger Binder erhöhen lässt, wobei auch gleichzeitig die Trübung bei konstanter Transmission reduziert werden konnte.

*Diffusionsbarrieren für $Cu(In,Ga)Se_2$ (CIGS) Solarkollektoren*
Im Projekt FlexNet wurden modifizierte glasartige Filme für die Photovoltaik entwickelt, die eine Diffusionsbarriere zwischen Substrat und CIGS-Material bilden, um so die Eindiffusion unerwünschter Elemente wie Eisen zu vermeiden. Gleichzeitig soll die Diffusion von Natrium aus der Schicht gefördert und eine Isolatorwirkung erzielt werden.

*Optische Materialien für das Design*
Ziel des Projektes EcoRepair ist die Entwicklung eines Reparaturmaterials für die keramische Industrie, das bei wesentlich niedrigeren Temperaturen als die Standardglasuren versintert werden kann. Gleichzeitig sollen die optischen, haptischen, chemischen und mechanischen Eigenschaften möglichst der umgebenden Glasur entsprechen. Dieses Projekt wird in enger Kooperation mit dem Programmbereich *Nanoprotect* durchgeführt.

The Program Division *Optical Materials* is a technologically orientated program area of INM. Its research is focused on the development of materials and methods for optical and micro-patterning applications. To increase the efficiency of this department, new strategies for the focusing of the research fields, as well as for the improvement of the sustainability of the selected research topics have been formulated. The increase of public funded projects, industry projects, and scientific journal publications is a result of this re-orientation. In 2009, the research of the department was funded mostly by targeted projects, which were mainly funded by German sources (BMBF, AiF, Leibniz-SAW, Europrofession, …), by Korean International Trade Association (KIAT), and by companies from Austria, Korea, Belgium, Luxembourg and the USA. In these projects new materials and technologies were developed for optical components and coatings for solar energy technology, display and printed electronics applications. A new research topic is the ontology for nanotechnology (funded by Leibniz-SAW), which will contribute to an improvement of knowledge transfer in nanotechnology.

Cooperations with other Program Divisions of INM and with Saarland University are: With *Nanomers* in the area of nanoparticle functionalization, with *Nano Cell Interactions* and Prof. J. Walter on DNA-based holographic material, and with *Nanoprotect* in the area of photopolymerizable ceramics. In cooperation with the Program Division *Functional Surfaces,* a joint up-scaling program for gecko structures has started, in which material properties and machinery for the embossing of structures with high aspect ratio are developed.

For this report, five following research topics have been selected for a more detailed description: Photovoltaic panels are primarily based on Si, CIGS, or CdTe. It is increasingly important to enhance the amount of light transported into the panels. During the development of the core-shell nanoparticles for the improvement of interference coatings, it was essential that a mixture of dispersed $SiO_2$ nanoparticles with a small amount of $TiO_2$ nanoparticles provided an excellent antireflective coating with a high abrasion resistance. A single layer coating from this sol can improve the average transmittance of the float glass by 8 % in the range of 380 nm to 1200 nm (Figure 1). The antireflective effect makes this sol attractive for the use in solar energy technology. Figure 2 shows that the reflectance of PET foils can be decreased from 5 % to 0.5 % at 650 nm. A homogeneous coating on large scale will be developed in the next phase.

The development of DNA-based composites for optical applications was funded by Europrofession. Fields of interest were holography and lithographic optical elements. In DNA the generation of double-strand breaks leads to changes of the refractive index. Another interesting point is the capability of DNA of forming radicals once irradiated with UV light. During this project, DNA was complexed with a cationic ligand and was thus soluble in an

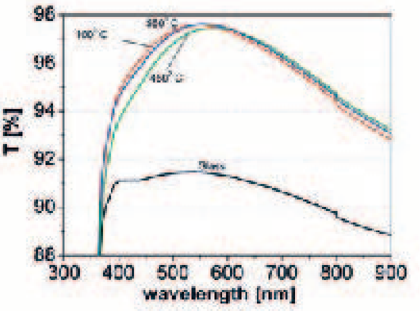


Figure 1: UV-VIS transmittance spectrum of uncoated glass and a coated glass with a porous single antireflective coating at different heat treatment temperature.

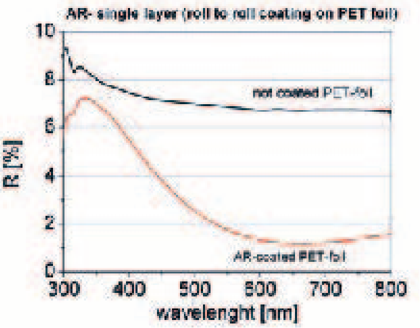


Figure 2: UV-VIS transmittance spectrum of uncoated and coated PET foils with a porous single antireflective coating.

organic matrix together with a monomer. With this mixture, the formation of a grid hologram by irradiation with an UV laser was possible. Subsequent real-time transmission measurement has shown an increase of the diffraction efficiency. Furthermore it could be shown that a rise of temperature led to a faster formation of a hologram and that the addition of ionic liquids significantly improved the diffraction efficiency (Figure 3). This feasibility study has shown that DNA can be used as bio-photoinitiator to induce a gradient of refractive index in micrometer scale and thus could find application in polymers for information storage or optical elements. The next research topic in this area will comprise the optimization of the writing time of the hologram in a biocompatible matrix to be used as data storage material for food industry.

For holographic and continuous roll-to-roll lithographic processes, a new ionic liquid (green solvent) based composite material, in combination with a new optical micro patterning technique, has been developed for optical management applications. Optical diffusers are key elements in liquid crystal displays (LCDs) as well as in security applications and photovoltaics. Generally our research has been focused on holographic diffusers due to their unique properties, such as controllable diffusion angle, directional property, volume refractive index variation and high transmittance. Hologram materials such as silver halide sensitized gelatine, dichromated gelatine, photopolymer and azobenzene polymer have been used.

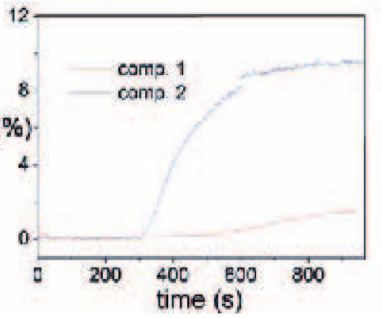


Figure 3: The diffraction efficiency (%) vs. time (s).
Comp. 1: TEGDMA (81 %), PVAC (17 %), DNA (2 %).
Comp. 2: TEGDMA (54 %), PVAC (11 %), Ionic Liquid (33 %), DNA (2 %).

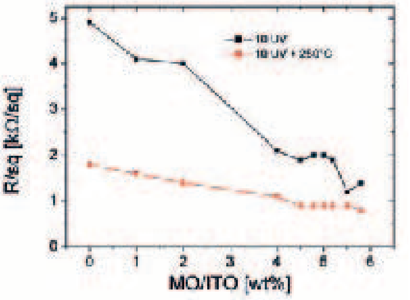


Figure 4: Partial replacement of the binder phase in the TCO paste by an *in situ* formed metal oxide phase leads to a reduction of the sheet resistance.

Ionic liquids are attracting considerable attention due to their unique physicochemical properties. They have high potential for the use in sustainable processes such as solvent replacement, catalytic reactions, electrochemical devices, and the synthesis of nanoparticles. Recently, we have reported that ionic liquids, based on dialkylimidazolium and used as additives in photopolymerizable hologram materials, can increase sensitivity, resolution, and diffraction efficiency. The material provides thin phase gratings with diffraction efficiency up to the theoretical maximum of 34 % in the thin hologram. In this context we used the material to fabricate optical diffusers for LCDs.

The need for thin conducting paths on plastic and glass substrates increases every year. This is not only due to the electronics or photovoltaics, but also to the packaging industry for tracking or labeling purposes. To overcome the time-consuming and expensive, but well established conventional photo-lithography, a new technique has been developed. Thereby, silver structures with lateral pattern sizes of some microns and more can be made within seconds to minutes by just irradiating a pre-coated substrate with UV-light through a photo mask. Due to the UV irradiation, the $Ag^{+}$-ions are converted to $Ag^{0}$ . For photovoltaics, sufficient conductivity is obtained. New studies to increase the silver path thickness will be performed in 2010.

Transparent conducting oxides (TCO) are of interest for many applications as displays, polymer electronics and thin film solar cells. Tin doped indium oxide (ITO, $In_2O_3$:Sn) coatings are most commonly used due to their high conductivity and high transmittance in visible light. Up to now, ITO coatings were usually fabricated on glass or plastic foils with cost intensive high-vacuum techniques. For rapid and inexpensive fabrication of polymer electronics, a cheaper deposition method of ITO coatings would be preferable. At INM, the fabrication of wet-chemically deposited ITO coatings was developed using a dispersion of ITO nanoparticles in a solvent and a UV curable binder. The coatings can be prepared by spin-coating or gravure printing and a sheet resistance R/sq of about 1 to 3 kΩ/sq can be obtained after UV-treatment. The printing of ITO coatings can be done by a low-cost roll-to-roll process on plastic foils. In order to decrease the sheet resistance, an enhancement of the matrix conductivity was studied by using metal oxides as additives in the binder matrix. An improvement of the matrix conductivity was achieved by introduction of conductive compound formed *in situ*, incorporated in the composite binder (Figure 4). The haze could be decreased to values smaller than 1 % (Figure 5).

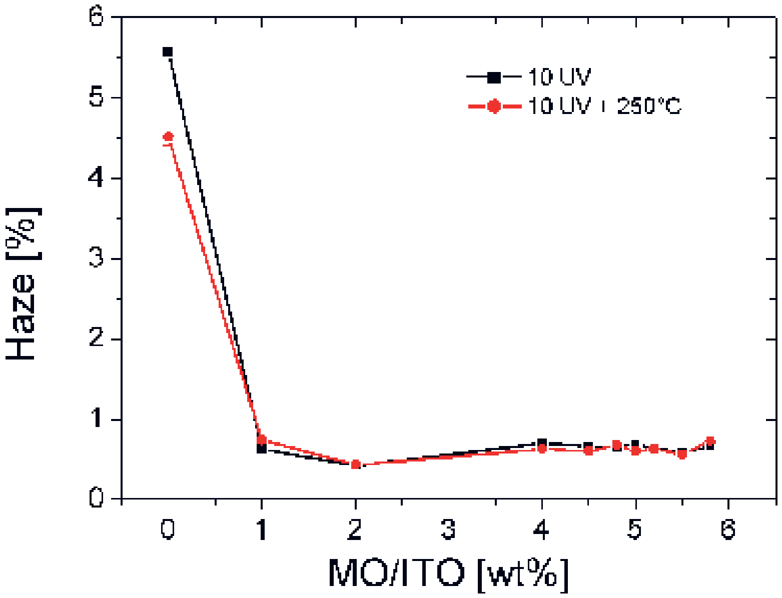


Figure 5: Partial replacement of the binder phase in the TCO paste by an *in situ* formed metal oxide phase leads to a reduction of haze.

In the course of the government-funded collaborative research project FlexNet, the development of modified glass-like films for use in photovoltaics has been pursued. The objective is to use flexible substrates, such as steel foil or polyimide, as a substrate for $Cu(In,Ga)Se_2$ (CIGS) thin film photovoltaic cells and monolithically integrated modules. The feature of the glass like film is to provide a diffusion barrier between the substrate and the CIGS absorber material, in order to avoid a reduction of the photovoltaic efficiency by in-diffusion of undesired elements, such as iron. Furthermore, the glass-like film is a source of sodium, which is known to be a beneficial dopant. A third function is to act as an electrical insulation layer. Single photovoltaic cells and integrated modules were produced by ZSW (Zentrum für Sonnenergie- und Wasserstoff-Forschung Baden-Württemberg, Stuttgart) on various steel substrates coated with glass-like films. Photovoltaic efficiencies up to 13.7 % for single cells on stainless steel substrates have been accomplished. Ongoing work is focusing on improving the reproducibility of the electrical insulation characteristics and the adhesion properties on both sides of the film.

In 2009, the work on a new project „EcoRepair“ has started in cooperation with the Program Division *Nanoprotect* and three industrial partners. In ceramic industry, production defects are machined away, refilled with glaze material and re-fired at 1200 °C for repair. The main target of EcoRepair is the development of an innovative repair material which can be cured at significantly lower temperatures than the standard glaze.

In the project, it was found that finely milled glaze is an excellent filler for repair Currently, the development and optimization of a glassy sol-gel-material for repair is performed.

Silver has been used for centuries as a conductor, as a reflector of light, as a photochrome or as a refractive index change agent. Our contribution in the area of silver thin films is to investigate how nano- and micro-structured silver can be used as a conductor or a transparent conductive coating for photovoltaics. The combination with actual transparent oxide coatings (TCOs) will be investigated in order to improve the electrical conductivity and the transparency of visible and near infrared light.

For the up-scaling of microstructured “Gecko surfaces” in continuous production processes, a new work group has been created in cooperation with the Program Divisions *Functional Surface* and *Nanomers*. The first goal was to define an optimal way for the up-scaling using methods like lithography, molding, casting or embossing. All methods have shown technical potential for the up-scaling of high aspect ratio structures. Embossed structures with high resolution were successfully obtained (Figure 6) with a well-defined shape, which depends strongly on the stiffness of the material. The next step will be the production of Gecko structures using a coating machine and a cylinder embossing setup. In this way a serious attempt is made to take the “Gecko technology” a crucial step further towards commercialization.

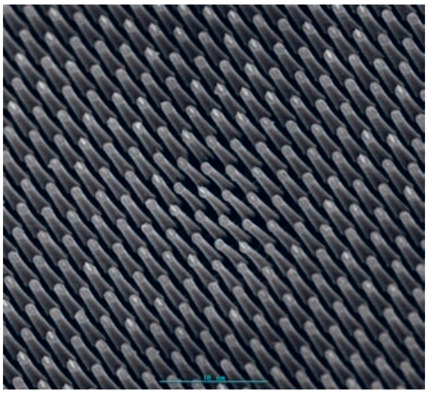


Figure 6: Embossed structures with high resolution.

# Funktionelle Oberflächen / Functional Surfaces

### Prof. Dr. Eduard Arzt

Der Programmbereich Funktionelle Oberflächen beschäftigt sich vorwiegend mit der Herstellung und Optimierung von mikrostrukturierten metallischen und Elastomer-Oberflächen mit neuartigen mechanischen Eigenschaften. Ziel ist die Erforschung und Anwendung von größenabhängigen Mechanismen, die die Einstellung neuer, vorzugsweise schaltbarer Oberflächenflächenfunktionalitäten erlauben.

Zentrale Fragestellungen des Programmbereichs sind:

*Herstellung von mechanisch schaltbaren Haftstrukturen*

Durch Verwendung von Shape-Memory-Polymeren kann die Haftkraft adhäsiver Strukturen durch Temperaturänderung beeinflusst werden. Das Einbringen von magnetischen Nanopartikeln erlaubt eine Strukturveränderung mittels eines externen magnetischen Felds.

*Hochpräzise Adhäsionsmessungen*

Der Neuaufbau eines Adhäsionsmessgeräts ermöglicht Adhäsionsmessungen mit sehr hoher Präzision. Mit Hilfe dieses Aufbaus sind erstmalig Messungen von adhäsiven Strukturen gegen unterschiedliche Oberflächenrauhigkeiten und -geometrien möglich.

*Entwicklung von Haftstrukturen für medizinische Implantate*

In einer Zusammenarbeit mit der HNO-Klinik des Universitätsklinikums in Homburg werden „Gecko“-Strukturen entwickelt, die als temporäre Implantate bei Verletzungen im Ohrbereich dienen können. Hierzu werden mechanische Untersuchungen zur Haftung an Haut sowie Untersuchungen zur Zellproliferation an strukturierte Polymeroberflächen durchgeführt.

*Up-scaling von Strukturierungsprozessen*

In enger Kooperation mit den Programmbereichen Optische Materialien und Nanomere wird intensiv an Strukturierungsverfahren gearbeitet, die auf größere Flächen angewendet werden können. Diese Arbeiten stoßen bereits auf vielfältiges Industrieinteresse.

*Oberflächen- und Größeneffekte in strukturierten Metalloberflächen*

Eine Reduktion der Probendimensionen führt bei metallischen Werkstoffen zu einer erheblichen Verbesserung der mechanischen Eigenschaften. Durch eine gezielte Mikro- bzw. Nanostrukturierung der Oberfläche können daher die tribologischen Eigenschaften von Metallen modifiziert werden.

Zum besseren Verständnis biologischer Haftsysteme wird die Auswirkung der Geometrie und der Materialeigenschaften der künstlichen Haftstrukturen auf die Haftung untersucht. Gleichzeitig werden weitere Möglichkeiten zur Schaltbarkeit künstlicher Haftsysteme entwickelt. Die so erhaltenen bioinspirierten Haftsysteme können dann mittels oberflächenchemischer Modifizierung weiter optimiert werden. Die großflächige Herstellung von Haftoberflächen wird intensiv weiter verfolgt, um Muster für verschiedenste Anwendungen bereit zu stellen. Im Gegensatz zu Polymerstrukturen zeichnen sich strukturierte Metalloberflächen durch ihre höhere mechanische und chemische Beständigkeit aus. Neue Verfahren für eine großflächige Strukturierung von Metalloberflächen werden entwickelt und die erhaltenen Strukturen auf ihre mechanischen Eigenschaften untersucht.

Der Programmbereich unterhält weitreichende internationale Kontakte und Kooperationen. Im Jahr 2009 verbrachten Frau Prof. Dr. Roya Maboudian und Dr. Carlo Carraro (University of California, Berkeley) ihr Sabbatical am INM. Für 2010 ist ein internationaler Workshop über Gecko-Materialien in Saarbrücken geplant.

The research of the *Functional Surfaces Group* is focused on the development of patterned surfaces with controlled mechanical and adhesive properties. The design of these surfaces is inspired by natural adhesive systems and by concepts of pattern formation in biology. Current research topics include geometry – adhesive property relationships, actuated polymeric and metallic adhesive systems, metallic nanocomposites and large scale surface patterning. We now also focus on the development of specific adhesive surfaces for industrial partners. Various research projects are highlighted:

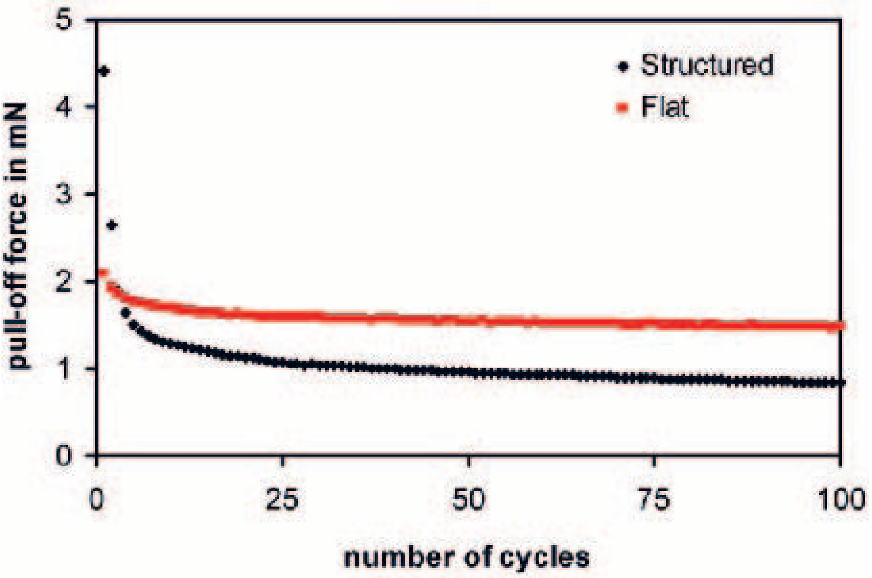


Figure 1: Effect of oligomer transfer from the sample to the substrate on the adhesion. The graph shows the pull-off force of a structured and a flat sample depending on the number of contact cycles. The structures had a diameter of ~ 4.5 µm, a height of ~ 2.2 µm and were hexagonally packed (packing density of ~ 4.7 %).

### Adhesion after repeated cycles

In a systematic study, we performed repeated adhesion measurements with the same poly(dimethylsiloxane) (PDMS) sample. It was found that the pull-off force drops significantly during the first several contacts and levels off after several hundreds of contacts (Figure 1). While the initial force values depend strongly on various parameters, such as surface chemistry of the mold and time between molding and adhesion measurement, a plateau is found after ~ 1000 contacts, which is independent of the fabrication protocol. This effect is explained by a transfer of free oligomers from the sample to the substrate. In this way, the surface energy and thus the pull-off force changes, reaching a dynamic equilibrium after a certain number of contacts (Figure 2). This effect was observed on both fibrillar and flat surfaces, but was much more pronounced for fibrillar arrays. Further experiments along these lines will be necessary to ascertain the mechanisms and to qualify certain polymers for repeated detachment applications (E. Kroner, R. Maboudian, E. Arzt, Adhesion characteristics of PDMS surfaces during repeated pull-off force measurements, Adv. Eng. Mater. 2010).

### In vitro adhesion experiments between skin and micropatterned PDMS

Another focus of the group is on the exploration of biomedical applications of “Gecko” surfaces. There is a growing need for biocompatible adhesives that can reversibly attach to soft, living and complex viscoelastic underlying tissue. In collaboration with the Medical School of Saarland University in Homburg (Department of Otorhinolaryngology, Prof. Schick) and with the Program Division *Biomineralization*, we investigated the adhesion performance of skin of mouse ear to micropatterned PDMS in comparison to flat PDMS substrates. No significant difference in separation force ($F_m$) was observed between flat substrates and micropatterned surfaces with pillar arrays. On the other hand, the energy necessary for separation of the substrate from the skin was sensitive to the topography (Figure 3). Furthermore, our results show that the force-displacement curves depended on the wetness of the skin: $F_m$ decreased as the skin dried out. Highest values for $F_m$ were obtained for fresh skin while the values dropped off significantly with increasing time between sample preparation and measurement (E. de Souza, M. Kamperman, G. Castellanos, E. Kroner, V. Armbrüster, M.-S. Romann, B. Schick, E. Arzt, 31st International Conference of the IEEE Engineering in Medicine and Biology Society Conference, Minneapolis, 2009). These results highlighted the great potential of our structures as temporary implants to support the healing of eardrum ruptures. In parallel, cell proliferation studies are conducted by our partners in Homburg.

## Adhesion measurements

To characterize the adhesive properties of these systems, we are building a second Macroscopic Adhesion measurement Device (MAD II) with high force and displacement resolution. New features of MAD II will include *in situ* visualization of material deformation during adhesion measurements using a (high-speed) camera, controlled humidity and temperature and lateral force measurements (Figure 4). These features will allow the exploration of a variety of novel systems and unexplored parameters, i.e. actuated fibrillar surfaces, effect of roughness and substrate geometries (e. g. flat punches or semi-cylinders).

In addition, first *in situ* adhesion tests in an environmental scanning electron microscope (ESEM) were performed (Figure 5). They give new insight into the details of detachment of a fibrillar structure. Contrary to most modeling approaches, detachment is found to be a stochastic event with defect control playing an important role. Another set of experiments was made in collaboration with the Program Division *Nanotribology*. Mechanical "communication" between different pillars through the backing material was discovered; it was successfully modeled by a continuum theory.

## Size-dependent plasticity of metals: towards micropatterned high-strength surfaces?

Microcompression tests were performed on focused-ion-beam-machined (FIB) micropillars of several body-centered-cubic (bcc) metals (W, Mo, Ta, and Nb) at room temperature (Figure 6). The relationship between yield strength and pillar diameter as well as the deformation morphologies were found to correlate with a parameter specific for bcc metals,

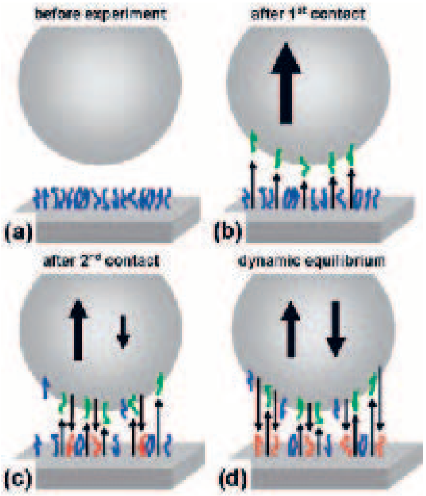


Figure 2: Schematic of the proposed mechanism for decrease in pull-off force upon repeated contact. (a) shows the system before the adhesion measurement. The probe is in a clean state, while free oligomers are present on the sample surface. (b): After the first contact, some free oligomers are transferred to the probe, changing its surface properties and thus influence the adhesion force. (c): After the second contact, more oligomers have been transferred to the probe, while back-transfer to the sample may occur. (d): Repeated contact experiments lead to a dynamic equilibrium. The transfer rate of the oligomers is constant and equal in both directions to and from the probe. The adhesive forces reach an equilibrium value.

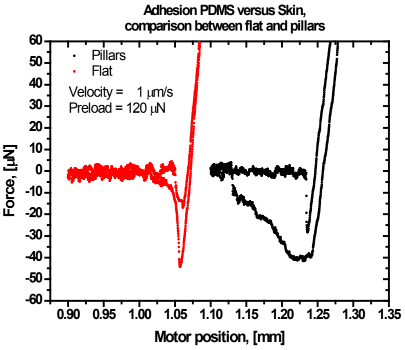


Figure 3: Force-displacement curves between PDMS and skin.

i.e., the critical temperature $T_c$. This finding sheds new light on the phenomenon of small-scale plasticity in largely unexplored non-fcc metals (Schneider et al., Phys. Rev. Lett. 2009). They are the basis for smart patterning of metal surfaces to achieve improved surface strengths and possible tribological properties.

The uniaxial compression behavior of single crystalline micropillars made of oxide-dispersion strengthened (ODS) alloys was also investigated. High critical resolved shear stress (CRSS) values were found which were independent of pillar diameter. This suggests that the deformation behavior is primarily controlled by the internal obstacle spacing, overwhelming any pillar-size dependent mechanisms, such as dislocation source activation or starvation. This study, for the first time, highlights an extreme of pillar studies, where a size effect is no longer measurable.

## Outlook

We have identified several design parameters that are important to control adhesion, among them pillar radius, aspect ratio and tip shape. The exploration of the parameter space is progressing and geometry and material property optimization are ongoing efforts. Parameters investigated are the influence of stiffness of the pillars, preload and backing layer thickness. These geometry-property relationships are used to guide the design of novel bioinspired artificial analogues.

We are currently exploring gecko-inspired switchable adhesive devices by combining patterning technologies with responsive polymer systems. Dependent on the particular system, switching can be induced using thermal, pressure or acoustic stimuli. In collaboration with the Leibniz Institute for Polymer Research in Dresden we aim to develop hierarchical responsive adhesives by a combination of photolithographic patterning techniques and chemical surface functionalization through polymer brushes. In collaboration with the Program Divisions *Optical Materials* and *Nanomers*, much effort is being devoted to the up-scaling of the patterning techniques to larger areas.

Microcompression tests have been performed on pure metals and oxide-dispersion strengthened (ODS) alloys to investigate the mechanical behavior of materials as their external size is reduced to sub-micron dimensions. Tests revealed that pure metals show a strong increase in strength with decreasing sample size, whereas the yield stress of ODS alloys is independent of sample dimensions. Due to this difference, pure metals reach the strength of ODS alloys in the submicron range. This clearly demonstrates the potential of small-scale metals structures: by reducing the sample size, pure metals can be as strong as highly alloyed, dispersion strengthened metals. To take advantage of this benefit, metal surfaces have to be micro- or nanostructured on a macroscopic scale. We are testing different approaches including nanoimprinting, template assisted electrodeposition and reactive ion etching to structure metal surfaces. The use of shape memory alloys may further lead to new actuated

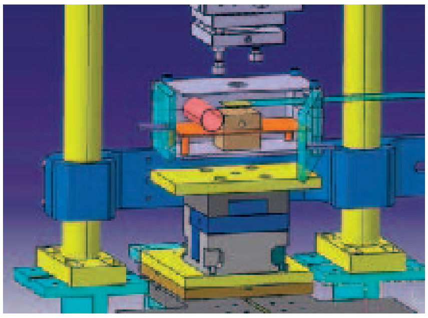


Figure 4: Design of the humidity control chamber for the Macroscopic Adhesion measurement Device (MAD II).

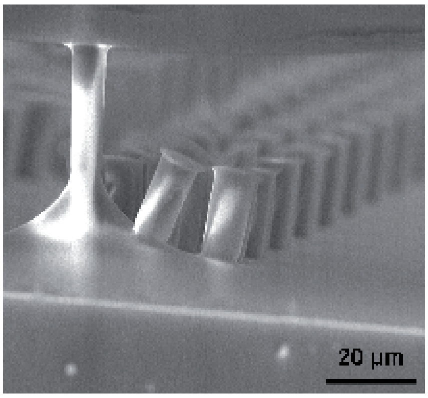


Figure 5: In situ adhesion experiment on a PDMS fibrillar surface.

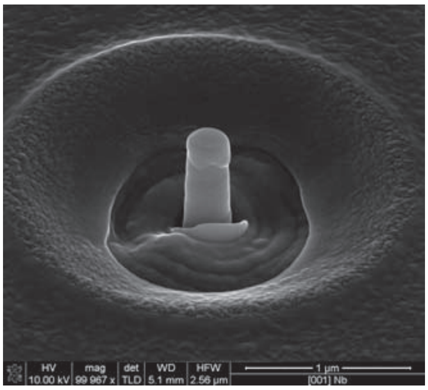


Figure 6: Scanning electron micrograph of a FIB machined, [001] oriented Nb pillar with a diameter of ~ 200 nm.

systems, due to their capability of changing shape under an external stimulus. To date, little fundamental understanding exists regarding shape memory surfaces. Further experimentation is critical for the optimization and customization of shape memory surfaces in order to make them useful for potential applications.

Our overall strategy is to advance the understanding and to improve the control of the properties of micro- and nanostructured surfaces. Ultimately, we aim to contribute substantially to the development of multifunctional surfaces with tunable properties. Such surfaces may find widespread applications ranging from household items and construction devices to biomedical gadgets and microtechnological systems.

# Nanotribologie / Nanotribology

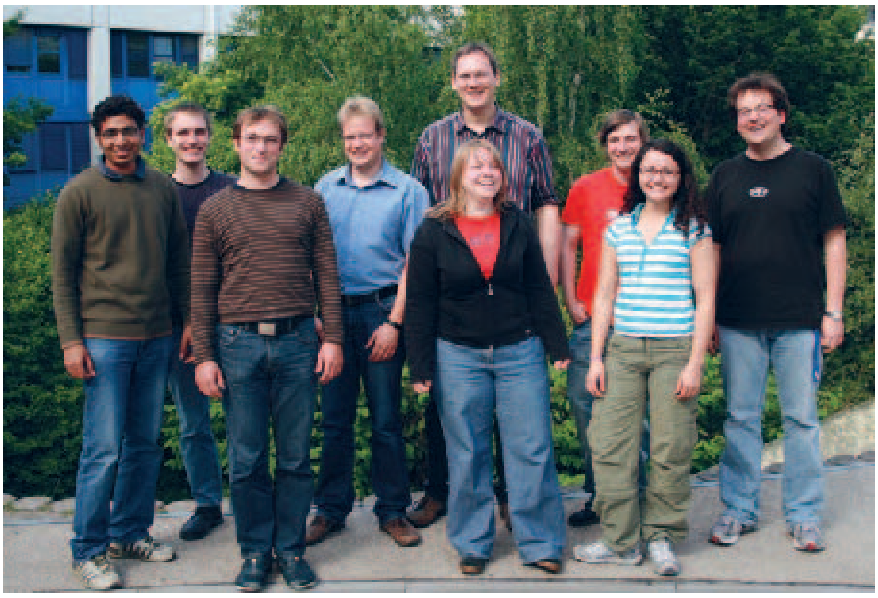
## Prof. Dr. Roland Bennewitz

Der Programmbereich *Nanotribologie* hat sich zum Ziel gesetzt, die mechanischen Phänomene Reibung, Abrieb und Verformbarkeit aus einer mikroskopischen Perspektive heraus zu verstehen. Dazu führen wir nanomechanische Experimente durch, meist mittels Rasterkraftmikroskopie (Atomic Force Microscope, AFM), die in hoher, oft atomarer Auflösung die grundlegenden Mechanismen der genannten Phänomene untersuchen. Eine Erweiterung unseres thematischen Spektrums auf Experimente, die mechanische Eigenschaften hierarchisch strukturierter Materialien auf allen relevanten Längenskalen prüfen, ist im Aufbau. In Zusammenarbeit mit internen und externen Partnern streben wir an, die Ergebnisse der grundlagenorientierten Nanotribologie für die Materialwissenschaften fruchtbar zu machen.

Der Programmbereich *Nanotribologie* wurde im Juni 2008 am INM eingerichtet, als Roland Bennewitz mit einem Teil seiner Arbeitsgruppe von der McGill Universität in Montreal, Kanada, an das INM wechselte. Die wichtigsten Aktivitäten im Jahr 2009 waren grundlegende Messungen an Modellsystemen, die die Methoden der Nanotribologie am INM etabliert haben. Dabei sind folgende Ergebnisse herauszuheben:

- Messungen zur atomaren Reibung wurden erfolgreich sowohl unter Vakuum als auch in einer elektrochemischen Zelle durchgeführt. Dabei konnte zum einen gezeigt werden, welche Rolle die Rekonstruktion einer Goldoberfläche durch Stapelfehler für die Reibung spielt, zum anderen wie die kontrollierte Oxidation und Reduktion die Reibungseigenschaften auf atomarer Skala beeinflusst.
- Bei der Untersuchung der ersten Stufen der plastischen Verformung gelang es, einzelne Stufenversetzungen an der Oberfläche nachzuweisen, sowie eine Methode zur zeitaufgelösten Detektion atomarer Gleitvorgänge während des Kriechens zu entwickeln.
- In der Reibung von mikrostrukturierten Elastomer-Proben gegen Glasoberflächen zeigte sich, dass die Ablösung einzelner Mikrokontakte in Wellen durch die gesamte Kontaktfläche läuft. Diese Beobachtung zeigt die Bedeutung der elastischen Kopplung zwischen den Mikrokontakten und wirft neues Licht auf den Übergang von statischer zu kinetischer Reibung.

Für die nächste Zukunft ergeben sich für den Programmbereich *Nanotribologie* zwei wesentliche Herausforderungen. Zum einen wollen wir durch herausragende experimentelle Ergebnisse zum fundamentalen Verständnis mechanischer Phänomene auf kleinster Skala beitragen. Zum anderen wollen wir durch den Aufbau von neuen Instrumenten und durch erste Versuche mit biologischen und biomimetischen Proben eine Expertise für das Studium der Mechanik hierarchisch strukturierter Materialien entwickeln.



The Program Division *Nanotribology* studies mechanical processes such as friction, wear, and plasticity from a fundamental scientific perspective. We follow three main directions: Firstly, we perform cutting-edge nanomechanical experiments, mostly based on Atomic Force Microscopy (AFM). Secondly, we develop novel experimental techniques which bridge the gap between nanomechanical and macroscopic studies. Finally, we seek collaborations with research groups in applied sciences in order to contribute to novel directions in materials sciences. High-resolution AFM imaging supports the mechanical experiments by revealing the surface structure, often with atomic resolution, and detecting the onset of wear and plasticity. The results of our work are presented at international conferences and in international scientific journals.

With its fundamental approach and methodological focus, our Program Division collaborates on projects across the INM. Typical areas of collaborative research include the tribological properties of micro-structured surfaces (Program Division *Functional Surfaces*) or the wear processes in nanoparticle-enforced polymer coatings (Program Division *Nanomers*). Multi-scale testing of mechanical properties in hierarchical structures is pursued in collaboration with the Program Divisions *Biomineralization* and *Functional Surfaces*.

The Program Division *Nanotribology* was established at INM in June 2008, when Roland Bennewitz moved here from McGill University in Montreal, Canada, together with part of his research group. The activities in 2009 have been focused on establishing three laboratories, obtaining cutting-edge experimental results on model systems, and starting collaborations with partners inside and outside INM.

## Atomic friction

Our group has a world-wide reputation for advanced atomic friction experiments. In 2009, our home-built AFM operating in Ultra High Vacuum (UHV) has produced data with an excellent signal-to-noise ratio for most of the year. Dr. Nitya Nand Goswami, a fellow of the Humboldt Foundation, has demonstrated that irregularities in atomic friction across the stacking-fault reconstruction of Au(111) surfaces can be recorded. The results have been accepted for publication (Tribology Letters DOI 10.1007/s11249-2009-9508-5) and are currently expanded towards molecular films on gold surfaces. In a project supported by the Deutsche Forschungsgemeinschaft within the European Science Foundation (ESF) project FANAS, Christian Held has started an experimental project towards his doctoral degree about atomic friction on ultra-thin films. He has already prepared single layers of graphene on a silicon carbide surface, which exhibit ultra-low-friction properties (Physical Review Letters 102, 086102 (2009)).

Furthermore, we began to study friction on surfaces under electrochemical control in order to explore friction and wear in corrosive environments. Towards this

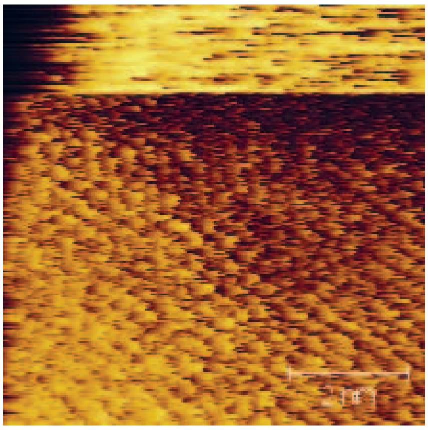


Figure 1: Map of lateral forces recorded on a perfectly flat gold surface in perchloric acid. The atomic structure of the gold surface is revealed through the atomic stick-slip mechanism in the lower part of the frame. Upon changing the electrochemical potential in the measurement cell, the surface undergoes oxidation with a dramatic effect on the friction signal, which now reflects the amorphous gold oxide structure.

goal, we have developed surface preparation and noise reduction strategies in order to obtain atomic friction resolution in a commercially available AFM operating in liquid environment. Florian Hausen, a chemist, has successfully revealed the atomic details in friction when switching electrochemically between oxidized and reduced states of an Au(111) surface (see Figure 1).

### Plasticity and wear

The permanent deformation of crystalline materials under stress occurs through the nucleation, multiplication, and movement of extended structural defects in the crystal, which are called dislocations. Understanding plasticity on the microscopic scale requires experiments which bridge the gap between continuum mechanics and the properties of individual dislocations. We contribute to this field through AFM-based indentation experiments combined with high-resolution imaging of the resulting surface structure (Nanotechnology 20 (2009) 264005). Our method detects the incipient stages of plasticity, i. e. the nucleation of individual dislocations. In 2009 Philip Egberts has extended the method towards the study of creep phenomena. The ongoing deformation under constant load can now be analyzed as a series of individual, atomic scale plastic events.

Our project on plasticity is a collaborative research project supported by the Canadian funding organization NSERC in which we are associate partners of Canadian and Indian groups. The goal of the collaboration is a description of the hardness of nanocrystalline materials. In 2009 we have presented a joint publication with our partners on the incipient plasticity of KBr single crystals comparing traditional nanoindentation and our AFM-based methodology (Mater. Res. Soc. Symp. Proc. Vol. 1185 (2009) 1185-II07-08).

### Friction of micro-structured surfaces

Friction between two sliding surfaces is critically determined by the roughness of the surfaces. A multitude of microscopic contacts is continuously formed, deformed, and ruptured in the course of sliding. Our activities using AFM explore the friction of single microscopic contacts. In a complementary approach, we study the friction of surfaces with thousands of microscopic contacts. However, these contacts are well-ordered and well-defined in shape to allow for an easier interpretation of the results. In collaboration with the Program Division *Functional Surfaces*, Katrin Brörmann has performed experiments using so-called Gecko surfaces. These surfaces comprise regular arrays of elastomer pillars with enhanced adhesion properties. Fundamental mechanisms of friction can be studied by optical microscopy when sliding a glass slide over the structured sample. One of the most striking observations is the motion of detachment waves travelling across the contact area (see Figure 2). The waves demonstrate the important role of long-range elastic interactions in these samples. Their analysis is under way and may shed new light on

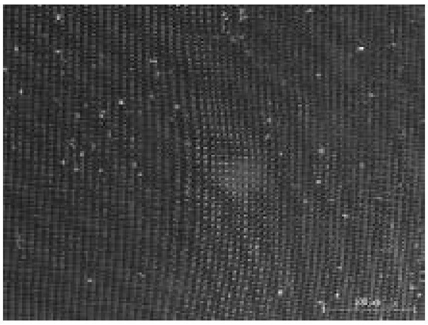


Figure 2: Optical micrograph of a micro-structured Gecko sample in contact with a sliding glass slide. The perfectly regular pattern of contacting pillars is locally distorted due to the interaction with the sliding glass and due to elastic coupling between the pillars through the backing layer. The distortion travels through the contact as a detachment wave.

the complex dynamics at the transition from static to kinetic friction.

## Outlook

The wealth of interesting results which the *Nanotribology* laboratories produced in 2009 on model materials motivates us to extend our methods and analyses to more complex systems. The fascinating low-friction properties of graphene on SiC will be studied on larger length scales. Furthermore, we plan to prepare and study graphene also on metal surfaces. These projects will be pursued in collaboration with the Fraunhofer Institute for Mechanics of Materials IWM and Saarland University; an application for financial support has been submitted to the BMBF. The plasticity studies will be extended towards metals. The tribology of patterned elastomer samples will be tested as a function of microstructure and materials properties, and will be modeled in collaboration with the Program Division *Modeling / Simulation* and with partners in the ESF FANAS project at Tel Aviv University.

We will also increase our activities in the field of multi-scale mechanical testing of materials. The scratch-resistance of polymer coatings is examined in collaboration with the Program Division *Nanomers*. Dr. Harald Tlatlik has already started to analyze the temporal development of surface topography and of stress distributions close to scratches. Finally, Dr. Griselda Guidoni and Felix Wählisch will initiate the Leibniz SAW project on multi-scale testing. In close collaboration with three Program Divisions, they will explore the mechanical response of hierarchically structured materials in biology and technology.

# Strukturbildung auf kleinen Skalen / Structure formation at small scales

## Dr. Tobias Kraus

Die Juniorforschungsgruppe *Strukturbildung auf kleinen Skalen* befasst sich mit Überstrukturen von Partikeln. Wir beobachten – wenn möglich *in situ* – die Bildung mesoskopischer Aggregate aus Nanopartikeln, um die Mechanismen zu identifizieren, die zur Bildung geordneter Strukturen statt ungeordneter Agglomerate führen. Unser Ziel ist es, diese Mechanismen in konventionelle Beschichtungsprozesse einzuführen, um so Hybridmaterialien mit definierten Mikrostrukturen effizient und skalierbar herstellen zu können.

Die Aufgabe, kontrollierte Partikelanordnungen zu schaffen, ist am INM weit verbreitet: Transparente, aber hoch brechende, kratzfeste oder dichte Schichten erfordern homogene Partikelverteilungen ohne Agglomerate. Lichtmanagement, Transportbarrieren und elektrische Eigenschaften basieren auf kontrollierter, anisotroper Verteilung der Partikel. Unser Ansatz nutzt die Interaktion der Partikel aus, um solche Anordnungen gezielt zu schaffen. Er ist geeignet, bestehende Materialien und Prozesse zu verbessern und neue Materialien zu ermöglichen. Neben grundlegenden Fragen der Strukturbildung untersucht die Gruppe auch die Eigenschaften der strukturierten Materialien, die entstehen. Wir arbeiten mit anderen Gruppen zusammen, die Anwendungen in den entsprechenden Gebieten erforschen, und nutzen deren Expertise in der Messtechnik.

Die Forschung in der Gruppe gliedert sich also in drei Phasen: die Synthese und Charakterisierung von Partikeln mit kontrollierter Geometrie, deren Anordnung in Überstrukturen und die Analyse der Eigenschaften, die sich in der Überstruktur gegenüber den Einzelpartikeln verändern oder neu auftreten.

Im Bereich der Partikelsynthese wurden in den vergangenen zwei Jahren Synthesen für drei Modellsysteme – Gold, Siliziumdioxid und Cadmiumselenid – etabliert. Diese Nanopartikel bilden die Basis unserer Forschung. Spezielle Partikel werden bei Bedarf synthetisiert, beispielsweise „weiche“ Partikel aus vernetzten Wachsen (Dr. Eoin Murray, Postdoc in der Gruppe) und Goldstäbchen im Jahr 2009.

Die Anordnung der Partikel ist die zentrale Tätigkeit der Gruppe und wird experimentell durchgeführt an Grenzflächen, in Emulsionen und direkt in der Suspension. Spezielle Versuchsaufbauten erlauben uns beispielsweise, Vorgänge während der Tauchbeschichtung detailliert zu steuern und zu beobachten. Simulationen werden mit den Messergebnissen verglichen, die während oder nach der Anordnung gewonnen wurden, um entscheidende Einflussgrößen zu identifizieren und schließlich Anordnungsmechanismen aufzuklären. Im Rahmen seiner Doktorarbeit, die seit 2009 von der DFG gefördert wird, hat Philip Born dabei überraschend scharfe kritische Temperaturen für die Agglomeration beobachtet und festgestellt, dass die Entstehung von Ordnung von der absoluten Temperatur und den Interaktionspotentialen abhängt.

Die Proben werden mikroskopisch auf ihre Struktur untersucht, und zwar sowohl mit lokal hoher Auflösung als auch in Hinblick auf die Homogenität der Strukturen. Makroskopische Eigenschaften der Überstrukturen, an denen wir besonders interessiert sind, sind strukturabhängiges optisches Verhalten, komplexe mechanische Eigenschaften und kontrollierbares elektrisches Verhalten. Johann Lacava (die zweite Doktorandin der Gruppe) untersucht solche Eigenschaften an Suprakolloiden, deren Herstellung in Emulsionstropfen im Jahr 2009 etabliert wurde.

Für grundlegende Untersuchungen zur Strukturbildung nutzen wir möglichst einfache Partikelsysteme. Gleichzeitig beschäftigen wir uns aber mit binären und höheren Mischungen aus Partikeln und mit anisotropen Partikeln, um Materialien mit gemischten Eigenschaften oder einstellbarem anisotropen Verhalten zu gewinnen.

The *Structure Formation* group is a junior research group which focuses on particle superstructures. We observe the formation of mesoscopic aggregates of nanoparticles using *in situ* methods wherever possible and identify mechanisms that lead to ordered superstructures instead of disordered agglomerates. Our goal is to invoke these mechanisms in standard coating and deposition processes to produce soft materials with defined microstructures in an efficient and scalable manner.

INM provides an ideal environment for this research. The *Structure Formation* group is using analytical methods that have been established at INM to analyze hybrid materials. Many of these methods have hitherto been used without considering details of particle arrangement. We strive to extend their capabilities, which will aid other users. The expertise that allows forming defined particle distributions is at the core of many other groups at INM, and we strive to collaborate with our colleagues to improve basic understanding and to develop innovative methods for the controlled integration of particles into new materials.

The group will continue to explore both the exciting fundamental questions of structure formation from interacting particles and novel properties of the superstructures that form, such as structure-dependent optical properties, complex mechanical behavior and tunable electrical behavior.

## Nanoparticle synthesis: from spheres to rods

Only particles with sufficiently narrow size distributions will assemble into regular superstructures. The group has established syntheses for particles from three material systems – gold, silica and cadmium selenide – as basis of research. Different surface modifications provide different inter-particle potentials and particle spacing. Anika Weber, the technician of the group, routinely prepares the particles in reproducible quality and characterizes their basic properties.

More specialized particles, for example, core-shell constructs (Figure 1) have been prepared in collaboration with other groups. Recently, we began exploring syntheses that yield anisotropic particles such as rods (Figure 1) as part of a larger project to create materials with highly anisotropic properties. In 2009, our Postdoctoral Associate Eoin Murray developed a route that yields apolar nanoparticles with narrow size dispersion in which a waxy bulk is held together by a silicate network. These "soft" particles complement the "hard" systems developed earlier and complete the basis for superstructures.

Particle synthesis is not only the basis of our activities, but also critical for the work of the Program Division *Nano Cell Interaction*, which has led to close collaboration in 2009, which will continue in the future.

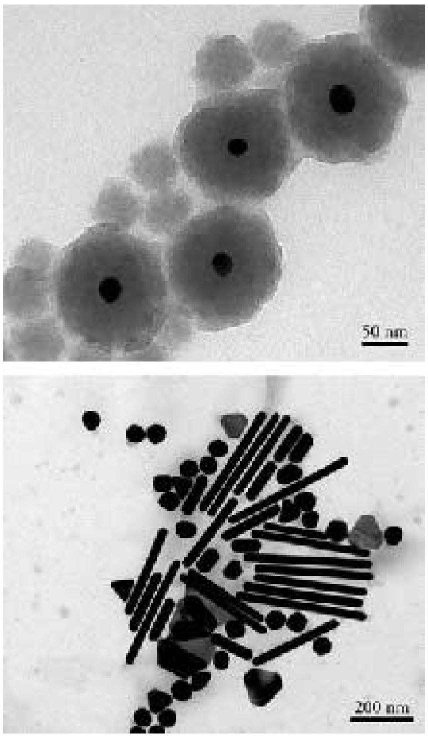


Figure 1: Core-shell nanoparticles (upper micrograph) containing a gold core surrounded by a silica shell and gold nanorods (lower micrograph) accompanied by some gold nanoparticles with various geometries.

### Particle behavior: atoms or grains?

Nanoparticles are Brownian objects and often regarded as “giant atoms” when it comes to their dynamics. During particle assembly, where these dynamics play a decisive role, we find deviations from this approximation. In a DFG-funded project (“Mobility and interaction in nanoparticle self-assembly”) that started in 2009, we analyze the actual particle behavior. Initial results suggest that nanoparticles can resemble both atoms and granular matter, depending on the situation.

Philip Born, one of the two doctoral students in the group, performs experiments that probe the ensemble behavior (measuring “thermodynamic” properties such as “melting point” of superstructures) as well as single-particle contributions (their position inside the superstructures, and the order therein). Using light scattering methods applied *in situ*, he has recently found surprisingly sharp, temperature-dependent transitions from single particle dispersions to agglomerates (Figure 2). We currently investigate their origin as well as the influence on the agglomerates’ structure. In collaboration with the bioinformatics department of the University of Saarland (Prof. Helms), we also tackle these questions using Brownian Dynamics simulation.

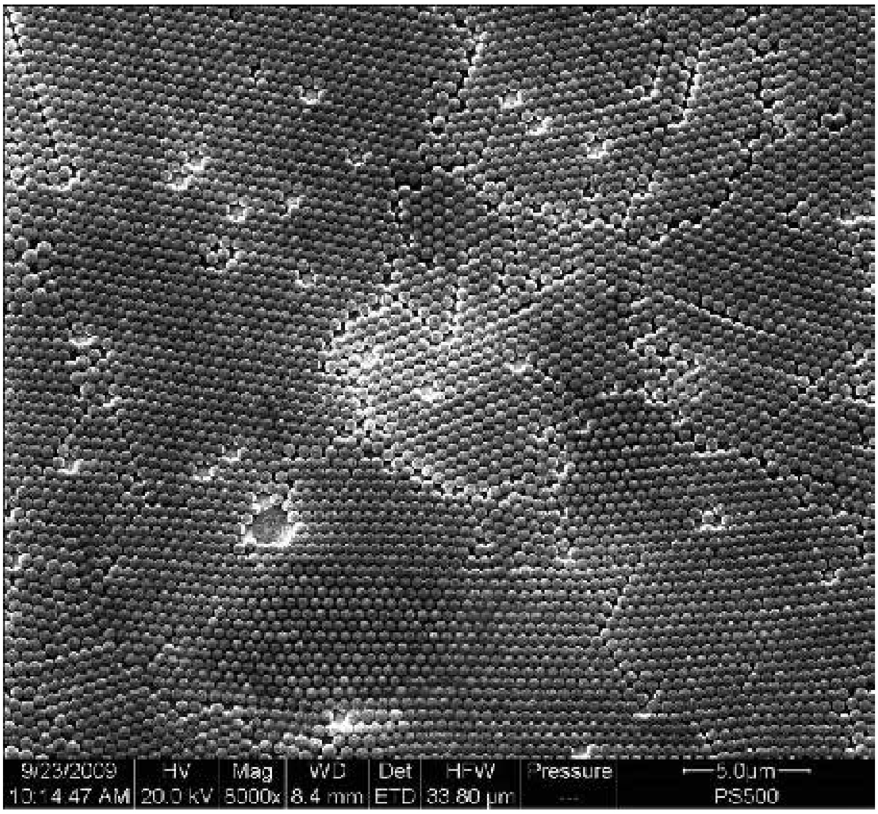


Figure 2: Measurement of the transition temperature of a gold colloid suspended in heptane. The DLS radius indicates induced agglomeration below 2 °C.

### Monolayers: dip-coating revisited

Particle layers are common coatings with applications ranging from wall paint to prosthetics. In this project, we aim to introduce order into monolayers and multilayers of nanoparticles with diameters between 500 nm and a few nanometers. The challenge is to use a coating process that is well-known in industry – dip-coating or painting – and still have the particles arrange into regular structures. With the aid of a microscope-based small-scale coating setup (the CAPA tool, for “Capillary Assisted Particle Assembly”, operated and programmed mainly by Susanne Blum, a student assistant), we deposit polystyrene spheres to analyze the stability of the coating process and the quality of the resulting layers (Figure 3). Coatings on usefully large areas with high quality and little defects require a very careful choice of parameters, which are still not known despite the intense international research activities on this topic throughout the last years. Our approach provides some of the insights necessary to make ordered, particle-based coatings industrially viable.

In addition to this hydrodynamic particle assembly process, we study systems in which particles autonomously segregate to liquid-gas interfaces (as in a drying paint), where they arrange into regular layers that form a coating upon complete evaporation of the solvent. The mechanisms that lead to ordered particle layers are probed by *in situ* monitoring the kinetics with optical spectroscopy, tensiometry and x-ray reflectometry. This project was initiated in 2009 by the work of an academic visitor from Oxford University, John Aveson.

### Particle supercrystals: tuned interactions

In the absence of geometrical confinement, attracting nanoparticles will grow into three-dimensional agglomerates. We are able to form agglomerates in which the particles arrange regularly into a supercrystal. It is often problematic to prepare macroscopic quantities of such supercrystals, as the constituent particles tend to be precious. To study the crystals' properties, we have thus developed routes to "supracolloids", in which the superstructures are present in colloidal form as stabilized groups comprising between dozens and millions of nanoparticles. Johann Lacava, the second doctoral student of the group (who joined us in 2009), prepares the superstructures and characterizes them using spectroscopic and microscopic methods.

## Outlook

Since its inception, the *Structure Formation* group has established the base materials for the preparation of nanoparticle superstructures, developed and refined analytical methods for their observation and started to collaborate with other groups towards the application of superstructures. We now concentrate on the preparation of regular monolayer coatings from nanoparticles that are functional or provide masking for surface structuring,

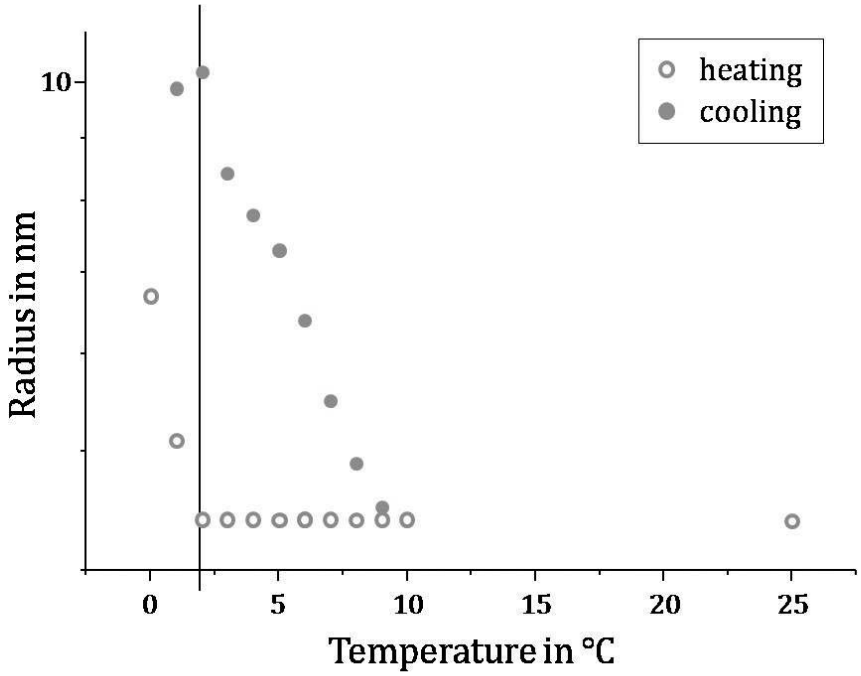


Figure 3: Electron micrograph of a 500-nm-diameter polystyrene particle monolayer, deposited with the CAPA-tool. Defects in one and two dimensions, such as grain boundaries and voids, are clearly visible.

the understanding of agglomeration processes that yield regular superstructures in suspension and in matrices, and on emulsion-templated superstructures.

In the near future, we will establish an optical setup to observe nanoparticle dynamics *in situ* with light scattering and adsorption methods to enable in-process monitoring. This setup will also be used in conjunction with the recently prepared, anisotropic nanoparticles for the fabrication of nanoparticle-polymer hybrids with direction-dependent properties. It will be built and operated in cooperation with the Program Divisions *Optical Materials* and *Nano Cell Interactions*.

The DFG-funded project on fundamental questions of nanoparticle assembly has unveiled intriguing dynamics, some of which will be further studied using x-ray scattering at a synchrotron source. We also collaborate with the group of Patrick Huber at the University of Saarland to apply scattering methods that probe ordering *in situ*.

After further development, the CAPA tool should enable us to fabricate particle monolayers as basis of functional structures with microstructure-controlled electrical conductivity, color, and adhesion. The relevant properties will be investigated in collaboration with the respective INM groups.

# Biomineralisation / Biomineralization

## PD Dr. Ingrid Weiss

Der Programmbereich *Biomineralisation* beschäftigt sich mit hierarchischen biologischen Materialien. Ziel ist es, die Konzepte zu verstehen, die hinter der Biosynthese hierarchischer Materialien stehen, und dieses Wissen in technologisch relevante Prozesse zu integrieren. Die Herausforderung besteht darin, die Natur auf allen Längenskalen zu analysieren und Wechselwirkungen zwischen diesen Skalen zu identifizieren.

Wichtige molekulare Schlüsselfaktoren zum Aufbau makroskopischer Komposite wie Perlmutt wurden bereits identifiziert. Nun geht es darum, daraus neue Materialien biologischen Ursprungs zu generieren, die sich zusätzlich zu den gewünschten Materialeigenschaften umweltfreundlich in bereits bestehende ökologische Kreisläufe für Um- und Abbau in die Natur integrieren lassen. Dadurch können Risiken der langjährigen Akkumulation in der Umwelt vermieden werden. Wir nutzen die Evolution im Labor, um basierend auf einfachsten Ausgangsstoffen, die in der Natur praktisch unbegrenzt zur Verfügung stehen, funktionell optimierte hierarchische Strukturen zu identifizieren.

Zusätzlich zu den bekannten Design-Prinzipien, wie beispielsweise selektive Permeabilität kombiniert mit bestimmten optischen Eigenschaften, wird der „Eco-Design"-Aspekt zunehmend wichtiger. Die Biologie stellt uns hierfür außerordentlich effiziente „Nano-(Fabrikations-)Technologie" zur Verfügung, deren wahre Effizienz jedoch darin liegt, sich der Vielfalt von Längenskalen bedienen zu können. Für diesen Zweck wurden großflächige Klima-Kammern eingerichtet, die nun die entscheidenden Experimente mit geeigneten Nutzpflanzen ermöglichen. Wir konzentrieren uns im Wesentlichen auf Zellwand-Aspekte von Modellorganismen, deren strukturelle Modifikationen wir mittels LC-Pol-Scope Bildverarbeitung (Eder et al., Protoplasma 2010, in press) und abbildender Raman-Spektroskopie analysieren.

In Zusammenarbeit mit anderen Programmbereichen des INM sowie den Service-Gruppen für *Chemische und Physikalische Analytik* sowie *Mechanische Prüfung* erarbeiten wir gegenwärtig ein breites Methodenspektrum für die schnelle, empfindliche und effiziente Analyse von Kompositmaterialien biologischen Ursprungs. Die metallographische Probenpräparation lässt sich effizient auf biogene Grenzflächen anwenden (Weiss et al., JSB 2009, 167:68-75), und die Interaktionen von extrazellulärer Matrix mit funktionellen Oberflächenstrukturen können zellbiologisch analysiert werden (Eder, Concors, Arzt & Weiss, Adv. Eng. Mat 2010, in press). Quantifizierbare Daten zur Grenzfläche zwischen lebenden Geweben und Materialien bilden einen wichtigen Ausgangspunkt für ein tieferes Verständnis einer Vielzahl strukturbildender Phänomene in der Natur, aber auch in der Anwendung auf medizintechnische Fragestellungen.

Zukünftig sollen auf Basis natürlicher Biomineralisationsprozesse, wie der Perlmuttbildung, mit bioinformatischen und experimentellen Methoden zelluläre und organismische Modellsysteme konzipiert werden, um die Biosynthese hierarchischer Materialien verstehen und in Form von „grünen Nanomaterialien" nutzbringend und effizient anwenden zu können. Umweltrelevante Parameter sind dabei von besonderer Bedeutung für einen nachhaltigen Umgang mit den verfügbaren Ressourcen.

## Biological Materials: Challenges and Perspectives

Biological materials are hierarchical materials. It is appealing to understand the physics underlying such hierarchical materials and to implement some basic concepts into man-made materials. On the other hand, it is challenging to elucidate the structure-function relationships of such materials. The general aim of our research is to study and to exploit natural resources at all hierarchical levels: from molecules to cells, to multi-cellular biofilms, tissues and even to whole organisms. In particular, we focus on selected protein catalysts involved in biomineralization, self-made biomimetic cell lines for studying particular aspects of biological materials in *statu nascendi*, and cellular feedback mechanisms related to functional materials interfaces. Materials derived from biological origins are naturally integrated into ecological cycles for degradation that already exist in nature, which minimizes risks of long-term accumulation. Biosynthetic routes usually start from simple compounds that are abundantly available in nature, whereas conventional processing routes towards sophisticated and efficient hierarchical systems require complex and energy demanding synthesis steps. The architecture of biological materials often meets multi-purpose demands, such as selective permeability for various substances, light management and so on. Biological materials have already implemented the aspect of "Eco-Design", in addition to the control of hierarchical assembly over a range of multiple length scales. Shortening evolutionary time-scales from millions of years to the duration of laboratory experiments by using micro-organism is the strategy we use for materials design.

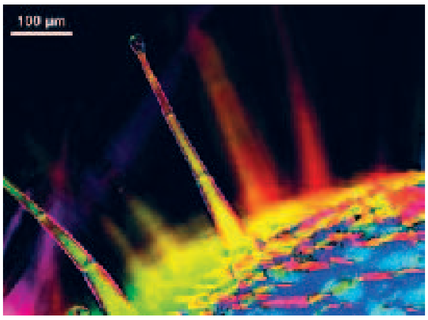


Figure 1: Towards application: Birefringent plant cell walls from tobacco (*N. benthamiana*) leaves analyzed using LC-PolScope imaging technology (Image courtesy of E. Weber).

## Towards application: Composite materials made by biological model organisms

The formation of defined shapes by cells is one of the challenging questions in biology. Due to the anisotropy of cell walls and of certain biominerals, the LC-PolScope (Abrio liquid crystal compensator image analysis system, CRi, Cambridge, U.K.) represents a promising tool for tracking dynamic structural changes in vivo non-invasively and, to some extent, quantitatively. A complex three-dimensional biogenic system, the in vitro precipitation of calcium oxalate induced by cellulose stalks produced by *Dictyostelium discoideum*, was analyzed. Although the retardance values and ori-

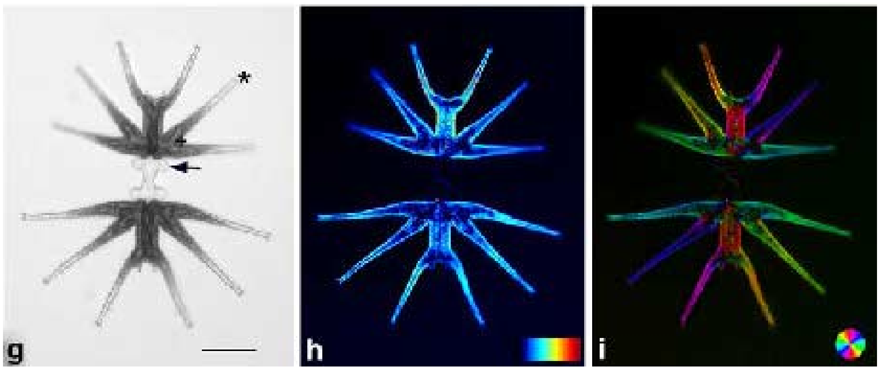


Figure 2: LC-PolScope analysis of living cells (*Micrasterias hardii*). Transmission light image (g), LC-PolScope retardance image (h, 0–34 nm), and orientation of the slow optical axis (i) are shown. SW-lobes, SW-indentations, and the primary cell wall are indicated by asterisks, plus signs, and arrows, respectively. Bars: 100 µm (Image courtesy of M. Eder).

entation of the crystals with respect to the stalk were quickly and easily detected, this study raised a number of issues that were addressed in this work. The effect of the refractive index of the embedding medium was examined by taking advantage of the homogeneous size and shape distribution of kiwifruit raphides, a biologically controlled calcium oxalate biomineral and of cotton (*Gossypium*) seed fibers. The retardance remained consistent when embedding these samples in media with increasing refractive indices from 1.33 to 1.42 or 1.46 for sucrose or glycerol gradients, respectively. The general applicability of LC-PolScope image processing for biominerals and cell wall formation during development in vivo was demonstrated in a particular group of green algae, the *Desmidiaceae*. Various organization levels of the cell wall were identified, thus confirming earlier findings based on electron microscopy and immunostaining investigations. It can be concluded that LC-PolScope microscopy is an attractive tool for studying dynamic ordering of biomolecules, such as plant cell walls (Figure 1), when additional parameters regarding the structure, composition, and refractive indices of the specimen are available (Figure 2, Eder et al., Protoplasma 2010, in press). The LC-PolScope Abrio system is suitable to study the synthesis of extracellular matrix polymers and their crystallization behavior as a function of intracellular cytoskeletal fibril assembly, and we currently apply this to explore the relationship between biogenic crystals and plant cells in a straight-forward manner. In order to expand towards application, the Program Division *Biomineralisation* has installed large scale plant growth facilities at INM for cultivating "renewable materials".

### Interdisciplinary approaches: Unconventional ways towards new biological materials

At INM, it became possible now to analyze biological materials from basic building blocks such as amino acids to the overall chemical composition and structure. Molluscs have a well-deserved reputation for being expert mineralizers of various shell types such as nacre. Nacre is defined as regularly arranged layers and stacks of 0.5 µm thick aragonite platelets that are extracellularly formed within a complex mixture of organic matrix. The control of species-specific layer thickness by the animal is still enigmatic. Despite the recent findings on the periodic layer-by-layer structures of

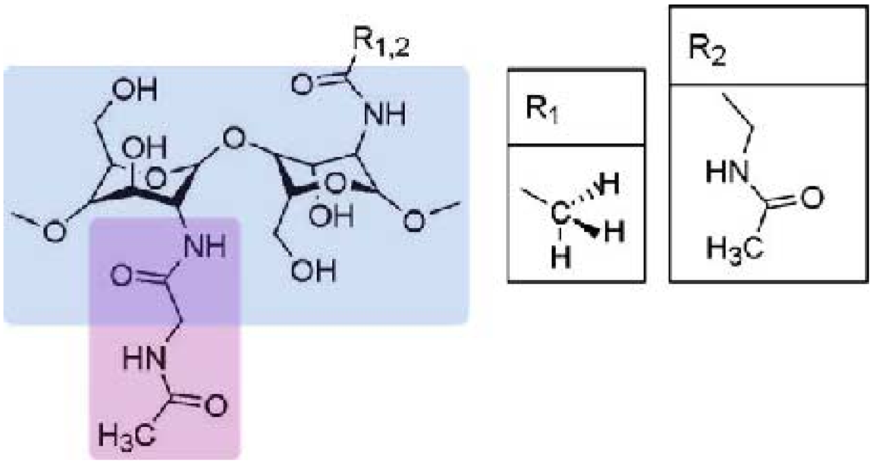


Figure 3: Structural model of modified chitooligosaccharides involved in biomineralization self-assembly processes as deduced fromMS data. For further details, see Weiss et al., JSB 2009 (Image reproduced from Elsevier).

chitin layers and silk-like protein layers in nacre-type biominerals, little is known about how the interface is defined between two different layers. We demonstrated the presence of covalently attached, hydrophobic amino acid side chains in the chitin matrix in the bivalve mollusc Mytilus galloprovincialis by the combination of infrared spectroscopy and mass spectroscopy. The accumulation of the modified chitin matrix at the interface is quantified by the critical aggregate concentration of the purified chitin matrix, which is approximately an order of magnitude smaller than that of pure chitin. Our finding suggests an active role of such chemically modified chito-oligosaccharides (Figure 3) in the creation of a defined interface and guidance of the periodic matrix textures, which would result in unique material properties of natural mollusc shells (Weiss et al., JSB 2009, 167:68-75).

Two new research foci in the area of biological materials were established. One is the interaction of multi-cellular aggregates with materials as a function of mechanical properties and surface structure. Gecko inspired adhesives are surfaces with many microscale pillars that form Van der Waals forces with other surfaces. They differ from conventional tape in that adhesion is reversible and has the potential for switchability. These properties make gecko adhesives interesting for various biomedical applications. The two objectives of this project were to investigate the formation of biofilms on such surfaces and how the surfaces affect cell development. The developmental stages of the model organism *Dictyostelium discoideum* were observed by time lapse photography using light and environmental scanning electron microscopy. This study shows that micropatterned surfaces can be used as a biophysical tool to interfere with multicellular tissue formation in multiple ways (Eder et al., Adv. Eng. Mat. 2010, in press).

The other new research focus in the area of biological materials deals with elucidating structure-function relationships from materials chemistry and design up to ecological implications and to application of natural materials. In quill embroidery, leather goods are beautified with patterns stitched with stripes of the cortex of peacock feathers (Figure 5). Our new structural, geometric and mechanical data for the tail cover feathers of the peacock allow an understanding of the mechanisms of embroidery (Weiss & Kirchner, Adv. Eng. Mat. 2010, in press; Weiss & Kirchner, J. Exp. Zool. 2010, submitted; Pabisch et al., J. Struct. Biol. 2010, submitted). This study serves as an example of how biological materials can be analyzed like engineering materials, giving insight into the optimization processes during evolution (Figure 6). Through the many interactions within INM, from materialographic processing to application of analytical tools, this knowledge is currently enormously expanded and will contribute to explore inconventional routes towards new biological materials well-adapted to compete with and replace hazardous man-made materials in the future.

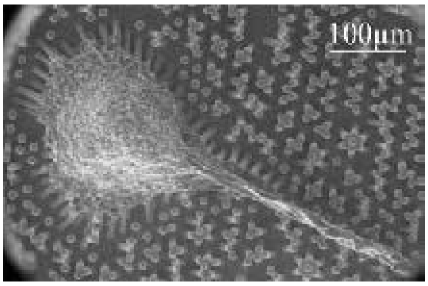


Figure 4: Cell accumulation and differentiation of the slime mold *Dictyostelium discoideum* shows that gecko inspired micropatterned surfaces can be used as a biophysical tool to improve our understanding of multicellular tissues and biofilm formation.

Figure 5: Detail of contemporary quill embroidery (Courtesy of K. Stecher). The technique exploits the remarkable mechanical properties of the cortical shell of the peacock's feathers (Weiss & Kirchner, Adv. Eng. Mat. 2010, in press).

## Outlook

We plan to transfer results of *in silico* studies on nacre formation into suitable experimental model systems using bioinformatic tools to study the formation of composite materials *in vivo* in a comparative manner. The main focus will be biosynthetic pathways and self-assembly of extracellular matrix polymers. A major challenge remains tracking the formation of mineralized composite materials in various systems as a function of time, surface interaction potentials, adhesion phenomena, phase separation and environmental parameters. Understanding these fundamental aspects will lead us to designing "green nanomaterials" with respect to various applications. Essential collaborations with established experts in the field of applied plant sciences and biophysical chemistry at UdS and other research labs at national and international institutes will be intensified.

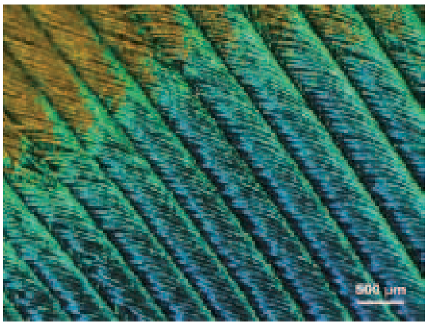


Figure 6: Ordered arrangement of native feather keratin, a high-performance hierarchical material in terms of optical and mechanical function (Image courtesy of B. Heiland).

# CVD/Biooberflächen / CVD/Biosurfaces

## Prof. Dr. Dr. h. c. Michael Veith, Dr. Cenk Aktas

Der Programmbereich *CVD/Biomaterialien* hat sich auf die Herstellung so genannter Single-Source-Prekursoren für den Einsatz bei der chemischen Gasphasenabscheidung (CVD) spezialisiert. Bei diesen Prekursoren handelt es sich um Moleküle, welche alle nötigen Elemente der Zielphase bereits in der korrekten Stöchiometrie enthalten und deren Sublimations- bzw. Verdampfungspunkte anhand der verwendeten Liganden gezielt eingestellt werden können. Zur Abscheidung dieser Moleküle aus der Gasphase werden in einem „bottom-up“-Ansatz die thermische CVD, die Plasma-unterstützte CVD (PECVD), die „liquid injection“ CVD und die Laser-unterstützte CVD genutzt. Überdies werden Schichten durch reaktives Kathodenzerstäuben erzeugt. Schwerpunktthemen der Gruppe sind Untersuchungen zu Wachstumsmechanismen aus der Gasphase sowie die Erforschung neuartiger Prekursoren zur Erzeugung von Strukturen wie beispielsweise Nanodrähten, Nanostäben oder Nanoröhren. Bei der Thermolyse dieser neuartigen Moleküle entstehen gezielt zwei- oder mehrphasige Feststoffe, die zu den beobachteten Strukturen führen. In aktuellen Projekten konnten über ebenfalls neuartige Prekursoren dichte Schichten, aber auch eindimensionale Strukturen der Mischoxide PZT (Bleizirkonattitanat) und ITO (Zinn-dotiertes Indiumoxid) erzeugt werden.

Die Herstellung eindimensionaler Nanostrukturen wird auch in künftigen Forschungsprojekten eine Hauptrolle spielen. Zur Integration dieser Strukturen in die Biomedizin, Sensoranwendungen oder Optik sollen Parameter wie Vorzugsorientierung, Morphologie und Phasenzusammensetzung erforscht und optimiert werden. Besonderes Augenmerk gilt hierbei der Weiterentwicklung nanostrukturierter Oberflächen für biomedizinische Anwendungen. Hierbei sollen mikro- und nanostrukturierte Oberflächen erzeugt werden, welche der extrazellulären Matrix (ECM) von organischem Gewebe gleichen, um so Zellen Bedingungen auf Substraten oder Implantaten anbieten zu können, die denen ihrer natürlichen Umgebung entsprechen. In diesem Zusammenhang sollen neue Projekte mit vorhandenen bzw. künftigen Projektpartnern initiiert werden.

In January 2009, the Program Divisions *CVD/PVD Technologies* and *Life Science/Biomimetics* were combined under the new division name *CVD/Biosurfaces*. Basically this new group focuses on the bottom-up gas phase synthesis of nanomaterials while keeping an eye on applications in the field of biology and medicine. In this context, the group benefits from the synthesis experience of the former *CVD/PVD Group* as well as medical science, bio- or food-technology background of the former *Life Science/Biomimetics Group*. In 2009, the group carried out extensive research on the gas phase synthesis of functional thin films for acoustic, optical and opto-electronic applications in addition to synthesis of biomedical coatings. Since energy storage materials are becoming a core research topic, the group set a special focus on the synthesis of porous materials for hydrogen storage applications.

The group has a strong background in the synthesis of single source precursors for CVD applications. Different gas phase deposition methods including thermal assisted CVD, plasma enhanced CVD (PECVD), liquid injection CVD (LICVD), laser assisted CVD (LCVD) and radio frequency (RF) reactive sputtering are employed within the group. Design of new molecular precursors is of our main interest and stays crucial for these gas phase bottom-up approaches. The main emphasis is on understanding how to control growth at the molecular level and to explore novel chemical routes to grow well-defined target structures such as nanowires, nanorods and nanotubes. In addition, some new chemical synthesis methods were developed for the synthesis of PZT (lead-zirconate-titanate) and ITO (tin doped indium oxide) thin films.

In 2009, the group intensified its activities on the synthesis of oxide nanostructures and the interactions of cells and tissues with these structures. The group has developed collaborations with a number of medical institutions including the Department of Trauma-, Hand- and Reconstructive Surgery and Department of Conservative Dentistry at Saarland University Hospital. Recently a collaboration contract was signed with the Department of Pediatric Cardiology for developing stable inorganic nanostructured thin films for stent applications. A post-doc and two medical doctorate students from Saarland University Hospital started work within the group to explore the cell-surface interactions. In addition to medical institutes, the group established a new collaboration with the Biotechnology Department of the University of Applied Sciences, Kaiserslautern to explore the interaction of neuronal cells with nanostructured surfaces.

## One dimensional oxide nanostructures

One-dimensional (1D) nanostructures have recently become the focus of intensive research owing to their unique chemical, physical and mechanical properties. Especially 1D hetero-nanostructures exhibit superior or new functional properties compared to their individual constituent materials. In this context the Program Division *CVD/Biosurfaces* focused on the synthesis of new 1D hetero-nanostructures such as Ga/$Ga_2O_3$ which find application in the field of sensors and semiconductors. In addition, a special attention was given to the characterization of similar bi-phasic systems for instance Al/$Al_2O_3$ 1D nanostructures; in order to get a better understanding of the growth mechanism and surface properties.

Recently, the group developed ultra-hydrophobic (Figure1a) to hydrophilic surfaces by depositing Al/$Al_2O_3$ nanowires on different substrates. Especially such surfaces are suited well for studying cell-surface interactions due to the biocompatible nature of $Al_2O_3$. The group identified a cell specific response to such chaotic nanostructures (Figure 1b). While osteoblast cells adhere and proliferate on such surfaces, the growth of fibroblasts is hindered. This cell specific response is promising for improving aseptic loosing and biocompatibility of orthopaedic implants. In addition to bio-adhesion studies on 1D nanostructures, the group works on mechanisms of the interaction between 1D ceramic nanostructures and polymers in collaboration with the Program Division *Functional Surfaces* within the frame of "Bio-inspired Adhesives" project funded by Volkswagen Foundation. Depending on the density and entanglement of deposited 1D nanostructures, surfaces exhibit adhering to non adhering regimes. This permanent adhesion opens up a possibility to incorporate fibre-like ceramic nanostructres in polymer matrices by embossing.

## Synthesis of Nanostructures in microgravity environment

Recently the Program Division *CVD/Biosurfaces* performed a CVD experiment during parabolic flights, organized by the German Aerospace Center (DLR), to explore the effect of gravity on the gas transport dynamics, nucleation and growth of 1D nanostructures. The main goal of this research is to develop a model which describes the effects of the gravity on CVD process.

For a typical chemical vapour deposition, the transport process is mainly governed by the combination of three parameters; temperature gradients, dynamic gas properties, and the gravitational force. In the presence of a gravitational field, there is an energetically unstable condition which is induced by the "downward" convection of colder, denser gas and a corresponding "upward" displacement of the hotter and less dense gas (this effect is often addressed as "thermal convection"). In addition to transport properties (like diffusion), the effect of the gravity on the growth and nucleation has been shown by simply changing the substrate position with respect to the gravitational field. On the other hand these approaches do not consider the change in the convection of gaseous reactants by the direction of the gravity field.

In this context a fully automated CVD apparatus with four different growth chambers was prepared to decompose

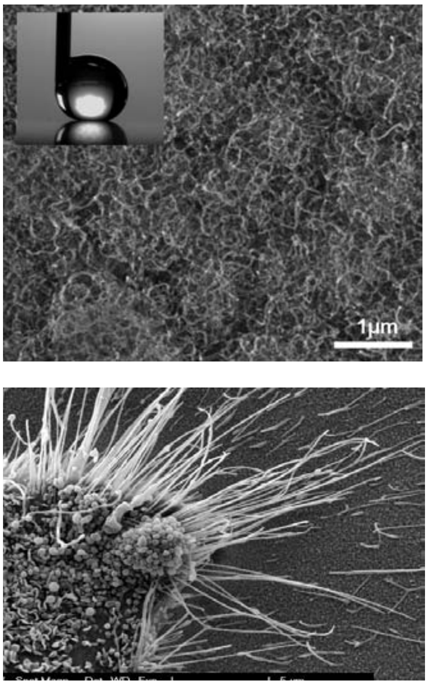


Figure 1: (a) (top) Ultra-hydrophobic coating composed of Al/$Al_2O_3$ nanowires. (b) (bottom) SEM image of an osteoblast cell on Al/$Al_2O_3$ nanowires.

Figure 2: Zero-G team in Airbus 300 before the parabolic flight.

a single source precursor which was developed in our group previously. In five flight days, 20 depositions were performed at different g conditions (0 g, 1 g and 2 g). During this extraordinary experiment, INM "Zero G-team (Figure 2)" struggled against the weightlessness and as well as the time limitation for the deposition since parabolic flights provide repetitively only up to 20 seconds of reduced gravity. Deposition experiments were successfully completed and characterization of samples is still going on. The results of this very interesting experiment will be reported very soon.

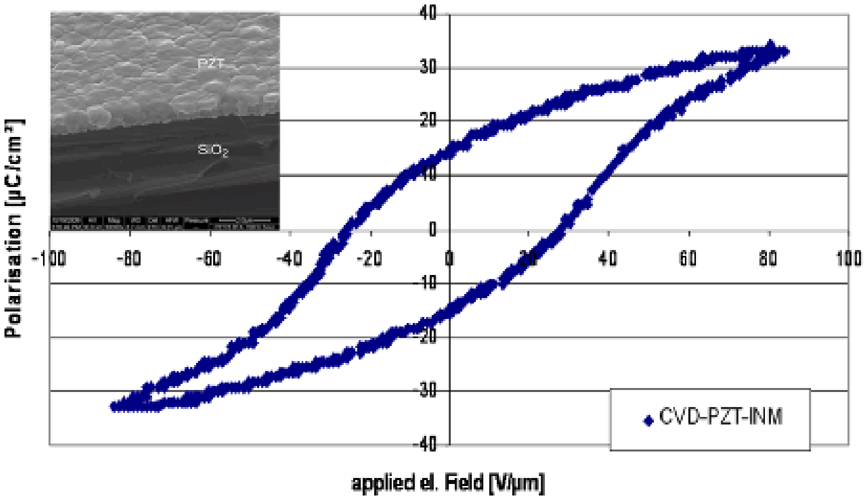


Figure 3: Hysteresis loop of the PZT coating deposited by CVD. Inset shows the SEM image of the deposited layer.

### Thermal CVD of PZT by a novel single source precursor

The interest in ferroelectric films increased during the last decades. The implementation in Micro-Electro-Mechanical Systems (MEMS) technologies, in Ferroelectric Random Access Memory (FeRAMS), in high-frequency components (WLAN) or in infrared-sensors led to a growing demand for those films. The challenge is to improve the film-quality and to reduce the cost of production. Thus, the aim of this work was to facilitate the film fabrication, especially the CVD-process, in using novel single-source-precursors for the deposition of PZT-films.

The design of two bimetallic alkoxide compounds, a lead titanate and a lead zirconate molecular source with identical properties and complement miscibility, resulted in a new single source PZT precursor which evaporates at a temperature of 25 °C and a pressure of 0.13 mbar. The composition of the precursor (Pb:Zr:Ti = 2:1:1) leads to transparent (100) oriented PZT films with a stoichiometry near the morphotropic phase boundary. An additional lead source is not required. After the CVD-process, the deposited films were thermally treated at 650 °C to obtain the desired perovskite phase. The SEM-images show the surface of a smooth 1 µm thick film with a grain-size of about 500 nm (Figure 3, inset). The dielectric constant $\varepsilon_r$ and the dielectric loss δ of the PZT-films were measured to be 412 and 0.025. The hysteresis loop (Figure 3) shows a remnant polarization of 25 µC/cm² and a coercive field of 30 V/µm.

### ITO coatings by CVD

Transparent conductive oxides (TCO) have attracted enormous attention over

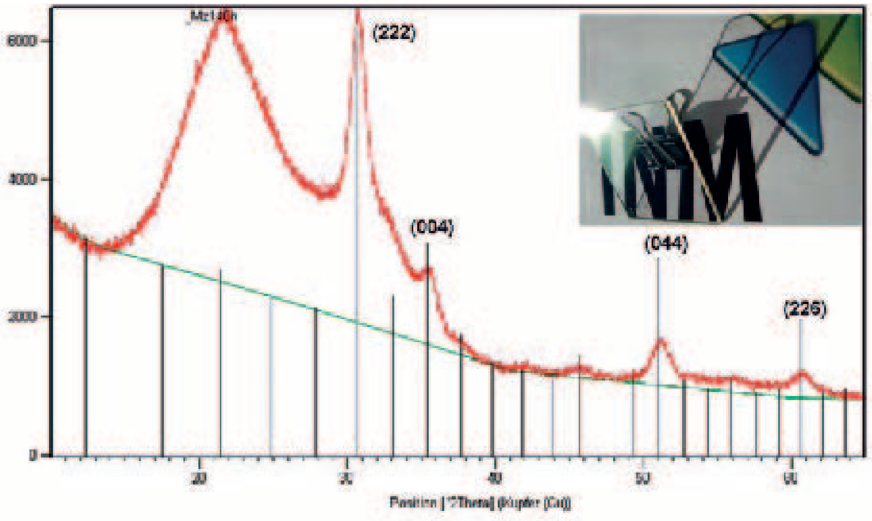


Figure 4: XRD diffractogram of the ITO layer. Inset shows the transparency of the deposited layer.

the last decades because of their unique combination of high visible transparency and good electrical conductivity. They are being used as transparent electrodes in electro optic devices such as solar cells, flat panel displays, liquid crystal displays, electroluminescent and electrochromic applications such as Light Emitting Diodes (LED) and electrochromic windows. The materials most widely used for TCO-applications are the doped and undoped oxides of indium, tin and zinc. Among them, Tin-doped Indium oxide ($In_2O_3$:Sn, ITO) offers the best combination of high electrical conductivity and transparency in the visible range, for which it is the material of choice for most applications.

Thin films of ITO can be applied by various techniques such as sputtering, spray pyrolysis, chemical vapor deposition (CVD) and by the sol-gel-process. For the CVD of ITO-coatings, suitable precursor materials should be volatile at moderate temperature and pressure, stable during evaporation and able to decompose on activated surfaces to build up the oxide layer. In most of the CVD approaches, precursors of tin and indium are separately deposited. In such a process, it is difficult to maintain a constant and stable flow rate of tin and indium which is a critical issue for achieving a controllable dopant concentration.

We developed a new precursor in which an organometallic indium compound is chemically bonded to the organometallic tin-compound. Decomposition of this precursor at 500 °C results in a one pot process and in a transparent film (Figure 4, inset) and this film exhibits a crystalline cubic indium oxide phase (Figure 4) obtained by XRD. The shift of the measured peaks compared to the reference diffraction peaks corresponds to lattice changes due to the incorporation of the dopant tin into the $In_2O_3$ host lattice. The thickness of the examined ITO-layer is 23 nm. The as-prepared samples without the general reducing treatment show a sheet resistance of 1640 kΩ/sq. After post-treatment in reducing atmosphere, the value has slightly decreased to 1542 kΩ/sq, corresponding to a specific electrical resistivity of $3.55 \times 10^{-3}$ Ωcm. This increase in electrical conductivity can be explained by the formation of oxygen vacancies in the oxide lattice by reduction treatment. Further enhancement of the layer growth might be achieved when oxygen is added to a carrier gas.

## Outlook

The research and development activities in *CVD/Biosurfaces Group* will be focused on developing new gas-phase synthetic approaches for fabrication of 1D nanostructures as functional nanomaterials in biomedical, sensor, optical and other relevant technological applications. The group plans performing further investigation on the quality of nanowires for instance how to produce well-aligned nanowires with uniform morphology and crystallinity to match the requirements for different applications including optics and electronics.

Special attention will be given to the design of nanostructured surfaces for biomedical applications. The main interest will be the fabrication of micro and nanostructured surfaces which can mimic the tissue's extracellular matrix (ECM) to provide cells a similar environment to their natural habitat and ensure the implant is analogue in terms of its physical and structural properties to the original tissue. In this context, we would like to establish new collaborative projects with our existing and new bio and medical partner institutions.

# Nano Zell Interaktionen / Nano Cell Interactions

## Dr. Annette Kraegeloh

Die Juniorforschungsgruppe *Nanotoxität* hat im November 2009 ihren Namen zu *Nano Zell Interaktionen* geändert. Der neue Name beschreibt die Zielsetzung der Gruppe etwas deutlicher. Ziel ist es, den Einfluss synthetischer Nanomaterialien, insbesondere von Nanopartikeln auf einzelne Zellen menschlicher Herkunft, festzustellen. Unsere Aufgabe besteht darin, die Wechselwirkungen technischer Nanopartikel mit Zellorganellen und biologischen nanoskaligen Strukturen detailliert zu beschreiben und Mechanismen aufzuklären, die eine mögliche Toxizität solcher Materialien hervorrufen. Wir konzentrieren uns dabei auf Phänomene wie die Adhäsion von Partikeln an der Zelloberfläche, die Partikelagglomeration und -aufnahme, den intrazellulären Transport und den Verbleib von Nanopartikeln. Eine methodische Besonderheit, die unsere Studien von denen anderer Gruppen abhebt, ist der Einsatz der neuen STED (Stimulated Emission Depletion)-Mikroskopie. Darüber hinaus wird die biochemische Antwort der Zellen bei Exposition mit Nanopartikeln anhand geeigneter Testsysteme festgestellt und den Strukturuntersuchungen gegenübergestellt. Die Kenntnis der Eigenschaften der eingesetzten Nanopartikel ist zentral, um ihre Auswirkungen auf lebende Zellen zu verstehen. Aus diesem Grund stellen wir wohldefinierte Nanopartikel her, die mit fluoreszenzbasierten Methoden detektierbar sind. Unser Ansatz nutzt eine enge Verknüpfung biologischer, chemischer und physikalischer Kenntnisse und Methoden.

Zu den von uns verwendeten Partikelsystemen gehören Silika-, Gold- und Silber-Nanopartikel, die wir zum Nachweis mittels fluoreszenzbasierter Methoden, wie z. B. der STED-Mikroskopie, mit speziellen Fluoreszenzmarkern versehen. Mit Hilfe mikroskopischer Untersuchungen wurde festgestellt, dass $SiO_2$-Nanopartikel unterschiedlicher Größen (45 und 130 nm) in die Zellen aufgenommen werden und dass die 130 nm Partikel nicht in den Zellkern eindringen. Auf die Stoffwechselaktivität der verwendeten Lungenepithel- und Darmepithel-Zellen hatte die Anwesenheit von $SiO_2$-Partikel keinen signifikanten Effekt. Die besondere Eignung der STED-Mikroskopie zur Aufklärung von Mechanismen konnte in einer ersten Studie belegt werden: Nur mit ihrer Hilfe war es möglich, die Agglomeration von $SiO_2$-Partikeln im Zellinneren quantitativ zu bestimmen (zur Publikation in Advanced Materials Engineering angenommen).

Die Gruppe profitiert bei ihren Untersuchungen von engen Kooperationen mit den Arbeitsgruppen Pharmazeutische Biologie, Theoretische Physik sowie Mathematik und Informatik der Universität des Saarlandes (UdS), mit denen sie im Rahmen eines vom Saarland Ministerium für Wirtschaft und Wissenschaft geförderten Projektes- den intrazellulären Transport von Gold-Nanopartikeln untersucht. Die Arbeitsgruppe unterstützt außerdem das durch das Institut für Arbeitsmedizin am INM durchgeführte „Arbeitsmedizinische Untersuchungsprogramm bei Exposition mit Nanopartikeln und neuen Materialien“. Weiterhin bereitet die Gruppe gemeinsam mit den Firmen Sarastro und Nanogate, Partnern der UdS und der Universität Mainz ein Vorhaben zur systematischen Bewertung der Gesundheitsauswirkungen nanoskaliger Kontrastmittel (NanoKon) vor. Das im Rahmen der BMBF-Ausschreibung „NanoCare“ beantragte Vorhaben wurde bereits zur Förderung vorgeschlagen.

In nächster Zeit werden wir uns intensiv mit den Aufnahmemechanismen und der intrazellulären Lokalisation der Partikel auseinandersetzen. Zu unseren unmittelbaren Arbeitsgegenständen gehören Untersuchungen zur Dynamik der Internalisierungs- und Transportprozesse sowie Untersuchungen zur möglichen Toxizität von Silber-Nanopartikeln.

In November 2009, the former junior research group *Nanotoxicity* was renamed as *Nano Cell Interactions*.. The new name specifies the objective of the group more precisely. The group aims at the investigation of the influence of nanoscaled materials, in particular nanoparticles, on single cells of human origin. Our objective is to describe in detail the interaction of nanoparticles with cellular organelles and biological structures of nanoscale dimension and to elucidate mechanisms potentially causing toxicity of such materials. We concentrate on phenomena like particle adhesion to cellular surfaces, nanoparticle agglomeration and uptake, intracellular transport and the fate of nanoparticles. The key method for our investigations, distinguishing our studies from others, is STED (Stimulated Emission Depletion) microscopy, enabling the visualization of biological as well as of engineered structures with appropriate spatial resolution. Microscopic data are complemented by analyzing the biochemical response of the cells to nanoparticle exposition, quantified by adequate assays. The results are set into context with the structural examinations. An important prerequisite for our investigations is the detailed knowledge of the accordant material properties. Therefore, we synthesize well-defined nanoparticles as model systems that allow the detection and visualization by fluorescence based methods. Our approach is highlighted by a tight combination of biological, chemical and physical skills and methods. The group benefits from cooperation with the groups Pharmaceutical Biology, Theoretical Physics, and Mathematics and Computer Science from Saarland University. Within a project funded by the Saarland Ministry for Economics and Science, the four partners investigate the intracellular transport of gold nanoparticles. The group supports the Institute of Occupational Medicine concerning the occupational medical diagnostic program regarding exposure to nanomaterials and new materials. Together with the companies Sarastro and Nanogate, partners of UdS, and University of Mainz the group prepares a project on the systematic evaluation of health impacts of nanoscale contrast agents. The proposed project has been recommended for funding by the Federal Ministry of Education and Research.

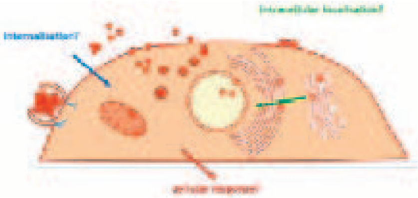


Figure 1: Potential uptake pathways and localization of nanoparticles in human cells.

## Nanoparticle systems

One of our key activities is the preparation of nanoparticles on the base of inorganic materials. Recently, silica, gold, and silver nanoparticles have been synthesized. During the last year, the synthesis of $SiO_2$ particles has been further optimized. As a result, core shell type nanoparticles have been synthesized, allowing the incorporation of different fluorescence dyes into the inner core of the particles. The dyes are either applied as a thin layer or used to label the whole particle core. Incorporation of dyes into the particle matrix minimizes potential effects of the dyes themselves. The size of the corresponding $SiO_2$ particles was varied between 25 and 130 nm (Figure 2a). Their spectral characteristics matched the characteristics of

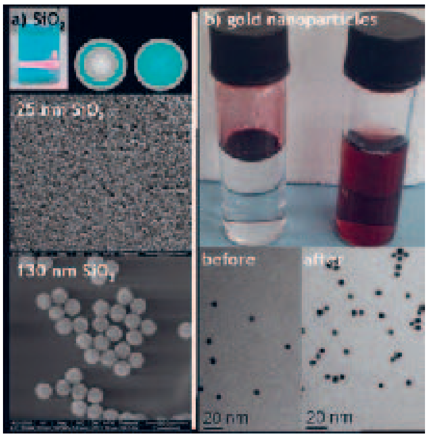


Figure 2: Silica and gold nanoparticles prepared for exposition to cells. a) top: suspension of labeled $SiO_2$-nanoparticles and scheme of their core shell structures, middle and bottom: SEM micrographs of labeled $SiO_2$-particles. b) top: suspension of gold nanoparticles before and after transfer into the water phase, bottom: corresponding TEM micrographs of the gold nanoparticles.

the pure dye in solution. Until now, $SiO_2$ particles were used without further surface modification. Using dynamic light scattering, the particles were found to be stable in cell culture media; they did not exhibit significant agglomeration. Also under experimental conditions, the zeta potential of the particles was reduced to less negative values, indicating wrapping by a protein layer.

Beside of silica, gold nanoparticles have been prepared, using a non polar synthesis route (Figure 2b). After phase transfer, the particles are surrounded by a polymer shell, enhancing particle stability in cell culture media. Gold particles synthesized thus far were negatively charged by carboxy groups, thus offering a broad variety of options for further functionalization, for example via peptide chemistry.

### Microscopical investigations

For *in vitro* investigations, we use epithelial cells derived from human lung and intestine tissues. In order to detect cellular building blocks – beside of nanoparticles – various cellular components are fluorescence labeled. Subsequently, cells are prepared for microscopy. By means of structural investigations we aim to identify components participating in particle uptake as well as to illustrate localization and state of the particles in detail.

Epithelial lung (A549) and intestine (Caco-2) cells were incubated with different sizes of $SiO_2$ nanoparticles up to 48 hours. Cellular structures like the actin cytoskeleton, the nucleus, and cellular membranes were labeled for microscopical investigations. 45 nm and 130 nm particles were shown to enter cells already after five hours of incubation, although to a moderate extent. The number of internalized particles increased with time, up to 48 hours. A great number of nanoparticles were attached to the cytoplasmic membrane of the cells, in particular to the surface of A549 cells. Over the experimental period the 130 nm particles were not detected to enter the cellular nucleus. The presence and internalization of nanoparticles did not fundamentally affect the structure of the actin cytoskeleton (Figure 3). Only STED microscopy enabled us to monitor and to quantify the agglomeration of 130 nm particles inside cells. The corresponding results are accepted to publication in Advanced Engineering Materials.

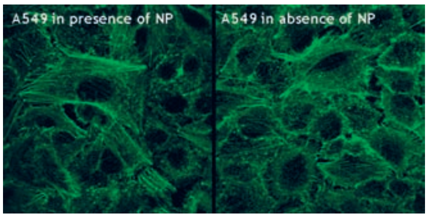


Figure 3: Structure of the actin cytoskeleton after incubation of A549 cells in presence or absence of $SiO_2$ nanoparticles.

### Cellular response

The presence and uptake of nanoparticles potentially affects the physiological status of the cells or induces generation of cellular mediators. In order to detect and quantify the biochemical response of the cells, we apply cell-based assays, as a start focusing on cytotoxicity, potentially caused by exposition to nanoparticles. Regarding cytotoxicity, an immense number of test systems exist, most of them relying on enzymatic conversion of the test substrate, resulting in a light absorbing, fluorescent or luminescent signal. Many of the quantitative assays indicate cellular viability in terms of energy content, reducing potential or membrane integrity, e. g. by detecting leakage of distinct compounds out of or into the cells. At early stages, before membrane damage or metabolic activity are reduced, the induction of apoptosis, an active mode of cellular death, can be measured.

To quantify the cellular response on exposition to $SiO_2$ nanoparticles, we applied a colorimetric assay system, indicating the metabolic activity and viability of the cells. This test is based on reduction of the substrate WST-1 (4-[3-(4-Iodophenyl)-2-(4-nitrophenyl)-2H-5-tetrazolio]-1,3-benzene disulfonate) to a soluble, yellow formazan by cellular enzymes. Cells were exposed to various sizes of nanoparticles for 24 hours (Figure 4). Using this assay system, no significant effect of the particles was detected, up to a concentration of 0.1 mg $SiO_2$ $ml^{-1}$.

## Outlook

A detailed analysis of uptake and intracellular localization of nanoparticles of various material compositions and other characteristics is central to our studies. In order to obtain deeper insights into these phenomena, we will proceed to expose the cells to nanoparticles of even smaller sizes. Later on, we will start to vary the surface modification of the particles. Uptake pathways will be analyzed by more specifically labeling of components, relevant for distinct uptake pathways. Additionally, we will apply pharmacological inhibitors to corroborate our findings. We intend to label particles by use of a pH sensitive dye, in order to be able to detect the physiological environment of internalized particles and to further elucidate their cellular localization. STED imaging and mathematical image processing will assist our effort to detect the state of agglomeration of nanoparticles for example on the cellular surface and to quantify the microscopic data. Additional test systems, indicating membrane integrity or oxidative stress will be used, in order to get further insights into the cellular response.

Besides the analyses of cellular uptake and potential effects of $SiO_2$ nanoparticles on human cells, two topics will capture our main attention in future. The first is to discover the dynamics related to particle internalization combined with the dynamics of distinct proteins involved in or affected by these processes. The other topic is related to the effects of silver nanoparticles on human cells. We aim to understand the mechanisms causing cellular toxicity in relation to the effects of silver ions.

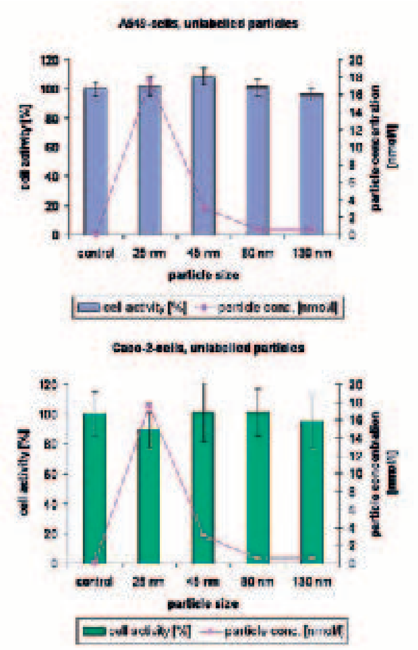


Figure 4: The metabolic activity of the cells was not affected significantly in response to the presence of various sizes of $SiO_2$ nanoparticles. Each particle type was added at a concentration of 0.1 mg $SiO_2$ $ml^{-1}$, the calculated particle concentration (number, pink data points) is indicated by the second y-axis. Values are averaged from eight replicates of one experiment.

# Modellierung/Simulation / Modelling/Simulation

**Prof. Dr. Robert McMeeking**

Der Programmbereich *Modellierung / Simulation*, seit 1. April 2008 kommissarisch geleitet von Prof. Dr. Robert McMeeking (University of California, Santa Barbara, UCSB), befindet sich im Aufbau. Bis 2011 soll der Programmbereich etabliert sein und neben der Bearbeitung von eigenständigen Projekten die anderen Programmbereiche im Hinblick auf Fragen der Modellierung und Simulation unterstützen.

Im Jahr 2009 wurde eine Reihe von Forschungsprojekten mit Bezug zu aktuellen INM-Forschungsthemen durchgeführt:

*Adhäsion*: Modelle der Adhäsion zwischen einer steifen, glatten Oberfläche und einer nachgiebigen, fibrillar sphärischen Oberfläche wurden entwickelt. Diese Modelle erlauben die Simulation von Experimenten, in denen die Abzugskräfte zwischen solchen Oberflächen gemessen werden. Die Ergebnisse der Simulationen lassen auch den Test von Hypothesen zu, die die Natur der Adhäsion zwischen den Fasern auf der sphärischen Oberfläche und dem flachen Objekt betreffen. Simulationen der Adhäsion zwischen einer nachgiebigen Oberfläche mit Vertiefungen mit einer flachen und steifen Oberfläche zeigten eine bistabile Adhäsion. Eine schwache Adhäsion kann durch druckloses Zusammenfügen der beiden Oberflächen erreicht werden, und die Oberflächen können wieder vollständig voneinander getrennt werden. Die Schwache kann durch Druck in eine starke Adhäsion umgewandelt werden. Die Oberflächen sind dann nicht mehr einfach zu trennen. Zu diesem bistabilen Adhäsionskonzept wurde ein Patent angemeldet.

*Zellmechanik*: Ein Modell für die Kontraktierbarkeit, das Remodelling des Zytoskeletts und die Adhäsion in biologischen Zellen wurde entwickelt. Dieses Modell erlaubt es, diverse experimentelle Beobachtungen wie zum Beispiel das Skalieren der kontraktilen Kräfte mit der Steifheit der Zellumgebung und der Orientierung der zytoskeletalen Stressfasern während einer zyklischen Anspannung der Zelle zu simulieren. Das Modell wird erweitert, um auch die Nutzung in Simulationen der Partikeltoxikologie zu ermöglichen, in denen Endozytose zur Aufnahme der Partikel führt und die Umbildung des Zytoskeletts stimuliert wird. Des Weiteren wurde damit begonnen, das Zellmodell in Richtung auf die Biomineralisation auszuweiten, da auch dieses Thema am INM aktiv verfolgt wird.

*Erstarrung nanopartikelhaltiger Schmelzen*: Es wurden Modelle zur Simulation der Erstarrungsfronten entwickelt, die mit einer Familie von Nanopartikeln wechselwirken, um Prozesse zu identifizieren, die die Dispersion solcher Partikel im erstarrenden Material verbessern. Dies soll zur Verstärkung des Materials dienen. Die Wechselwirkung zwischen Zugkraft auf die Nanopartikel, ihrer Trägheit und die Oberflächenspannung zwischen festen, flüssigen und Partikeloberflächen dominieren die involvierten Prozesse und bestimmen, ob die Nanopartikel in die Flüssigkeit vor der Erstarrungsfront gezogen oder in den erstarrenden Festkörper eingebaut werden. Die Simulationen werden durchgeführt, um den Bereich der Prozessparameter – z. B. Kühlrate, Erstarrungsgeschwindigkeit etc. – zu identifizieren, der den Einbau der Nanopartikel in den Festkörper und ihre gleichmäßige Dispersion sicherstellt.

Folgende Themen werden aus heutiger Sicht für die zukünftige Entwicklung des Programmbereiches *Modellierung / Simulation* von Interesse sein:

- Kontaktmechanik strukturierter Systeme;
- Tribologie von Hybridschichtsystemen;
- Benetzung und Kapillarität;
- Adhäsion;
- Optimierung von mikrooptischen Systemen;
- Mikromechanik natürlicher und künstlicher Kompositsysteme;
- Simulation von Wachstumsprozessen;
- Modellierung von Zelladhäsion und zellbiologischer Prozesse, speziell in Wechselwirkung mit Substraten oder Nanopartikeln.

This Program Division is in a set-up stage. Since 1 April 2008, Prof. Dr. Robert McMeeking from the University of California, Santa Barbara (UCSB) has been its provisional head. Currently, Prof. Dr. Daniel Strauss is a senior member of the division, and he and McMeeking collaborate on both research projects and planning for the future of the Program Division. By 2011, the division should be established, with the aim of providing support to the other program divisions, as well as having on-going research projects selected according to the research interests and activities of division personnel.

**Research Projects**

McMeeking pursued a small number of research projects relevant to topics currently of importance within INM:

*Adhesion*: Models of adhesion between a stiff smooth surface and a compliant, fibrillar spherical surface have been developed. These models allow simulation of experiments carried out at INM and elsewhere in which the pull-off forces between such surfaces has been measured. The results of the simulations allow hypothesis testing to be carried out regarding the nature of adhesion between the fibrils on the spherical surface and the flat object. For example, assessments can be made in regard to whether the pull-off condition for an individual fibril is deterministic, or if it obeys a probabilistic behavior in which the force at which separation occurs is controlled by defects in the surfaces that are adhering. In addition, simulations of the adhesion of a compliant dimpled surface with a flat, stiff one have been developed and show that bi-stable adhesion can be developed. In this phenomenon, weak adhesion can be achieved by placing the surfaces together without compression. In this state, the surfaces can be separated readily. The weak adhesion condition can be converted to strong adhesion by application of pressure to press the apices of the dimples against the flat surface. The surface now cannot be easily detached. A patent has been applied for regarding this bi-stable adhesion concept.

*Cell mechanics*: A model for contractility, cytoskeleton remodeling, and adhesion in biological cells has been developed, coupled to signaling controlled by proteins generated in response to mechanical stimulations of the ligaments to which the cell is attached. This model is able to simulate various experimental observations such as the scaling of contractile forces with the stiffness of the cell's environment, and the orientation of cytoskeletal stress-fibres during cyclic straining of the cell. The model is being extended to allow for its utilization in particle toxicology simulations, where endocytosis ingests particles, and stimulates remodeling of the cytoskeleton. Such models should be relevant to issues of nanotoxicology that are being considered at INM. In addition, preliminary thought has been developed for developing the cell model in the direction of biomineralization, another topic that is actively pursued at INM.

*Solidification of melts containing nanoparticles*: Models are being developed for simulating solidification fronts that interact with a family of nanoparticles to identify processes that will enable the dispersion of such particles within the solidified material for purposes of strengthening. Competition among drag on the nanoparticles, their inertia and surface tension among the solid, liquid and particle surfaces can dominate the processes involved, determining whether the nanoparticles are driven into the liquid ahead of the solidification front or are ingested into the solidifying solid. The simulations are being pursued to identify the range of processing parameters (i. e. cooling rate, speed of the solidification front, etc.) that ensures incorporation of the nanoparticles into the solid and their even dispersion.

## Outlook

From today's perspective, the following topics are assessed to be of significance for future developments in modeling and simulation, given directions within INM, and will be considered for future effort as the division builds in strength and resources:

- contact mechanics of structured systems;
- tribology of hybrid layered systems;
- wetting and capillarity;
- adhesion;
- optimization of micro-optical systems;
- micro mechanics of natural and artificial composite systems;
- simulation of growth processes;
- modeling of cell adhesion and of cell biological processes, especially in interaction with substrates or nanoparticles.

# Anwendungszentrum NMO/Verfahrenstechnik / Application Center NMO/Chemical Engineering

Das *Anwendungszentrum NMO* (Neue Materialien für die Oberflächentechnik) ist seit 14 Jahren eine zentrale Schnittstelle des INM für den Technologietransfer in die Industrie. Seit seiner Gründung im Jahr 1995 wurden vielfältige Entwicklungsarbeiten im Bereich von Nassbeschichtungstechnologien mit neuen, im INM entwickelten Beschichtungswerkstoffen unter Ausnutzung einer breit gefächerten technischen Ausstattung mit Pilotanlagen zur Materialsynthese bis zum 100 L-Maßstab, zur Serienbeschichtung von Formteilen mit verschiedenen Nassbeschichtungsverfahren (u. a. Sprüh-, Tauch-, Schleuder- und Rollenverfahren) sowie Anlagen zur Oberflächenvorbehandlungs- und Härtungstechnik durchgeführt. Nach dem Ende der Förderperiode durch das BMBF im Jahr 1999 wurde das Anwendungszentrum in den folgenden Jahren strategisch als Forschungs- und Entwicklungsdienstleister für Industrieunternehmen in Form einer INM-Abteilung mit eigenständiger Kostenrechnung unter der Maßgabe von hundertprozentiger Kostendeckung durch Drittmitteleinnahmen fortgeführt. Im Zuge des Veränderungsprozesses des gesamten Institutes während der vergangenen Jahre befindet sich auch das *NMO* aktuell in einer Umstrukturierungsphase. Zudem erfolgt eine thematische Neuausrichtung, welche sich nicht allein auf das Gebiet der Nassbeschichtungstechnik beschränkt. Vielmehr soll das *NMO* zukünftig als Ansprechpartner für die technologische Umsetzung von verschiedensten Forschungsthemen aus allen Programmbereichen des INM dienen.

Im Rahmen von internen Kooperationen mit anderen Programmbereichen leistete das *NMO* Beiträge zu vier Entwicklungsprojekten, sechs Klein-Projekten sowie einer Untersuchung im Grundlagenforschungsbereich. Die Kooperationsprojekte beinhalteten u. a. Untersuchungen zum Up-Scaling von Rezepturen, die Entwicklung von Applikationswerkzeugen zur Innenbeschichtung von zylindrischen Formteilen sowie Versuche zur Sprühapplikation von glasartigen Sol-Gel-Materialien, Glas-Keramik-Materialien und von Nanomer-Korrosionsschutzschichten auf verschiedenen Metall-Formteilen. Zusätzlich wurde ein separates Kleinprojekt mit Beratung und Nutzung von technischer Ausstattung durchgeführt.

Als Erweiterung der bisherigen technischen Ausstattung wurde im Berichtszeitraum zur Entwicklung von maschinengesteuerten Sprühbeschichtungsverfahren für komplexe Probengeometrien eine neue Lackierkabine mit integriertem Industrieroboter konzipiert. Der Aufbau und die Inbetriebnahme dieser Anlage sind zu Beginn des Jahres 2010 geplant.

Innerhalb der *Chemischen Verfahrenstechnik*, welche durch Eingliederung im Jahr 2007 zusammen mit dem *NMO* den Programmbereich *NMO / Verfahrenstechnik* bildet, wurde eine eigenständige, von Industrieprojekten unabhängige Grundlagenforschung betrieben. Das Thema einer laufenden Doktorarbeit liegt auf dem Gebiet der elektrochemischen Synthese von nano-skaligen Metalloxiden. Neben dem System Indium-Zinn-Oxid liegt der Schwerpunkt der Arbeit auf dem System Zinkoxid, welches sowohl direkt unter Einstellung spezifischer Prozessparameter während der Synthese, als auch über den Umweg über Zwischenstufen verschiedener Hydroxid- und Schichthydroxidsysteme und deren thermischer Behandlung mit entsprechenden Eigenschaften erhalten werden kann.

## Application Center NMO (New Materials for Surface Technologies)

Since 14 years, the *Application Center NMO* represents the central INM interface group for the transfer of lab-scaled research results into industrial application. A vast number of development activities were performed in the area of wet coating applications of newly developed sol-gel and nano composite materials using a variety of technical equipment for pilot-scale material synthesis, pilot-plant coating technologies (e. g. spray-, dip-, spin-, roller-coating etc.), surface pretreatment and curing machinery. The *NMO* presented a direct partner for industrial partners to introduce new products using INM material- and coating-technology. After the end of the financial support by the German ministry of education, science, research and technology in 1999, the *NMO* was continued as INM department with separate financial accounting and a budget covered 100 % from project revenues. Due to the INM restructuring during the last years, a reorganization of the *NMO* structure is also in progress. Development activities will no longer focus on wet coating technology only. The *NMO* is supposed to operate as internal cooperation partner for all INM R&D departments for technology transfer of a variety of research topics.

As a service group with three employees in 2009, the *NMO* supported all Program Divisions of INM. In 2009, we cooperated in four R&D projects, six small-scale projects and one basic research topic including:

- Investigations for scaling-up of a Nanomer coating material (cooperation with the Program Division *Nanomers*).
- Development of spray coating device for the application of a Nanomer coating material on the inside of cylindrical samples (cooperation with Program Division *Nanomers*).
- Application of a glass-ceramic coating with corrosion inhibitant and anti-adhesive properties on stainless steel engine parts using spray coating (cooperation with Program Division *Optical Materials*).
- Investigations for spray coating of different corrosion protective Nanomer coatings on metal samples (cooperation with Program Division *Nanoprotect*).
- Spray coating experiments for application of glass-like and glass-ceramic coatings with wear resistant properties on aluminum parts, for application of glass-ceramic coating materials on stainless steel parts for improving corrosion protection and slip properties (both cooperation with Program Division *Optical Materials*) and for the application of coatings with high temperature anti-oxidative properties on steel (cooperation with Program Division *Nanoprotect*).
- Rendering of technical service and renting technical equipment for synthesis of liquid coating materials as support for a small sized enterprise.

A new spray cabin (24 m$^2$ area size) with an integrated industrial robot was

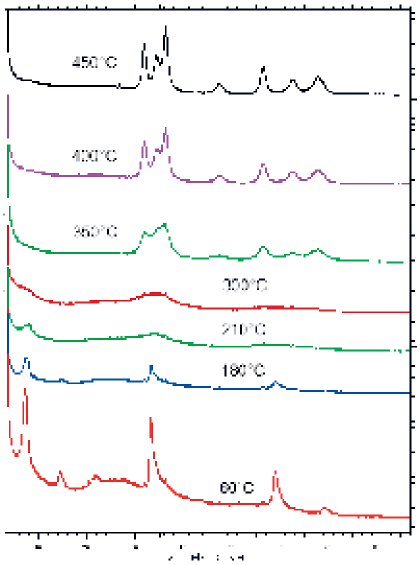


Figure 1: X-ray diffraction patterns of zinc oxide / hydroxide at various temperatures: phase evolution of a layered zinc hydroxide structure to nano scaled zinc oxide particles.

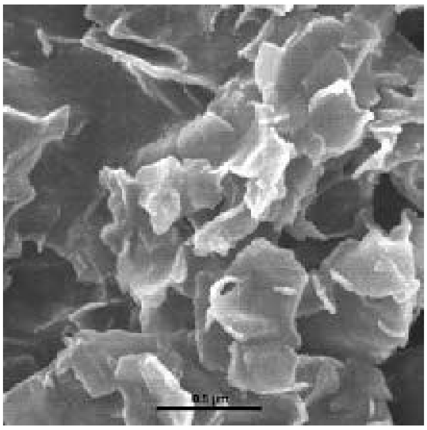


Figure 2: SEM image of a layered zinc hydroxide structure, before thermal treatment.

designed as additional technical equipment for the development of automatic spray coating technologies for complex 3-dimensional sample geometries. The installation and setup is scheduled for early 2010.

### Chemical Engineering

The Chemical Engineering group was integrated into the *NMO* in 2007 to form the Program Division *Application Center NMO/Chemical Engineering*. In the *Chemical Engineering* part of the division basic research independent of industrial projects was performed. Currently, one doctoral student is working on his thesis investigating electrochemical deposition processes of metal oxides for forming nano scaled particles. In 2009, research activities were focused on the synthesis of ZnO. In addition to existing experience of hydroxide to oxide conversion during the synthesis procedure controlled by process parameter adjustment, a new synthesis route with a modified experimental setup could be developed. Laminated hydroxide salts accessible by this procedure could serve as precursors for high purity metal oxide materials with possible applications, e.g. as materials for drug delivery, anion exchange, catalysis etc. These materials and their properties were further investigated. Thereby, the parameters of the dehydration step using different methods were found to be equally influential as the electrochemical deposition process parameters (e.g. inert atmosphere, temperature and counter part ions). The doctoral thesis is planned to be finished in 2010.

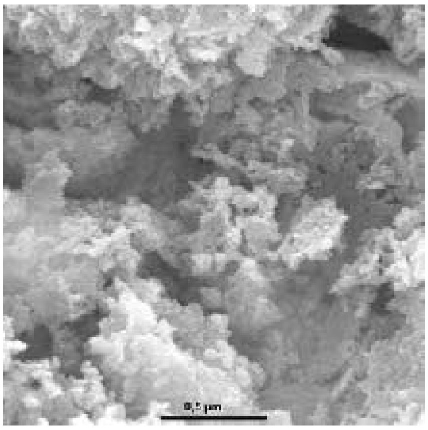


Figure 3: SEM image of nano scaled ZnO particles, after heat treatment (> 200 °C) of a layered zinc hydroxide structure.

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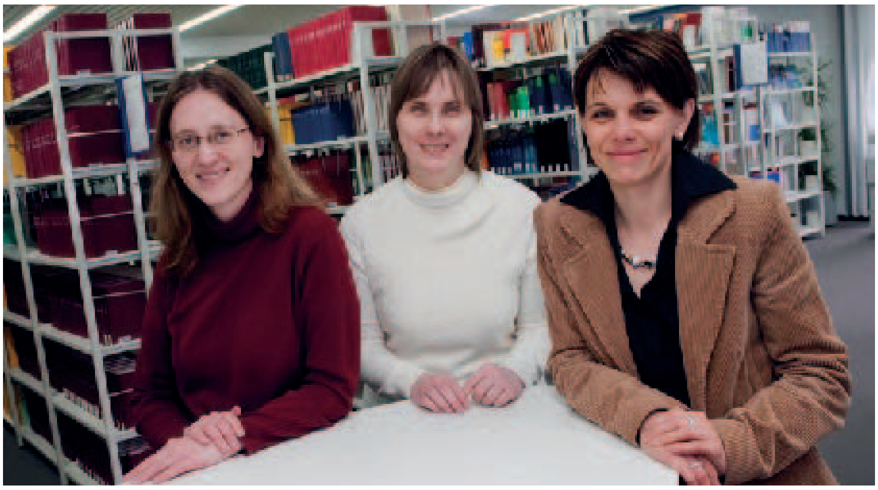
Ziel der Open-Access-Bewegung ist es, wissenschaftliche Literatur und wissenschaftliche Materialien für alle Nutzerinnen und Nutzer kostenlos im Internet zugänglich zu machen. In ihrer Leitlinie zu Open Access formuliert die Leibniz-Gemeinschaft das Ziel, die Forschungsergebnisse ihrer Mitgliedseinrichtungen möglichst digital und frei zugänglich zu publizieren und langfristig an zentraler Stelle nachzuweisen. Die INM-Bibliothek setzt diese Leitlinie über den sogenannten „Grünen Weg“ um, einer Open-Access-Strategie, mit der die zeitverzögerte elektronische Zweitveröffentlichung von Publikationen gemeint ist. Unter Berücksichtigung der urheberrechtlichen Bestimmungen veröffentlicht die INM-Bibliothek hausinterne Publikationen auf SciDok (http://scidok.sulb.uni-saarland.de/), dem Wissenschaftsserver der Saarländischen Universitäts- und Landesbibliothek.

### Dokumentation von INM-Publikationen

Wissenschaftliche Publikationen gelten als quantitativer Leistungsindikator bei Audit und Evaluation innerhalb der Leibniz-Gemeinschaft. In der INM-Bibliothek werden an zentraler Stelle sämtliche Veröffentlichungen und Vorträge des Hauses kontinuierlich und vollständig dokumentiert, um Analysen nach evaluationsrelevanten Kriterien zu ermöglichen. Als Basis dient die Literaturverwaltungssoftware Endnote, für die im Berichtszeitraum Schulungen auch für interessierte Wissenschaftlerinnen und Wissenschaftler des Hauses organisiert und durchgeführt worden sind.

### Interne Kommunikation und Information

Innerhalb der Arbeitsgruppe PR / Öffentlichkeitsarbeit des INM ist die Bibliothek an der Konzeption und dem Erstellen von Medien und Kommunikationsmitteln des Instituts beteiligt. Dazu gehören die Mitarbeit bei der Erstellung der Mitarbeiterzeitschrift *nanonews*, die Administration und Weiterentwicklung des INM-Internet-Auftritts sowie die Pflege des hausinternen Intranet-Angebots.



# Servicegruppe Chemische Analytik / Service group Chemical Analysis

## Dr. Claudia Fink-Straube

Für die chemische Charakterisierung der am INM synthetisierten Materialien werden Methoden der Flüssig- (HPLC, LC/MS und SEC) und Gaschromatographie (GC, GC/MS), atomspektrometrische Messverfahren (AAS, ICP OES) sowie die Flüssig- und Festkörper-NMR-Spektroskopie eingesetzt. Im Jahr 2009 wurden vom Servicebereich *Chemische Analytik* ca. 70 % der analytischen Arbeiten für interne Forschungsaufgaben und laufende Projekte des INM, ca. 20 % für Kooperationen mit der Universität des Saarlandes und ca. 10 % für externe Auftraggeber durchgeführt. Neben den analytischen Untersuchungen zu den laufenden Projekten des INM lag ein weiterer Schwerpunkt auf der Anpassung, Erweiterung und Optimierung der bestehenden Methoden auf die Anforderungen der neuen Arbeitsgruppen und dem Ausbau der Kooperationen mit der Universität des Saarlandes.

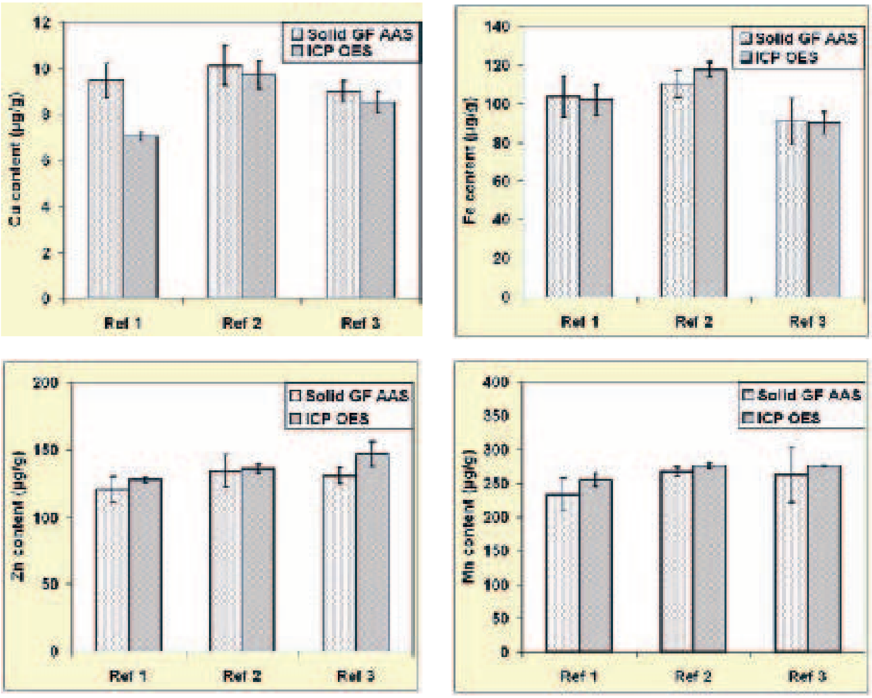


Bild 1: Fe-, Mn-, Cu- und Zn-Gehalte von drei Referenzproben (Arabidopsis thaliana), analysiert mit GF-AAS mit direkter Feststoff-Zufuhr und ICP OES nach Mikrowellen-Aufschluss.

Eine neue Kooperation wurde mit dem Institut für Biopharmazie und pharmazeutische Technologie (Prof. C.-M. Lehr und Prof. M. Schneider) im Juli 2009 gestartet. Im Rahmen einer Dissertation werden Gold-Nanopartikel als Transporter für Pharmawirkstoffe untersucht. Für die Bindung des Wirkstoffes an die Gold-Nanopartikel wird ein Komplex aus Porphyrinderivat und Polystyrolsulfonat durch die sog. „layer-by-layer“-Technik elektrostatisch an die Oberfläche der Gold-Nanopartikel gebunden. Die Servicegruppe analysiert quantitativ die Au-Konzentrationen in den kolloidalen Lösungen mit ICP OES. Zur Quantifizierung des Wirkstoff-Komplexes werden

CHNS-Analysen durchgeführt, aus deren Ergebnissen der Masseanteil an Porphyrinderivat und Polystyrolsulfonat berechnet wird.

Die Kooperation mit Frau Prof. P. Bauer von der Arbeitsgruppe Molekulare Pflanzenbiologie und Botanik des Fachbereichs Biowissenschaften wurde intensiviert. Die Arbeitsgruppe von Frau Bauer beschäftigt sich mit molekulargenetischen Aspekten zur Regulierung der Mineralstoffaufnahme und -verteilung in Pflanzen. Da es durch die Beobachtung der Gen- und Proteinexpression allein nicht möglich ist, absolute Aussagen zur Metallverteilung in der Pflanze und daraus resultierender Phänotypen zu treffen, analysiert die Servicegruppe quantitativ Metallgehalte (Fe, Cu, Zn und Mn) in gefriergetrocknetem Pflanzenmaterial (Arabidopsis thaliana). Durch die Bestimmung der Metallgehalte in den einzelnen Pflanzenorganen können molekulare Mechanismen, die für die Aufnahme und Verteilung verantwortlich sind, analysiert werden. Da von den einzelnen Pflanzenorganen nur kleinste Mengen (ca. 1 mg) zur Verfügung stehen, bietet sich direkte Feststoff-AAS an (Einwaagen 50-200 µg). In Bild 1 sind die analysierten Metallgehalte der direkten Feststoff-AAS und ICP OES nach Mikrowellenaufschluss anhand von drei Referenzproben dargestellt. Der Vergleich beider Messmethoden zeigt, dass die analysierten Metallgehalte, mit Ausnahme von Cu in Referenz 1, innerhalb der statistischen Abweichungen liegen.

Eine weitere Kooperation wurde im Juli 2009 mit dem Arbeitskreis von Herrn Prof. Hempelmann an der Physikalischen Chemie gestartet. Im Rahmen einer Dissertation zum Thema „Aufklärung des Mechanismus der Direkthärtung von hochmolekularen Silanen durch Säuren und Basen“ werden Polyurethan-funktionelle Bindemittel hergestellt und mit den bei der Firma NANO-X erhältlichen SiliXanen® verglichen.

Die Servicegruppe analysiert dabei quantitativ die bei der Direkthärtung freigesetzten Abspaltprodukte mit GC/MS und untersucht die Reaktionsprodukte mit 29Si- und 13C-NMR-Spektroskopie. Beide Methoden dienen der Reaktionskontrolle und der Aufklärung des Reaktionsmechanismus während der Härtung.

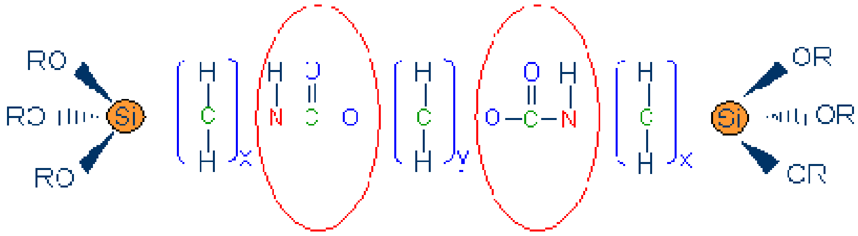


Bild 2: Allgemeine Struktur eines SiliXan®.

# Servicegruppe Physikalische Analytik / Service group Physical Analysis

## Dr. Herbert Schmid

In der *Physikalischen Analytik* stehen Einrichtungen für eine umfassende Charakterisierung nanostrukturierter Materialien bezüglich deren Struktur, Phase, Morphologie und chemischer Zusammensetzung zur Verfügung. Der Bereich Röntgenanalytik ist mit drei Röntgendiffraktometern (XRD) neuester Bauart für konventionelle Pulver-XRD, Vier-Kreis-XRD speziell für Dünnschicht-Charakterisierung, Hochtemperatur-XRD für *in situ* Messungen, sowie mit Fluoreszenzspektrometer (XRF) für quantitative chemische Analyse ausgestattet. Für mikroskopische Untersuchungen stehen derzeit ein 200 kV TEM, zwei SEM für Hoch- und Niedervakuum (ESEM), sowie zwei Raster-Kraftmikroskope (AFM) und ein konfokales Laser-Raster-Mikroskop (CLSM) zur Verfügung.

Die Hauptaktivitäten der *Physikalischen Analytik* gliedern sich in allgemeine Serviceleistungen wie die Gerätebetreuung, Justierung und Kalibrierung von Geräten, die Einweisung und Schulung von Gerätenutzern, sowie Serviceleistungen für die Programmbereiche des INM und Kooperationen im Rahmen von Projekten mit internen und externen Partnern. An umfangreicheren laufenden Aktivitäten im Jahr 2009 sind zu nennen:

*INM-interne Kooperationen/Serviceleistungen:*

- Charakterisierung von Nanopartikeln und Nanowires/-rods bezüglich Struktur, Kristallinität, Morphologie, Größenverteilung und chemische Zusammensetzung,
- Aufklärung von Core-Shell-Strukturen im System Al/Al-Oxid mittels hochauflösender TEM,
- Untersuchungen zur Strukturbildung von Ag-Nanopartikeln mittels TEM, SEM und WET-STEM,
- ESEM-Untersuchungen zur Wechselwirkung von Nanopartikeln (Ag, $ZrO_2$) in biologischen Materialien.

*Methodische Entwicklungen:*

- Methode zur Charakterisierung des Ordnungsgrades zweidimensionaler Partikel-Ensembles aus der Paarverteilungs Funktion,
- Erfassung des Ordnungsgrades zweidimensionaler Anordnungen von Ag-Nanopartikeln aus der Autokorrelationsfunktion,
- Untersuchungen zur Korrelation von Elektronen-Spinzuständen in 3d-Über-

gangsmetallen und Ionisations-Kantenfeinstrukturen (ELNES) in hochauflösender Elektronen-Spektroskopie (HR-EELS).

*Externe Kooperationen:*

- ESEM-Untersuchungen zum Agglomerationsverhalten magnetischer Ni-Nanostäbchen in Glycerin-Wasser-Matrix (Technische Physik/Universität des Saarlandes),
- Charakterisierung von $SnO_2$-Nanostrukturen mittels hochauflösenden TEM-Methoden (Anorganische Chemie, Universität Köln),
- analytische TEM-Untersuchungen zur Struktur von Ni/a-C-Sensorschichten (HTW/Saarbrücken).

Das INM ist bestrebt, die Analytik bezüglich Geräteausstattung und Methodik weiter zu entwickeln. Um die Elektronenmikroskopie auf den neuesten Stand der Technik zu bringen, wurden im Jahr 2009 erhebliche Investitionen zur Beschaffung von analytischen TEM/STEM- und SEM-Systemen der neuesten Generation getätigt. Im Rahmen des Auswahl- und Ausschreibungsverfahrens wurden umfangreiche Testmessungen an verschiedenen analytischen TEM/STEM-Systemen durchgeführt und daraus resultierend ein System mit folgender Ausstattung in Auftrag gegeben:

- 200 kV TEM/STEM mit kalter FEG (0.3 eV Energieauflösung),
- Cs-Korrektor im Kondensorsystem zur Korrektur der sphärischen Aberration in STEM,
- EDS System für Röntgen-Spektroskopie und Element-Mapping in STEM,
- EELS/abbildendes Energiefilter (GIF) für Spektroskopie und energiegefilterte Abbildung,
- Tomographiesystem für 3D-Visualisierung in TEM und STEM.

Außerdem wird das seit 1992 dem INM zur Verfügung stehende Raster-Elektronenmikroskop (SEM) durch ein hochauflösendes SEM, ausgestattet mit kalter FEG und EDS-Analysesystem, ersetzt. Die Auftragsvergabe konnte 2009 abgeschlossen werden. Beide Mikroskope werden 2010 am INM installiert werden, wodurch unsere zukünftigen analytischen Möglichkeiten beträchtlich erweitert werden.

# Servicegruppe Engineering / Service group Engineering

## Dietmar Serwas

Im Berichtszeitraum wurden der Ausbau und die Modernisierung der Ausstattung konsequent fortgesetzt. So wurde die CATIA V5-Prozesskette des CAD/CAM-Systems im Bereich CNC-Drehen um das Modul CAM-Drehen und im Frässektor um das Modul NC-Simulation ergänzt. Damit sind nun auch komplexe Geometrien im Drehbereich herstellbar. Durch das NC-Simulationsmodul werden im 5-Achs-Fräsbereich die Arbeitsvorgänge komplett, einschließlich Maschine, Werkzeugbewegung und Werkstück mit Einspannung, dargestellt. Durch diese Visualisierung des Arbeitsprozesses können Fehler aufgedeckt und Kollisionen verhindert werden. Mit der vorhandenen Ausrüstung steht damit u. a. als Ausstattung zur Verfügung:

- Präzisionsdrehmaschine,
- 5-Achs-Fräsbearbeitungszentrum,
- Schneid- und Fügebearbeitung einschließlich 6-Achs-Wasserstrahlschneidanlage,
- 3D-CAD-System CATIA V5,
- CAM für vorgenannte Anlagen einschließlich Simulationsmodule.

### Aufgaben

Das Hauptarbeitsgebiet liegt in der Entwicklung und im Bau von wissenschaftlichen Anlagen und Komponenten für die Forschungsabteilungen im Rahmen von Projekten und im Bereich der Grundlagenforschung. Die Bandbreite reicht hierbei von kleinen Laborgeräten bis hin zu großen Pilotanlagen. Aus den Vorgaben der Forschung werden Konzepte entwickelt, mit denen nach Präzisierung der Anforderungen eine Konstruktion erstellt wird. Planung, Konstruktion und Bau erfordern eine enge Verzahnung mit den wissenschaftlichen Abteilungen des Hauses. Die praktische Umsetzung erfolgt in den Werkstätten durch weitestgehend eigene Fertigung sowohl von individuellen Steuerungen und Softwareentwicklungen als auch der mechanischen Herstellung der einzelnen Komponenten einschließlich Zusammenbau zur kompletten Anlage. Ein weiteres Arbeitsgebiet ist die Messwerterfassung zur Charakterisierung elektrischer Materialeigenschaften. Weiterhin führt die Arbeitsgruppe im Rahmen einer Kooperation die Werkstattaufgaben für den Lehrstuhl „Technische Physik“ der Universität des Saarlandes durch.

## CVD-Anlage für Parabelflug

Erwähnenswert im Berichtszeitraum ist der Bau einer CVD-Anlage für den Einsatz bei der 14. Parabelflugkampagne des Deutschen Luft- und Raumfahrtzentrums. Mit dieser Anlage sollten die Auswirkungen der Schwerelosigkeit auf das Wachstum von Nano-Drähten auf einem Substrat beobachtet werden. Von besonderem Interesse sind hierbei die Wachstumsrichtung sowie die Verteilung, Größe und Struktur der Nanowires. Aufgrund der möglichen Belastungen muss die Anlage mit allen Komponenten für Beschleunigungen und Verzögerungen bis zu 9 g ausgelegt sein. Die ständigen Veränderungen der Einbaulage durch die Parabelform des Fluges waren ebenso zu berücksichtigen wie das Handling unter Schwerelosigkeit und die strengen Sicherheitsvorschriften. Für die Erzeugung des erforderlichen Druckes von $10^{-3}$ mbar konnte eine Pumpe gefunden werden, die nach dem Prinzip der archimedischen Spiralen arbeitet. Um möglichst viele Substrate beschichten zu können, wurde die Anlage mit vier CVD-Kammern bestückt. In jeder Kammer werden über ein Strömungsleitsystem fünf Substrate beschichtet. Dieses System wurde aus bearbeitbarer Glaskeramik gefertigt, um gleichzeitig auch als Wärmedämmung zu dienen. Die üblicherweise verwendete induktive Heizung zur schnellen Erwärmung der Substrate auf Temperaturen bis zu 650 °C ist wegen der Kühlung und der im Flugzeug erforderlichen Abschirmung der Hochfrequenzeinrichtung problematisch. Deshalb wurden vakuumtaugliche Widerstandshochleistungsheizelemente verwendet. Die Steuerung der Anlage erfolgt so, dass das notwendige Handling in der Schwerelosigkeit auf ein Minimum reduziert wird. Die Beschichtungsversuche wurden bei der Parabelflugkampagne ohne Probleme durchgeführt. Die Auswertung der Versuche ist noch nicht beendet.

# Servicegruppe Werkstoffprüfung/Pulversynthese / Service group Materials Testing/Powder Synthesis

**Karl-Peter Schmitt, Robert Drumm**

Der Servicebereich *Werkstoffprüfung/ Pulversynthese* umfasst hauptsächlich die Prüfverfahren, mit denen das Verhalten und die Werkstoffkenngrößen von normierten Werkstoffproben oder fertigen Bauteilen unter mechanischen, thermischen oder chemischen Beanspruchungen ermittelt werden. Die verwendeten mechanischen Prüfverfahren dienen zur Charakterisierung der Festigkeit, des Verformungs- und Bruchverhaltens sowie der Härte und des Verschleißwiderstandes von Werkstoffen. Der Servicebereich unterstützt die Programmbereiche bei verfahrenstechnischen Entwicklungen zum Up-Scaling bestehender Pulversynthesen in den Technikumsmaßstab. Er führt Synthesen sowie Dispergierungen von nanoskaligen Partikeln im Auftrag der Programmbereiche sowie externer Kunden durch.

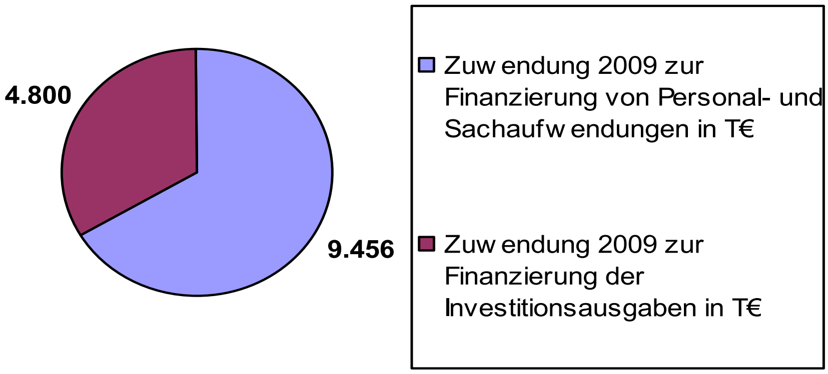
# Fakten und Zahlen / Facts and Figures

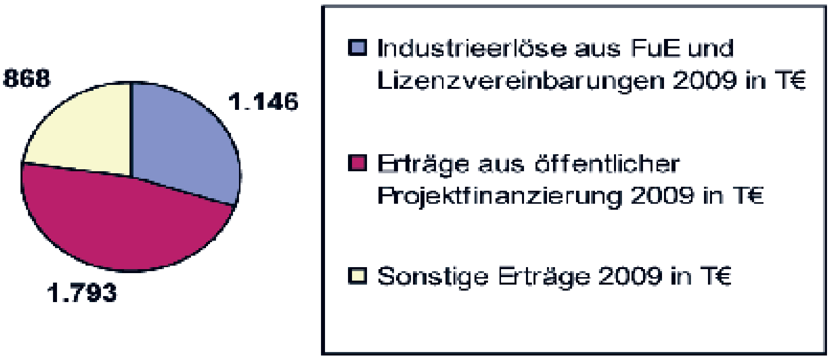
## Statusbericht

**Finanz- und Ertragslage / Vermögenslage der Gesellschaft**

Als Forschungseinrichtung der Leibniz-Gemeinschaft hat das INM auch im Haushaltsjahr 2009 eine gemeinsame Förderung durch den Bund und die Länder erhalten. Diese belief sich auf 14.256 T€; hiervon 9.456 T€ zur Finanzierung von Personal- und Sachaufwendungen sowie 4.800 T€ für erforderliche Neu- und Ersatzinvestitionen.

Die nominale Steigerung der Zuwendung gegenüber dem Vorjahr um 1.806 T€ ist durch eine allgemeine Zunahme zum Ausgleich von Tariflohn- und Preissteigerungen (250 T€); eine Bewilligung im SAW-Verfahren der Leibniz-Gemeinschaft (56 T€) sowie eine Sonderfinanzierung zum Aufbau neuer Forschungsschwerpunkte (1.500 T€) bedingt.





Im Geschäftsjahr 2009 erzielte das Leibniz-Institut für Neue Materialien eigene Erlöse aus Forschung und Entwicklung sowie sonstige betriebliche Erträge in Höhe von 3.807 T€ (Vorjahr: 4.692 T€). Die Industrieerlöse aus Forschung und Entwicklung sowie aus Lizenzvereinbarungen beliefen sich hierbei auf 1.146 T€ (Vorjahr: 1.405 T€). Im Rahmen öffentlicher Projektfinanzierungen erzielte das INM im Jahr 2009 Erträge in Höhe von 1.793 T€ (Vorjahr: 2.792 T€). Hierbei ist als „Einmaleffekt“ im Jahr 2008 eine BMBF-Förderung zu berücksichtigen, im Rahmen derer die Anschaffung eines STED-Mikroskops (1.179 T€) möglich war. Sonstige Erträge resultierten im Geschäftsjahr 2009 aus Konjunkturprogrammen (306 T€) und aus der Weiterbelastung von Gebäude-, Patent- sowie sonstigen Kosten.

Im EU-Projekt „Multiprotect“ ist das Leibniz-Institut für Neue Materialien Projektkoordinator und hat in dieser Funktion im Geschäftsjahr 2009 weitere Fördermittel der Europäischen Union in

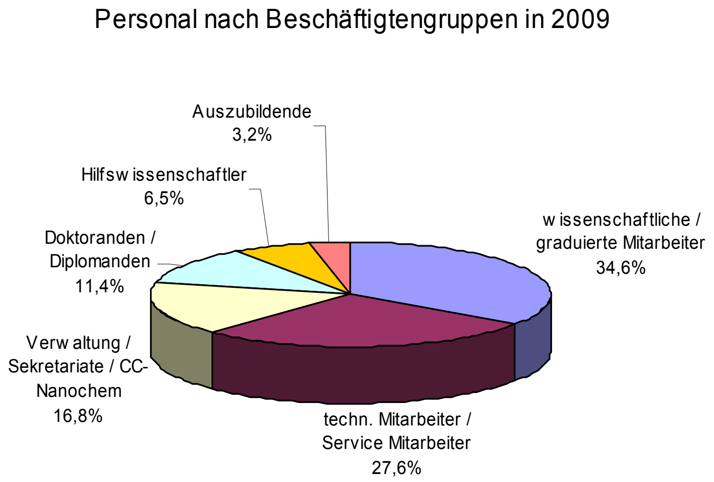
Höhe von 1.451 T€ vereinnahmt und an die Projektpartner weitergeleitet.

Der Gesamtumsatz 2009 der Gesellschaft betrug 17.916 T€ (Vorjahr: 17.053 T€). Die Erhöhung resultiert aus den Erträgen aus der gemeinsamen Finanzierung durch Bund und Länder sowie aus den Konjunkturprogrammen des Bundes.

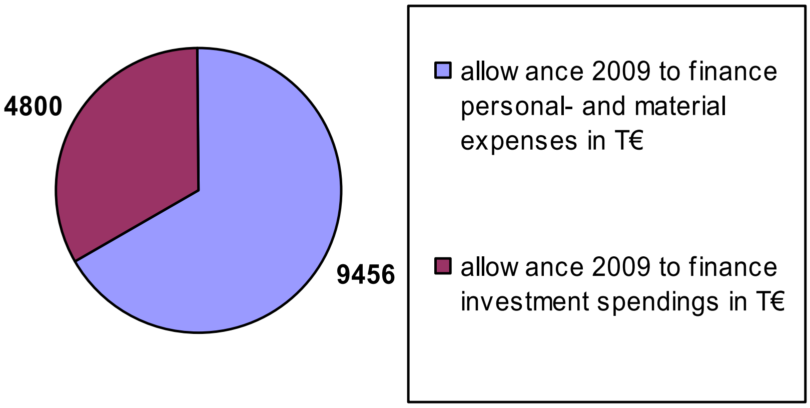
Die Bilanzsumme der Gesellschaft zum 31. Dezember 2009 betrug 18.745 T€; gegenüber dem Vorjahr (16.253 T€) eine deutliche Erhöhung um 2.492 T€. Während sich das Umlaufvermögen gegenüber dem Bilanzstichtag des Vorjahres um 457 T€ erhöhte, ist beim Anlagevermögen der Gesellschaft eine beträchtliche Zunahme um 1.970 T€ zu verzeichnen. Die Investitionstätigkeit (4.347 T€) überstieg in erster Linie durch den Aufbau neuer Forschungsbereiche im Geschäftsjahr 2009 erneut deutlich die Abschreibungsquote in Höhe von 2.369 T€. Die aktiven Rechnungsabgrenzungs-posten haben sich gegenüber dem Vorjahr um 65 T€ erhöht. Rückstellungen wurden in Höhe von 441 T€ (Vorjahr: 326 T€) bilanziert. Die Verbindlichkeiten der Gesellschaft beliefen sich zum Bilanzstichtag auf 1.238 T€ gegenüber 895 T€ im Vorjahr.

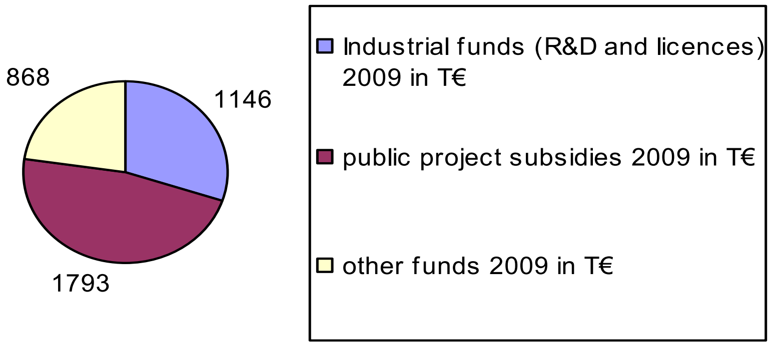
## Personalentwicklung

Die Anzahl der Beschäftigten in 2009 ist gegenüber dem Jahr 2008 leicht angestiegen. So waren Ende 2009 185 Mitarbeiter (162 Vollzeitäquivalente) gegenüber 176 Mitarbeitern (160 Vollzeitäquivalente) Ende 2008 beschäftigt. Hiervon waren 46 Mitarbeiterinnen und Mitarbeiter (dies entspricht 39 Vollzeitäquivalenten) im Drittmittelbereich beschäftigt. Die Anzahl der Auszubildenden sank bedingt durch die erfolgreichen Abschlüsse dreier Azubis auf sechs; der Anteil der Mitarbeiterinnen und Mitarbeiter im Verwaltungsbereich / Sekretariate / CC-Nanochem erhöhte sich leicht auf 16,8 Prozent. Der Anteil der Doktoranden/ Diplomanden bleib mit 11,4 Prozent auf dem Niveau des Vorjahres, der der Hilfswissenschaftler stieg von 2,3 Prozent auf 6,5 Prozent. Der Anteil der wissenschaftlichen und graduierten Mitarbeiter verringerte sich gegenüber dem Vorjahr um 4 Prozentpunkte auf 34,6 Prozent, während der Anteil der Servicemitarbeiter und der Mitarbeiter im technischen Bereich mit 27,6 Prozent gegenüber 27,3 Prozent in 2008 nahezu konstant blieb.



### Financial and income situation of the company





As a research institute of the Leibniz Community, INM also obtained common grants from the federal government and the states in the financial year 2009. These amounted to 14,256 T€, of which 9,456 T€ were used to finance personal- and material expenses and 3,250 T€ for necessary new investments and reconstruction measures.

The nominal increase of the obtained common grant amounting to 1,806 T€ results from a general rise to equalize the increase of the standard wages and price rise (250 T€), a grant within the SAW procedure of the Leibniz Association (56 T€) and also from a special grant for the development of new main research fields (1,500 T€).

In the financial year 2009, INM – Leibniz Institute for New Materials internally generated proceeds of 3,807T€ (preceding year 4,692 T€) from research and development as well as from other operating income. Industry revenues from research and development as well as from patents/licences amounted to 1,146 T€ (preceding year 1,405 T€). Within public project subsidies, INM made a profit in the amount of 1,793 T€ in 2008 (preceding year 2,792 T€). Here, a grant from the BMBF in 2008 has to be considered as a “one-time effect” in the scope of which the acquisition of a STED microscope was possible. Other income in 2009 resulted from economic stimulus packages (306 T€) and from cost transfer for buildings, patents and other costs.

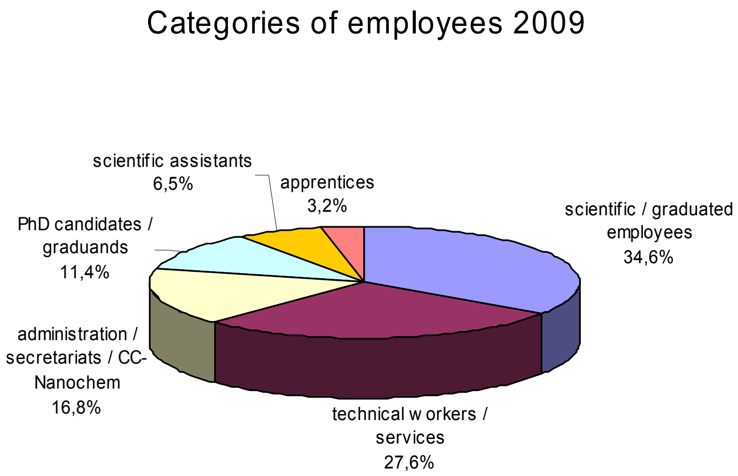
INM is the project coordinator of an EU-project named “Multiprotect” and collected in this function another subsidies amounting to 1,451 T€ from the European Union. These subsidies were transferred to the corresponding project partners.

The total turnover of INM in 2009 added up to 17,916 T€ (preceding year 17,053 T€). This increase primarily results from obtained common grants from the federal government and the state as well as from economic stimulus packages from the federal government.

The balance sheet total of the corporation was 18,745 T€ on 31 December 2009, compared to the preceding year (16,253 T€) a significant increase of 2,492 T€. While current assets increased by 457 T€ compared to the reporting date of the previous year, the non-current assets of the corporation increased remarkable by 1,970 T€. The investment activity of the corporation (4,347 T€) exceeded noticeably the allowance rate amounting to 2,369 T€ in the financial year 2009. The liabilities of the corporation amounted to 1,238 T€ at the reporting date (preceding year 895 T€).

## Personnel development

In comparison to 2008, the number of employees increased moderately. At the end of 2009, 185 employees (162 full-time equivalents) worked at INM, compared to 176 employees (160 full-time equivalents) the preceding year. 46 employees (39 full-time equivalents) were financed by third-party funds. The number of apprentices declined from nine to six, while the proportion of the administration staff / secretariats / CC-Nanochem increased from 15.3% to 16.8%. The proportion of PhD and other graduate students remained constant at 11.4% while the proportion of scientific and graduated employees declined about 4 percentage points from 38.6% to 34,6%. The proportion of manual workers and workers in technical services remained nearly constant (27.6% in 2009, 27.3% in 2008), and the proportion of scientific assistants increased from 2.3% in 2008 to 6.5% in 2009.



# Mitglieder des Kuratoriums / Members of the Board of Directors

# Mitglieder des wissenschaftlichen Beirats / Members of the Scientific Board

# Aktivitäten in Gremien / Activities in committees

## Mitglieder des Kuratoriums (Stand: Ende 2009) / Members of the Board of Directors (Status: End of 2009)

Dr. Christian Ege (bis Dezember 2009)
Staatssekretär
Ministerium für Wirtschaft und Wissenschaft des Saarlandes
– Vorsitzender –

Peter Hauptmann (seit Dezember 2009)
Staatssekretär
Ministerium für Wirtschaft und Wissenschaft des Saarlandes
– Vorsitzender –

Prof. Yves Berthelot
Präsident
Georgia Tech Lorraine, Metz

Dr. Gerhard Felten
Geschäftsleiter Zentralbereich Forschung und Vorausentwicklung
Robert Bosch GmbH, Stuttgart

Prof. Dr. Horst Hahn
Geschäftsführender Direktor, Institut für Nanotechnologie
Forschungszentrum Karlsruhe, Eggenstein-Leopoldshafen

Dr. Max Häring
Vorstandsvorsitzender a. D.
Landesbank Saar Girozentrale, Saarbrücken

Liane Horst
Bundesministerium für Bildung und Forschung, Bonn
– Stellvertr. Vorsitzende –

Prof. Dr. Volker Linneweber
Präsident der Universität des Saarlandes
– Stellvertr. Vorstizender –

Prof. Dr. Dr. E.h. Kurt Mehlhorn
Wissenschaftlicher Direktor
Max-Planck-Institut für Informatik, Saarbrücken

Prof. Dr. Frank Mücklich
Lehrstuhl für Funktionswerkstoffe
Universität des Saarlandes

Dr. Peter W. de Oliveira
Wissenschaftlicher Mitarbeiter
INM gGmbH, Saarbrücken

Dr. Roland Rolles
Leiter Abteilung C – Mittelstand und Innovation
Ministerium für Wirtschaft und Wissenschaft des Saarlandes

Ralf Zastrau
Vorstandsvorsitzender
Nanogate AG, Göttelborn

## Mitglieder des wissenschaftlichen Beirats (Stand: Ende 2009) / Members of the Scientific Board (Status: End of 2009)

Prof. Dr. Horst Hahn
Geschäftsführender Direktor, Institut für Nanotechnologie
Forschungszentrum Karlsruhe, Eggenstein-Leopoldshafen
– Vorsitzender –

Ralf Becker
Leitung Geschäftsfeld Sanitäterkeramik und Küche
Villeroy & Boch AG, Mettlach

Prof. Dr. Rainer Birringer
Lehrstuhl für Technische Physik
Universität des Saarlandes

Prof. Dr. Ludwig Gauckler
Institut für Nichtmetallische Werkstoffe
ETH-Hönggerberg Zürich, Schweiz

Dr. Klaus Harste
Vorstandsvorsitzender
Saarstahl AG, Völklingen

Prof. Dr. Martin Möller
Lehrstuhl für Textilchemie und Makromolekulare Chemie
RWTH Aachen

Prof. Dr. Andreas Mortensen
Ecole Polytechnique Fédérale de Lausanne (EPFL), Schweiz

Prof. Dr. Erich Sackmann
Lehrstuhl für Biophysik
Technische Universität München, Garching

Dr. Stefan Sepeur
Geschäftsführer
NANO-X GmbH, Saarbrücken

Prof. Dr. Robert F. Singer
Lehrstuhl Werkstoffkunde und Technologie der Metalle
Universität Erlangen-Nürnberg

## Aktivitäten in Gremien / Activities in committees

**Prof. Dr. Eduard Arzt**

Mitglied bei
- Österreichische Akademie der Wissenschaften (Korrespondierendes Mitglied)
- Deutsche Akademie der Naturforscher Leopoldina, Halle
- Beirat des Programms Nano-Mikrosysteme, Feld Werkstoffe und Materialien, KIT, Karlsruhe

- Scientific Committee des IUTAM Symposiums zu „Mechanics of Soft Active Materials“, Technion - Israel Institute of Technology, Haifa, Israel
- Professorial Committee, IST Austria, Vienna, Austria
- Internationaler Beirat der Christian-Doppler-Gesellschaft, Vienna, Austria
- Scientific Advisory Board, CCMX - Comptenece Centre for Materials Science and Technology, Lausanne, Switzerland
- Wissenschaftlicher Beirat der Alfried Krupp von Bohlen und Halbach Stiftung, Essen
- Strategiebeirat, Material Engineering Centre Saarland (MECS), Saarbrücken
- Findungskommission, Karlsruher Institut für Technologie
- Berufungskommission, Allgemeine und Anorganische Chemie, Universität des Saarlandes
- Berufungskommission, Chemische Materialwissenschaft, Universität des Saarlandes und INM
- International Evaluation Panel, Ecole Polytechnique Federal Lausanne, School of Engineering, Lausanne, Switzerland

Gutachtertätigkeit bei
- Karl Heinz Beckurts-Stiftung, Beckurtspreis
- Universitätsklinik Homburg (Forschungsförderung HOMFOR)
- University of California, San Diego, CA, USA
- Clemson University, Clemson, SC, USA
- DAAD – Deutscher Akademischer Austausch Dienst
- Nachwuchsakademie der DFG – Deutsche Forschungsgemeinschaft
- ETH – Eidgenössische Technische Hochschule Zürich, Switzerland
- Harvard University, Cambridge, MA, USA
- Massachusetts Institute of Technology, Cambridge, MA, USA
- Stanford University, Stanford, CA, USA
- Lehigh University, Bethlehem, PA, USA
- Columbia University, New York, NY, USA
- University of Wyoming, Laramie, WY, USA
- University of Utah, Salt Lake City, UT, USA
- Sandia National Laboratories, Albuquerque, NM, USA
- Alexander-von-Humboldt-Stiftung

Editor von Progress in Materials Science, Oxford, UK (Reviewzeitschrift)

Mitglied im Editorial Board der Zeitschriften
- Materials Science and Technology, London, UK
- Advanced Engineering Materials, Weinheim
- International Journal of Materials Research (früher: Zeitschrift für Metallkunde), München
- Materials Science and Engineering / C, Materials for Biological Applications

Referee der Zeitschriften (u.a.):
Acta Materialia, Advanced Materials, Applied Physics Letters, Journal of Applied Physics, Journal of Micromechanics and Microengineering, Journal of the Royal Society / Interfaces, Langmuir, Nanotechnology, Nature, Nature Materials, Philosophical Magazine, Proceedings of the National Academy of Science, Science, Scripta Materialia

### Dr. Carsten Becker-Willinger

Gutachtertätigkeit bei Forschungsanträgen „Forschungsverbund Baden-Württemberg“

### Prof. Dr. Roland Bennewitz

Adjunct Professor, Physics Department der McGill University, Montreal, Canada

Honorarprofessor der Universität des Saarlandes, Saarbrücken

Mitorganisator beim Focus Workshop „Energy Dissipation in Nanocontacts and Molecular Bonds“, 28.09.-01.10.2009, MPI für die Physik komplexer Systeme, Dresden

Mitglied im Editorial Board der Zeitschrift Review of Scientific Instruments

Gutachtertätigkeit für Agence Nationale de la Recherche

Referee der Zeitschriften:
Applied Physics Letters, Journal of Physics / D, Applied Physics, Nature Materials, Physical Review / B, Physical Review Letters, Review of Scientific Instruments, Thin solid films, Tribology letters

### Jochen Flackus

Vorstandsvorsitzender des NanoBioNet e.V.

Gründungsmitglied von Saarland Empowering Nano

Editor der Zeitschrift Empowering Nano

### Dr. Annette Kraegeloh

Referee der Zeitschrift:
Microbiology

### Dr. Tobias Kraus

Gutachtertätigkeit für Schweizer Nationalfonds (SNF)

Referee der Zeitschriften:
Applied Physics Letters, Surface and interface analysis, Tribology Letters

### Dr. Thomas Müller

Referee der Zeitschrift:
Thin Solid Films

### Dr. Peter W. de Oliveira

Mitglied, Round Table Lateinamerika des BMBF

Mitorganisator beim Brazilian German Workshop on Nanotechnology and Applications, 07. – 08.10.2009, Belo Horizonte, MG, Brazil

Editor des Proceedings of the Brazilian German Workshop on Nanotechnology and Applications, 07. – 08.10.2009, Belo Horizonte, MG, Brazil

Referee der Zeitschrift:
Materials Letters

### Dr. Mario Quilitz

Gutachtertätigkeit bei Machbarkeitsstudien im Rahmen des AGeNT-D Netzwerkes der nationalen Kompetenzzentren für Nanotechnologien und Nanoanalytik

Mitorganisator beim Brazilian German Workshop on Nanotechnology and Applications, 07. – 08.10.2009, Belo Horizonte, MG, Brazil

Editor des Proceedings of the Brazilian German Workshop on Nanotechnology and Applications, 07. – 08.10.2009, Belo Horizonte, MG, Brazil

Referee der Zeitschriften:
Solid State Ionics, Electrochemical and Solid State Letters

### Dr. Peter Rogin

Referee der Zeitschrift:
Plasma Processes & Polymers

### Prof. Dr. Dr. Daniel J. Strauss

Mitglied bei

- Empower Deutschland / Cluster Medizintechnik
- Cognitive Neuroscience Society CNS
- Institute of Electrical and Electronic Engineers IEEE
- Engineering in Medicine and Biology Society EMBS
- Society for Industrial and Applied Mathematics SIAM

Gutachtertätigkeit bei

- Medical Research Council, UK
- University Malaysia Perlis

Referee der Zeitschriften:
Journal of Neuroscience Methods, Artificial Intelligence in Medicine, IEEE Trans. on Neural Networks, IEEE Trans. on Biomedical Engineering, IEEE Trans. on Neural Systems & Rehabilitation Engineering, Medical Engineering and Physics, Annals of Biomedical Engineering, IEEE International Conference Neural Engineering, IEEE International Conference of the Engineering in Medicine and Biology Society, Computers in Medicine & Biology

### Prof. Dr. Dr. h.c. Michael Veith

Lehrstuhl für Anorganische und Allgemeine Chemie der UdS Saarbrücken

Berater der Universität Lyon, France

Bevollmächtigter der DFH für den Studentenaustausch mit Strasbourg, France (ECPM)

Externes Beratungsmitglied, LCC Toulouse, France

Sprecher, Internationales Graduiertenkolleg GRK 532

Stellvertretender Leiter, Frankreichzentrum, Universität des Saarlandes, Saarbrücken

Vorstand des AGeNT-D Netzwerk der nationalen Kompetenzzentren für Nanotechnologien und Nanoanalytik

1. Vorsitzender des cc-NanoChem

Vorstandsmitglied, International Ring Systems (IRIS), International Meetings: Germanium, Tin, Lead (GTL)

Mitglied bei

- Akademie der Wissenschaften und der Literatur, Mainz (Korrespondierendes Mitglied)
- Deutschen Akademie der Naturforscher Leopoldina, Halle
- Fellow of the Royal Society of Chemistry, London, UK
- Rat der Universität des Saarlandes, Saarbrücken
- Wissenschaftlicher Beirat, Papiertechnische Stiftung PTS, München
- Ecole Doctorale Metz-Nancy, France
- Expertengruppe Metropolprojekt Saarbrücken - Moselle Est, France
- Verwaltungsrates der EEIGM Nancy, France
- Arbeitsausschuss Angewandte Anorganische Chemie DECHEMA e.V
- International Advisory Board der Zeitschrift für Anorganische und Allgemeine Chemie ZAAC
- Steering Komitee MiNaT
- Advisory Board Nanotech Europe, Berlin
- Advisory Board, IRIS 12, Goa, India

Gutachtertätigkeit bei

- Deutsche Forschungsgemeinschaft (DFG)
- FWF Wissenschaftsfonds, Vienna, Austria
- Deutsche Akademie der Naturforscher Leopoldina (Stipendien)
- Qiagen GmbH (Innovation Award)
- Laboratoire UCCS, Lille, France (Evaluation)
- National Science Foundation, Arlington VA, USA (Forschungsantrag)
- UPR 8241 + UMR 5069 + FR 2599, Toulouse, France (Evaluation)
- Alexander-von-Humboldt-Stiftung (Stipendien)
- Universität des Saarlandes, UdS, Saarbrücken
- Humboldt-Universität Berlin
- College de France, Paris, France
- Philipps-Universität Marburg

Mitglied im Editorial Board der Zeitschriften

- New Journal of Chemistry (NJC)
- Comptes Rendus
- Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry (European Ed.)

Referee der Zeitschriften:
Acta Biomaterialia, Angewandte Chemie, Applied Organometallic Chemistry, Chemistry – an Asian Journal, Chemistry – a European Journal, Chemistry of Materials, Comptes Rendus Chimie, Journal of Organometallic Chemistry, Journal of Solid State Chemistry, Main Group Chemistry, Materials Science and Engineering / C, Organometallics, Progress in Materials Science, Zeitschrift für Anorganische und Allgemeine Chemie ZAAC

### Dr. Ingrid Weiss

Gutachtertätigkeit, German-Israeli Foundation for Scientific Research and Development

Gutachtertätigkeit, COST External Expert Panel 2009

Referee der Zeitschriften:
ChemBioChem, Chemical Reviews, CompBiochemPhysiol, Journal of Structural Biology, Marine Biology, Zoology

### Dr. Alexandra Wittmar

Referee der Zeitschrift:
Journal of Non-Crystalline Solids

### Dr. Matthias Wittmar

Mitglied bei Working Party 14 „Coatings“ of the European Federation of Corrosion (EFC)

Referee der Zeitschrift:
Corrosion Science

# Auszeichnungen / Awards

# Abgeschlossene Dissertationen / Completed doctoral theses

# Abgeschlossene Bachelor- & Masterarbeiten / Completed Bachelor & Master theses

## Auszeichnungen / Awards

Dr. Cenk Aktas

Auszeichnung der Dissertation „Functional applications of Al/Al$_2$O$_3$ nanowires: laser assisted alpha-Al$_2$O$_3$ synthesis and fabrication of micro-/nanostructured surfaces for cell compatibility studies" (Saarbrücken, Univ., Diss., 2009) durch den Preisrat der Chemiker der Universität des Saarlandes aus Mitteln der Hardt-Stiftung

Prof. Dr. Eduard Arzt

Distinguished Award
„Thermec'2009 – International Conference on Processing and Manufacturing of Advanced Materials", Berlin, 25.-29-08.2009

Si Chen

DAAD Undergraduate Scholarship
01.10.2009-31.07.2010

Christina Guth

Landesbeste Prüfungsteilnehmerin des Saarlandes im Ausbildungsberuf Chemielaborantin – Auszeichnung durch IHK des Saarlandes

Birgit Heiland, Prof. Dr. Eduard Arzt, PD Dr. Ingrid M. Weiss

Best Poster Award, 2. Preis der Deutschen Gesellschaft für Materialkunde e.V. für „Polarisationsmikroskopie an Zwiebelschalen"
43. Metallographietagung, Aachen,
16.-18.09.2009

Elmar Kroner

Excellent Poster Award für „Measuring Adhesion of Gecko-Inspired Surfaces"
Gordon Research Conferences, Science of Adhesion 2009, New London (NH), USA, 26.-31.07.2009

Prof. Dr. Dr. h.c. Michael Veith

Verleihung des Wilhelm-Klemm Preises (09/2009)

Dr. Ulf Werner (INM), Prof. Dr. Günter Schultes (HTW)

Verleihung des 10. SaarLB-Wissenschaftspreises am 08.07.2009

## Abgeschlossene Dissertationen / Completed doctoral theses

Aktas, Cenk O.

Functional applications of Al/Al$_2$O$_3$ nanowires: laser assisted alpha-Al$_2$O$_3$ synthesis and fabrication of micro-/nanostructured surfaces for cell compatibility studies
Saarbrücken, Univers., Diss (2009)
Prof. Dr. Dr. h.c. M. Veith

Altmayer, Jessica

Homo- und Heteroleptische Übergangsmetall- und Lanthanoidverbindungen und deren Einsatz in der Materialforschung
Saarbrücken, Univers., Diss (2009)
Prof. Dr. S. Mathur

Cavelius, Christian

Chemische Wege zur Herstellung metallischer und oxidischer Nanopartikel: Charakterisierung und Oberflächenmodifikation
Saarbrücken, Univers., Diss (2009)
Prof. Dr. S. Mathur

Danzebrink, Rolf

Herstellung und Charakterisierung mikrostrukturierter Beschichtungen mittels Ink-jet und Pad-printing
Saarbrücken, Univers., Diss (2009)
Prof. Dr. R. Clasen

Filleter, Tobin

Nanometer-scale studies of friction, dissipation, and plasticity
Montreal, Kanada, Univers., Diss (2009)
Prof. Dr. R. Bennewitz

Moh, Karsten

Darstellung und Charakterisierung metallischer und oxidischer Nanostrukturen
Saarbrücken, Univers., Diss (2009)
Prof. Dr. Dr. h.c. M. Veith

Ndiaye, Amadou

Synthesis and physico-chemical studies on dithiolene complexes fort he closed-shell (d10) metals and trivalent lanthanide ions
Saarbrücken, Univers., Diss (2009)
Prof. Dr. Dr. h.c. M. Veith

Ren, Shuhua

Development of a novel parallel synthesis by injection moulding and it's application to study dielectric materials
Saarbrücken, Univers., Diss (2009)
Prof. Dr. Dr. h.c. M. Veith

Schönitzer, Veronika

Dictyostelium discoideum als Expressionssystem für die transmembrane Myosin-Chitinsynthase Ar-CS1 aus Atrina rigida (Mollusca, Bivalvia) – einem Modellorganismus der Biomineralisation – und Charakterisierung der Myosindomäne
Regensburg, Univers., Diss (2009)
PD Dr. I. Weiss

## Abgeschlossene Bachelor- & Masterarbeiten / Completed Bachelor & Master theses

Kaiser, Jessica

Ultrasound actuated gecko-inspired pillar arrays
Saarbrücken, Univers., Master (2009)
Prof. Dr. Dr. D. J. Strauss

Lee, Ju Seok

Nanostructured Alumina Surfaces for Neuron Cell Adhesion

Saarbrücken, Univers., Master (2009)
Prof. Dr. Dr. h.c. M. Veith

Martinez-Miro, Marina
Osteoblast adhesion on nanostructured surfaces
Saarbrücken and Barcelona, Univers., Master (2009)
Prof. Dr. Dr. h.c. M. Veith

Schulzendorf, Mathias
Synthesis and characterization of oxide-metal core-shell particles
Berlin, Freie Univers., Bachelor (2009)
Prof. Dr. E. Arzt

## Doktoranden / Doctoral Students

Bender, Michael
Prof. Dr. Dr. h.c. M. Veith

Born, Philip
Prof. Dr. E. Arzt

Brörmann, Katrin
Prof. Dr. R. Bennewitz

Bubel, Carsten
Prof. Dr. Dr. h.c. M. Veith

Dufloux, Cecile
Prof. Dr. Dr. h.c. M. Veith

Egberts, Philip
Prof. Dr. R. Bennewitz

Hausen, Florian
Prof. Dr. R. Bennewitz

Held, Christian
Prof. Dr. R. Bennewitz

Jochum, Marlon
Prof. Dr. Dr. h.c. M. Veith

Kasper, Christoph
Prof. Dr. Dr. h.c. M. Veith

Kroner, Elmar
Prof. Dr. E. Arzt

Lacava, Johann
Prof. Dr. E. Arzt

Lee, Ju Seok
Prof. Dr. Dr. h.c. M. Veith

Lehnert, Tobias
Prof. Dr. Dr. h.c. M. Veith

Martinez Miro, Marina
Prof. Dr. Dr. h.c. M. Veith

Moll, Jana
Prof. Dr. Dr. h.c. M. Veith

Paretkar, Dadhichi
Prof. Dr. E. Arzt

Rabung, Benjamin
Prof. Dr. Dr. h.c. M. Veith

Ullah, Hameed
Prof. Dr. Dr. h.c. M. Veith

Wählisch, Felix
Prof. Dr. R. Bennewitz

Weber, Eva
PD Dr. I. Weiß

## Gastwissenschaftler / Guest Scientists

Akkan, Çagri Kaan
Türkei

Aktas, Dr. Cenk
Türkei

Ali, Awadelkareem
Sudan

Ali, Dr. Budiman
Republik Indonesien

Araujo de Itriago, Yani Carolina
Venezuela

Caparrotti, Dr. Hinka
Bulgarien

Carraro, Dr. Carlo
USA

Castellanos, Graciela
Spanien

Chen, Si
Kanada

De Souza, Dr. Emerson
Brasilien

Del Campo, Dr. Aránzazu
Spanien

Dufloux, Cecile
Frankreich

Eder, Dr. Magdalena
Österreich

Egberts, Philip
Kanada

Egorov, Dr. Yuri
Russland

Figiel, Pawel
Polen

Gabriel, Dr. Urszula
Polen

Girault, Dr. Baptiste
Frankreich

Gosvami, Dr. Nitya Nand
Indien

Guidoni, Dr. Griselda
Argentinien

Kamperman, Dr. Marleen
Niederlande

Lacava, Johann
Frankreich

Lee, Ju Seok
Südkorea

Lin, Dr. Hechun
China

Lin, Leyu
China

Maboudian, Prof. Dr. Roya
USA

Martinez Miro, Marina
Spanien

Mattila, Dr. Tomi
Finnland

McMeeking, Prof. Dr. Robert
USA

Murray, Dr. Eoin
Irland

Ndiaye, Dr. Amadou
Senegal

Nielsen, Mette Skovgaard
Dänemark

Paretkar, Dadhichi
Indien

Ramos Costa, Silvia Alexandra
Portugal

Ren, Dr. Shuhua
China

Sam, Dr. Ebru Devrim
Türkei

Shanmugasundaram, Dr. Sakthivel
Indien

Smail, Dr. Hakima
Frankreich

Turak, Dr. Ayse
Türkei

Ullah, Hameed
Pakistan

Wittmar, Dr. Alexandra
Rumänien

Yazdani-Assl, Dr. Omid
Iran

## Publikationen / Publications

### Book publications / Buchveröffentlichungen

M. Quilitz, P. W. Oliveira

Proceedings of the Brazilian-German Workshop on Nanotechnology and Applications, October 07-08, 2009, Belo Horizonte, Brazil, 2009, p 75 S.

### Book chapter / Buchkapitel

M. R. S. Castro, P. W. Oliveira, M. Veith

Transparent conducting oxide nanofilms: Properties, growth and applications
In: Metal Oxide Nanostructures and Their Applications, American Scientific Publishers (Valencia): 2009

A. Del Campo, E. Arzt

Gecko-inspired adhesives: Nanofabrication
In: The Dekker Encyclopedia of Nanoscience and Nanotechnology, C. I. Contescu and K. Putyera Eds., CRC Press: Boca Raton [u. a.], 2009, Vol. II, pp 1384-1393

F. Hernandez-Ramirez, J. D. Prades, S. Barth, A. Romano-Rodriguez, S. Mathur, A. Tarancon, O. Casals, R. Jimenez-Diaz, J. Rodriguez, E. Pellicer, M. A. Juli, T. Andreu, S. Estrade, E. Rossinyol, J. R. Morante

Fabrication of nanodevices based on individual SnO2 nanowires and their electrical characterization
In: Metal Oxide Nanostructures and Their Applications, A. Umar Ed., American Scientific Publishers (Valencia): 2009

### Journal articles / Publikationen in Journalen

E. Arzt, A. Del Campo

Functional surfaces for controlled adhesion
Annual Report, Jahresbericht 2008 - INM Leibniz-Institut für Neue Materialien 2009, 29-32 [-]

F. Barroso-Bujans, R. Serna, E. A. Sow, J. L. G. Fierro, M. Veith

Grafting of poly(acrylic acid) onto an aluminum surface
Langmuir 2009, 25, (16), 9094-9100 [04.097 (2008)]

S. Barth, S. Estrade, F. Hernandez-Ramirez, F. Peiro, J. Arbiol, A. Romano-Rodriguez, J. R. Morante, S. Mathur

Studies on surface facets and chemical composition of vapor grown one-dimensional magnetite nanostructures
Cryst Growth Des 2009, 9, (2), 1077-1081 [04.215 (2008)]

C. Becker-Willinger, S. Schmitz-Stöwe, D. Bentz

Research on the synthesis and applicability of surface modified nanoscaled metal oxide particles as curing catalysers for UV-print-colours and lacquers

Annual Report, Jahresbericht 2008 - INM Leibniz-Institut für Neue Materialien 2009, 13-17 [-]

P. Braunstein, M. Veith
Physical Methods for the structural investigation of new materials. Foreword
CR Chim 2009, 12, 1109 [01.529 (2008)]

S. Buhl, C. Greiner, A. del Campo, E. Arzt
Humidity influence on the adhesion of biomimetic fibrillar surfaces
Int J Mater Res 2009, 100, (8), 1119-1126 [00.819 (2008)]

M. R. S. Castro, N. Al-Dahoudi, P. W. Oliveira, H. K. Schmidt
Multi-walled carbon nanotube-based transparent conductive layers deposited on polycarbonate substrate
J Nanopart Res 2009, 11, (4), 801-806 [02.299 (2008)]

M. R. S. Castro, P. W. Oliveira, H. K. Schmidt
Optical, structural and electrical investigations of TiO2/multi-walled carbon nanotube composites
J Nanosci Nanotechno 2009, 9, (6), 4016-4021 [01.929 (2008)]

F. I. Corona-Strauss, W. Delb, B. Schick, D. J. Strauss
Phase stability analysis of chirp evoked auditory brainstem responses by Gabor Frame Operators
IEEE T Neur Sys Reh 2009, 17, (6), 530-536 [02.934 (2008)]

J. K. Deuschle, H. M. Deuschle, S. Enders, E. Arzt
Contact area determination in indentation testing of elastomers
J Mater Res 2009, 24, (3), 736-748 [01.743 (2008)]

P. Egberts, R. Bennewitz
Kelvin Probe Force Microscopy of charged indentation-induced dislocation structures in KBr
Annual Report, Jahresbericht 2008 - INM Leibniz-Institut für Neue Materialien 2009, 33-37 [-]

P. Egberts, T. Filleter, R. Bennewitz
A kelvin probe force microscopy of charged indentation-induced dislocation structures in KBr
Nanotechnology 2009, 20, (26), 264005 (7pp) [03.446 (2008)]

T. Filleter, J. L. McChesney, A. Bostwick, E. Rotenberg, K. V. Emtsev, T. Seyller, K. Horn, R. Bennewitz
Friction and dissipation in epitaxial graphene films
Phys Rev Lett 2009, 102, (8), 086102-4 [07.180 (2008)]

B. C. Garcia, M. Kamperman, R. Ulrich, A. Jain, S. M. Gruner, U. Wiesner
Morphology diagram of a diblock copolymer - aluminosilicate nanoparticle system
Chem Mater 2009, 21, (22), 5397-5405 [05.046 (2008)]

C. Greiner, E. Arzt, A. Del Campo
Hierarchical gecko-like adhesives
Adv Mater 2009, 21, (4), 479-482 [08.191 (2008)]

C. Greiner, S. Buhl, A. Del Campo, E. Arzt
Experimental parameters controlling adhesion of biomimetic fibrillar surfaces
J Adhes 2009, 85, (9), 646-661 [00.685 (2008)]

C. Greiner, R. Spolenak, E. Arzt
Adhesion design maps for fibrillar adhesives: The effect of shape
Acta Biomater 2009, 5, 597-606 [03.727 (2008)]

R. Gross, C. Schumann, M. M. N. Wolf, J. Herbst, R. Diller, N. Friedman, M. Sheves
Ultrafast protein conformational alterations in bacteriorhodopsin and its locked analogue BR5.12
J Phys Chem B 2009, 113, (22), 7851-7860 [04.189 (2008)]

R. Gross, M. M. N. Wolf, C. Schumann, N. Friedman, M. Sheves, L. Li, M. Engelhard, O. Trentmann, H. E. Neuhaus, R. Diller
Primary photoinduced protein response in bacteriorhodopsin and sensory rhodopsin II
J Am Chem Soc 2009, 131, (41), 14868-14878 [08.091 (2008)]

P. A. Gruber, E. Arzt, R. Spolenak
Brittle-to-ductile transition in ultrathin Ta/Cu film systems
J Mater Res 2009, 24, (6), 1906-1918 [01.743 (2008)]

S. Heusing, P. W. Oliveira, E. Kraker, A. Haase, C. Palfinger, M. Veith
Wet chemical deposited ITO coatings on flexible substrates for organic photodiodes
Thin Solid Films 2009, 518, 1164-1169 [01.884 (2008)]

W. Hofbauer, R. J. Ho, R. Hairul Nizam, N. N. Gosvami, S. J. O'Shea
Crystalline structure and squeeze-out dissipation of liquid solvation layers observed by small-amplitude dynamic AFM
Phys Rev B 2009, 80, (13), 134104 [03.322 (2008)]

M. Klatte, M. Schuler, M. Wirtz, C. Fink-Straube, R. Hell, P. Bauer
The analysis of arabidopsis nicotianamine synthase mutants reveals functions for nicotianamine in seed iron loading and iron deficiency responses
Plant Physiol 2009, 150, (1), 257-271 [06.110 (2008)]

E. Kraker, A. Haase, G. Jakopic, J. Krenn, S. Köstler, C. Konrad, S. Heusing, P. W. Oliveira, M. Veith
Organic photodiodes on flexible substrates
Thin Solid Films 2009, 518, 1214-1217 [01.884 (2008)]

T. Kraus
The scale-up of material microstructuring: a perspective
Annual Report, Jahresbericht 2008 - INM Leibniz-Institut für Neue Materialien 2009, 38-41 [-]

E. Kroner, E. Arzt
Was wir von Geckos lernen können
Nachr Chem 2009, 57, (2), 137-139 [00.128 (2008)]

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## Posters / Poster

K. Brörmann

Friction induced deformation of microstructured PDMS surfaces
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M. Eder, E. Weber, I. M. Weiss

Fast and sensitive screening of composite materials using polarized light imaging
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M. Eder, I. M. Weiss

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B. Girault

Loss of mechanical size effect in micropillars of an ODS superalloy
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N. N. Gosvami

Atomic scale friction studies on metal surfaces

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F. Hausen

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Polarisationsmikroskopie an Zwiebelschalen
43. Metallographietagung, September 16-18, 2009, Aachen
Best Poster Award, 2. Preis

M. Kamperman

Beetle inspired adhesives
Gordon Research Conference on the Science of Adhesion, July 26-31, 2009, New London, NH, USA

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Measuring adhesion of gecko-inspired surfaces
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Measuring adhesion of gecko-inspired surfaces
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Winner of the “Excellent Poster Award”

A. Schneider

Correlation between critical temperature and strength of small-scale bcc pillars
Nanomechanical Testing in Materials Research and Development, October 11-16, 2009, Barga, Italy

C. Schumann, S. Schübbe, C. Cavelius, M. Koch, A. Kraegeloh

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Heterologous biomineralization in plants
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## Vorträge / Talks

### Eingeladene Vorträge / Invited talks

J. Adam

Verschiedene chemische Verfahren zur Herstellung von Nanopartikeln. a) Methoden zur Oberflächenmodifikation und Dispergierung, b) Top-down: Naßmahlverfahren
GDCh Fortbildungskurs „Chemische Nanotechnologien“, June 16-17, 2009, Saarbrücken

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Printable memory solutions for sensor, ID, and media applications (PriMeBits)
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THERMEC, August 26, 2009, Berlin

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Biomimietic surfaces – from principles to applications
Plenarvortrag Österreichische Chemietage, University of Vienna, August 25, 2009, Vienna, Austria

**E. Arzt**

Bio-inspired adhesion
Gordon Research Conference, July 28, 2009, Boston, MA, USA

**E. Arzt**

INM – Smarte Grenzflächen von den Grundlagen zur Anwendung
DGM-Tagung, Juni 23, 2009, Saarbrücken

**E. Arzt, E. De Souza, M. Kamperman**

Klebefreie Klebetechnik – Lernen von Geckos und Fliegen
126. Kongress der Deutschen Gesellschaft für Chirurgie, April 30, 2009, München

**E. Arzt**

Materials research from fundamentals to application – a portrait of INM
Luncheon – Sustainable Innovation: Nano Buildings, April 23, 2009, Chicago, IL, USA

**E. Arzt**

Biomimetic adhesion surfaces: from fundamentals to applications
DFG-Nachwuchsakademie, 30.03.2009, Aachen

**E. Arzt**

Biomimetic adhesion surfaces: from fundamentals to applications
Soft Matter Colloquium, March 22, 2009, Rehovot / Tel-Aviv, Israel

**E. Arzt**

Was hält den Gecko an der Decke?
Schüler-Uni – Materialwissenschaft und Werkstofftechnik, Saarland University, January 27, 2009, Saarbrücken

**C. Becker-Willinger**

Polymer matrix nanocomposites by the Nanomer approach
Korea-Germany Seminar on Materials and Components Technology, April 22, 2009, Hannover

**C. Becker-Willinger, G. Heppe, M. Opsölder, M. Veith, J. Cho, J.-R. Lee**

Wear resistant Nanomer additives for dispersion type polymer resin coatings for steel plates
The Asia-Pacific Galvanizing Conference 2009, November 08-12, 2009, Jeju, South Korea

**R. Bennewitz**

Feynman's talk, nanomachines, and friction force microscopy
Seminar at the Institute of Experimental Physics, Saarland University, November 6, 2009, Saarbrücken

**R. Bennewitz**

Jumps in friction
International Conference "Trends in Nanotribology"; October 19, 2009; Trieste, Italy

**R. Bennewitz**

Friction experiments from atomically flat graphene to micro-structured elastomers
Symposium in honour of Hans-Joachim Güntherodt's retirement, University of Basel, June 19, 2009, Basel, Switzerland

**R. Bennewitz**

Dissipation phenomena in atomic scale mechanics
SFB 602 Seminarserie, University of Göttingen, May 29, 2009, Göttingen

**R. Bennewitz**

Onset of plasticity as observed by force microscopy
DPG-Frühjahrstagung, March 26, 2009, Dresden

**R. Bennewitz**

Dissipation in single-asperity experiments
428. Wilhelm und Else Heraeus Seminar „Physics of Tribology", Physikzentrum, March 23-25, 2009, Bad Honnef

**R. Bennewitz**

Friction experiments from epitaxial graphene to rough elastomers
20. Edgar-Lüscher-Seminar, February 11, 2009, Klosters, Switzerland

**R. Bennewitz**

Single-asperity mechanics: Nanoscale friction and plasticity
nanoSeminar, TU Dresden, January 29, 2009, Dresden

**R. Bennewitz**

Atomic friction on atomically thin films
Seminar Oberflächenforschung, University of Bonn, January 16, 2009, Bonn

**P. Born, E. Murray, T. Kraus**

Temperature induced nanoparticle self-assembly
EMRS Spring Meeting. Symposium D: Nano-scale energetic materials: fabrication, cha-

racterization and molecular modelling, June 08-12, 2009, Strasbourg, France

C. Carraro
Nanostructure imaging by inelastic scattering of light
Department of Chemistry, Wageningen University, April 17, 2009, Wageningen, Netherlands

C. Carraro
Processing and characterization of SiC MEMS and nanowires
INM-Leibniz Institute for New Materials, July 08, 2009, Saarbrücken

C. Carraro
Processing and characterisation of SiC MEMS, nanowires, and graphene
CAPE Lecture, University of Cambridge, July 17, 2009, Cambridge, UK

C. Carraro
Silicon carbide thin film technology for Microsystems in harsh environment
German-Chinese Summer School on Microsystems Technology, University of Saarland, September 15, 2009, Saarbrücken

C. Carraro
Controlled structural strain of epitaxial graphene layers on hexagonal SiC
10th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN10), September 25, 2009, Granada, Spain

C. Carraro
Silicon carbide thin film technology for Microsystems in Harsh Environment
The American Vacuum Society (AVS) 56th National Symposium, November 12, 2009, San Jose, CA, USA

J. Flackus
The INM Business Model
Workshop / Seminar mit IDEC, May 21, 2009, Yokohama, Japan

M. Kamperman
Bioinspired systems for enhanced adhesion and catalytic function
Leibniz-Institut für Polymerforschung Dresden, Prof. M. Stamm, May 06, 2009, Dresden

M. Kamperman
Bioinspired systems for enhanced adhesion and catalytic function
Universität Köln, Prof. K. Meerholz, May 08, 2009, Köln

M. Kamperman
Bioinspired Hierarchical Systems
Universität Bayreuth, Prof. J. Breu, October 15, 2009, Bayreuth

M. Kamperman
Micropatterned Adhesive Surfaces: Lessons from Nature
Munich Adhesives and Finishing Symposium, October 19, 2009, München

A. Kraegeloh
Eigenschaften, Herstellung und Anwendung von Nanomaterialien
Arbeitsmedizinisches Symposium, INM Leibniz-Institut für Neue Materialien, June 27, 2009, Saarbrücken

A. Kraegeloh
Interaction of nanoparticles with human cells
AG Nanostrukturforschung und Nanotechnologie, Universität des Saarlandes, Prof. Dr. Hartmann, Seminar Nanostrukturforschung, December 04, 2009, Saarbrücken

T. Kraus
Engineering nanoparticle assembly
University of Toronto, July 06, 2009, Toronto, Canada

R. Maboudian
Manipulating surface forces in MEMS
INM – Leibniz Institute for New Materials, February 2009, Saarbrücken

R. Maboudian
Surface and materials engineering for Microsystems in harsh environment
Department of Mechanical and Process Engineering, ETH, February 2009, Zurich, Switzerland

R. Maboudian
Manipulating surface forces in MEMS
Department of Chemistry, Wageningen University, April 2009, Wageningen, Netherlands

R. Maboudian
Technology of Miniaturization and Implications for Sensing
Eni S.p.A., Exploration and Production Division, May 2009, Milan, Italy

R. Maboudian
Surface and materials engineering for enhanced Microsystems technology
Robert Bosch GmbH, Microsystems Research & Development Division, June 2009, Stuttgart

R. Maboudian
Surface and materials engineering for enhanced MEMS reliability
German-Chinese Summer School on Microsystems Technology, University of Saarland, September 2009, Saarbrücken

R. Maboudian
Surface and materials engineering for enhanced Microsystems technology
STMicroelectronics Srl, September 2009, Milan, Italy

R. Maboudian
Surface and Materials Engineering for Microsystems in Harsh Environment
Commissariat a l'Energie Atomique, October 2009, Saclay, France

R. Maboudian
Surface and Materials Engineering for Microsystems in Harsh Environment,

Department of Chemistry, Imperial College, December 2009, London, UK

R. Maboudian

Surface and materials engineering for Microsystems in harsh environment
Department of Materials, Oxford University, December 2009, Oxford, UK

P. W. Oliveira

Innovation through material development
Brazilian-German Workshop on Nanotechnology and Applications, October 07, 2009, Belo Horizonte, Brazil

M. Quilitz

Chemische Nanotechnologie für die Architektur
Netzwerktreffen & Partnering Day Saarland-Steiermark, Schloss Piber, September 18, 2009, Köflach, Austria

M. Quilitz, P. W. Oliveira

Optical materials
IDEC, Industrial Development Corporation Seminar, May 21, 2009, Yokohama, Japan

M. Quilitz, P. W. Oliveira

Nanopartikel für die Optik
Kolloquium Makromolekulare Chemie, Philips Universität Marburg, July 10, 2009, Marburg

M. Quilitz, P. W. Oliveira, M. Veith

Material development for optical devices
Korea-Germany Seminar on Materials and Components Technology, April 22, 2009, Hannover

M. Quilitz, P. W. Oliveira, M. Veith

Transparent, conductive oxides for coating applications
Brazilian-German Workshop on Nanotechnology and Applications, October 07, 2009, Belo Horizonte, Brazil

M. Quilitz

Chemische Nanotechnologie - Grundlagen der Herstellung und Oberflächenmodifikation von Nanopartikeln über chemische Verfahren
GDCh-Kurs „Chemische Nanotechnologien“, June 16-17, 2009, Saarbrücken

K.P. Schmitt

Nass-Chemische Herstellung keramischer Nanopartikel
GDCh Fortbildungskurs „Chemische Nanotechnologien“, Juni 16-17, 2009, Saarbrücken

M. Veith

Nano- to micro-structured ceramic wires as surfaces for cell adhesion
NanoMed, March 04, 2009, Berlin

M. Veith

Smart Surfaces
Hannover Messe, Seminartag KITECH, April 22, 2009, Hannover

M. Veith

Funktionale Oberflächen - die neue Vielfalt
Smarte Oberflächen - Neue Produkteigenschaften, IHK Ostwestfalen, April 29, 2009, Detmold

M. Veith

Präsentation mit Experimenten
3. Empower-Kongress, May 04, 2009, Saarbrücken

M. Veith

Keramische Nano-Partikel im Baubereich für besondere Beanspruchungen
Beschichten von Beton, TAW Wuppertal, May 05, 2009, Bochum

M. Veith, C. Aktas, E. Sow

Biphasic nano-materials and applications in life sciences: 1D Al/$Al_2O_3$ nanostructures for improved neuron cell culturing
PAC RIM Meeting der American Ceramic Society, May 31-June 05, 2009, Vancouver, Canada

M. Veith

Eröffnung des Wissenschaftssommers 2009, mit Experimenten
Wissenschaftssommer 2009, June 20-26, 2009, Saarbrücken

M. Veith

Nanotechnologie und ihre Anwendungen in der Metalltechnik
Metallforum, July 06, 2009, Wallerfangen

M. Veith

Einführungsvortrag Kick-off Meeting AiF-Projekt
Firma Seidel, October 05, 2009, Marburg

M. Veith

Smart surfaces
Korea-Germany Seminar on Materials and Components Technology, April 22, 2009, Hannover

M. Veith

From polycyclic molecular alumosilicates to core-shell nano-loops with alumina
IRIS 12, August 16-21, 2009, Gao, India

M. Veith

Nanowires, nanoloops and nanorods by CVD
ALT 2009, September 27-29, 2009, Antalya, Turkey

I. M. Weiss

The myosin-chitinsynthases of molluscs -hypotheses for the evolution of biological materials
Weizman Institute, Department of Structural Biology, March 22, 2009, Rehovot, Israel

I. M. Weiss

Biomineralization from a biologist’s viewpoint - glycosyltransferases, molecular motors, and the properties of biological materials
Biologisches Kolloquium, Saarland University, June 02, 2009, Saarbrücken

M. Wittmar, A. Wittmar, M. Veith
Chromfreier Korrosionsschutz mit dünnen Schichten
KooperationsForum “Moderne Beschichtungs- und Oberflächentechnologien”, Dezember 9, 2009, Köln

## Sonstige Vorträge / Other talks

J. Adam
WP2-Materials. Synthesis and characterization of ferroelectric $BaTiO_3$ nanoparticles and pastes
1st PriMeBits Review Meeting, European Commission, February 10, 2009, Brussels, Belgium

J. Adam
WP2-Materials. Synthesis and characterization of ferroelectric $BaTiO_3$ nanoparticles and pastes. Particulate FRAM cells
Intermediate PriMeBits Review Meeting, European Commission, September 17, 2009, Brussels, Belgium

J. Adam, J. Dietz, M. Koch, M. Veith
Bonding of porous alumina structures with zirconia nanoparticles
11th Conference of the European Ceramic Society, June 21-25, 2009, Krakow, Poland

M. Amlung, P. W. Oliveira, P. Rogin, M. Veith
Kratzfeste glaskeramische Korrosionsschutzschichten mit Antihaft-Eigenschaften
Workshop “Schichten aus Nanopartikeln - Abscheidung aus Dispersionen, Flammen und Plasmen”, Europäische Forschungsgesellschaft, September 29, 2009, Dresden

M. Amlung, P. Rogin, P. W. Oliveira, M. Veith
Neue glaskeramische Schutzschichten für Gläser und Stähle mit Korrosionsschutz und Antihaft-Eigenschaften
83. Glastechnische Tagung, May 18-20, 2009, Amberg

C. Becker-Willinger
Polymer matrix nanocomposites by the Nanomer approach
Lange Nacht der Wissenschaft, Universität des Saarlandes, June 20, 2009, Saarbrücken

C. Becker-Willinger
Polymer matrix nanocomposites - new properties in polymer via nanoparticles
Minisymposium “From Molecules to Materials”, Universität des Saarlandes, September 10-11, 2009, Saarbrücken

C. Becker-Willinger, P. Kalmes, M. Veith
Investigation on new functional materials surfaces for the use in food production
European Coatings Conference 2009 „Easy-to-clean/Self-cleaning coatings II“, December 08-09, 2009

R. Bennewitz
Single dislocation plasticity probed by force microscopy
MRS Spring Meeting, April 16, 2009, San Francisco, CA, USA

P. Born, E. Murray, T. Kraus
Temperature induced nanoparticle assembly
EMRS Spring Meeting 2009, Symposium D: Nano-scale energetic materials: fabrication, characterization and molecular modelling, June 8-12, 2009, Strasbourg, France

M. Busse, L. Haab, M. Mariam, C. Krick, T. Weis, W. Reith, D. J. Strauss
Assessment of aversive stimuli dependent attentional binding by the N170 VEP component
31st International Conference of the IEEE Engineering in Medicine and Biology Society, September 02-06, 2009, Minneapolis, MN, USA

F. I. Corona-Strauss, W. Delb, B. Schick, S. Hussain, D. J. Strauss
Gabor frame phase stability analysis of chirp evoked auditory brainstem responses
4th International IEEE EMBS Conference on Neural Engineering, April 29-May 02, 2009, Antalya, Turkey

F. I. Corona-Strauss, D. J. Strauss, B. Schick, W. Delb
A series of notched-noise embedded chirps for objective frequency specific hearing examinations
31st International Conference of the IEEE Engineering in Medicine and Biology Society, September 02-06, 2009, Minneapolis, MN, USA

P. Egberts
Identation and wear of KBr(100)
428. Wilhelm und Else Heraeus Seminar “Physics of Tribology”, Physikzentrum, March 23-25, 2009, Bad Honnef
Vortrag (contributed talk)

J. Flackus
Nano to Market
Nanotechnology-Workshop beim Illinois Institute of Technology (IIT) – Sustainable Innovation: NanoBuildings – April 24, 2009, Chicago, IL, USA

N.N. Gosvami
Atomic friction on ultrathin films
Annual Meeting of the AFRI cooperation within the FANAS project, Universität Münster, November 20, 2009, Münster
Vortrag (contributed talk)

N. N. Gosvami
Atomic scale friction studies on metal surfaces
428. Wilhelm und Else Heraeus Seminar “Physics of Tribology”, Physikzentrum, March 23-25, 2009, Bad Honnef
Vortrag (contributed talk)

L. Haab, C. Trenado and D. J. Strauss
Neurofunctional model of limbic influences on electroencephalographic correlates of selective attention governed by stimulus-novelty
4th International IEEE EMBS Conference on Neural Engineering, April 29-May 02, 2009, Antalya, Turkey

L. Haab, E. Wallhäußer-Franke, C. Trenado, D. J. Strauss

Modeling limbic influences on habituation deficits in chronic tinnitus aurium
31st International Conference of the IEEE Engineering in Medicine and Biology Society, September 02-06, 2009, Minneapolis, MN, USA

A. R. Harris, K. Schwerdtfeger, Y. F. Low, D. J. Strauss

Effects of transcranial magnetic stimulation on auditory attention: An electroencephalographic study
4th International IEEE EMBS Conference on Neural Engineering, April 29-May 02, 2009, Antalya, Turkey

M. Kamperman

Adhesion of gecko-inspired surfaces: Material properties and geometry
Materials Research Society Spring Meeting, April 13-17, 2009, San Francisco, CA, USA

M. Kamperman

Bioinspired systems for enhanced adhesion and catalytic function
Groningen University, Prof. A. J. Schouten, June 19, 2009, Groningen, Netherlands

M. Kamperman

Bioinspired systems for enhanced adhesion and catalytic function
Clausthal University, Prof. D. Johannsmann; June 23, 2009; Clausthal

T. Kraus

The process engineering of nanoparticle assembly
Gordon Research Conference Supramolecules & Assemblies, June 28-July 3rd, 2009, Waterville Valley, NH, USA

T. Kraus, P. Born, E. Murray

Regular particle superstructures: science and engineering
Symposium “From molecules to materials”, Saarland University, September 10, 2009, Saarbrücken

E. Kroner

Neue Haftsysteme aus der Materialforschung - Was wir von Geckos lernen können
Lange Nacht der Wissenschaft, Universität des Saarlandes, June 20, 2009, Saarbrücken

E. Kroner

Gecko-inspired adhesives: measurement effects
EUROMAT 2009, September 06-10, 2009, Glasgow, UK

T. Lehnert

Vorstellung des Arbeitskreises Veith - anorganische und allgemeine Chemie
Doktorandentag der Chemie der Universität des Saarlandes, October 21, 2009, Saarbrücken

T. Lehnert, P. Herbeck-Engel, J. Adam, M. Veith

Ferroelectric characterization of low temperature sol-gel bonded particles
8th ECerS Students‘ Meeting, December 02-05, 2009, Novi Sad, Serbia

T. Lehnert

Ferroelektrische Charakterisierung von Nanopartikeln
Skilizium, March 16-20, 2009, Zweisimmen, Switzerland

Y. F. Low, K. Schwerdtfeger, A. R. Harris, D. J. Strauss

An investigation on the effects of single pulse transcranial magnetic stimulation in a modified maximum entropy auditory stimulation paradigm
31st International Conference of the IEEE Engineering in Medicine and Biology Society, September 02-06, 2009, Minneapolis, MN, USA

Y. F. Low, D. J. Strauss

An inverse transform technique for EEG phase reset
4th International IEEE EMBS Conference on Neural Engineering, April 29-May 02, 2009, Antalya, Turkey

M. Mariam, W. Delb, D. J. Strauss

Differentiation of perceived sound levels by electroencephalographic data: a novelty detection approach using habituation correlates
4th International IEEE EMBS Conference on Neural Engineering, April 29-May 02, 2009, Antalya, Turkey

I. Mustaffa, C. Trenado, H. R. A. Rahim, K.-H. Schäfer, D. J. Strauss

Sharpening of neurite morphology using complex coherence enhanced diffusion
31st International Conference of the IEEE Engineering in Medicine and Biology Society, September 02-06, 2009, Minneapolis, MN, USA

S. Ren, M. Wittmar, M. Aslan, I. Grobelsek, M. Quilitz, M. Veith

Dielectric properties of the composites in the $CaO-CuO-TiO_2$ system
11th Conference of the European Ceramic Society, June 21-25, 2009, Krakow, Poland

P. Rogin

Microstructured and nanostructured optical materials
Summer School der Universität des Saarlandes, mit der Peking Universität und der Chinesischen Akademie der Wissenschaften, September 14-25, 2009, Saarbrücken

H. K. Schmid

ELNES in transition metal oxides recorded by HR-EELS
International EELS Workshop (EDGE 2009), May 17-22, 2009, Banff, Canada

D. J. Strauss, F. I. Corona-Strauss, C. Bernarding, W. Reith, M. Latzel, M. Froehlich

On the cognitive neurodynamics of listening effort: a phase clustering analysis of large-scale neural correlates
31st International Conference of the IEEE Engineering in Medicine and Biology Society, September 02-06, 2009, Minneapolis, MN, USA

D. J. Strauss, F. I. Corona-Strauss, M. Latzel, M. Froehlich
On the feasibility of objective listening effort estimations by electroencephalographic correlates of corticofugal modulations
4th International IEEE EMBS Conference on Neural Engineering, April 29-May 02, 2009, Antalya, Turkey

C. Trenado, L. Haab, W. Reith, D. J. Strauss
Toward a realistic simulation framework for large-scale neural correlates in clinical applications
4th International IEEE EMBS Conference on Neural Engineering, April 29-May 02, 2009, Antalya, Turkey

M. Veith
General objectives and results in MULTIPROTECT
Final Review Meeting of the EU-Project MULTIPROTECT, May 8, 2009, Saarbrücken

M. Veith
Advanced environmental-friendly multifunctional corrosion protection by nanotechnology: Introduction Part 1
MULTIPROTECT and MUST Dissemination Workshop, January 21-22, 2009, München

M. Veith
Safety and risks of nanotechnology
MULTIPROTECT and MUST Dissemination Workshop, January 21-22, 2009, München

I. M. Weiss
New materials based on biomineralization concepts
Symposium "From Molecules to Materials", Saarland University, September 10, 2009, Saarbrücken

I.M. Weiss
Mechanical signals as a trigger for onset of cyclic biomineralization
Kick-off Meeting in the frame of Marie Curie ITN People Program, November 12, 2009, Manchester, UK

M. Wittmar, A. Wittmar, H. Caparrotti, M. Veith
Simple preparation routes for corrosion protection hybrid sol-gel coatings on AA 2024
5th Aluminium Surface
Science & Technology - ASST2009, May 10-14, 2009, Leiden, Netherlands

A. Wittmar, H. Caparrotti, M. Wittmar, M. Veith
Investigations on synergistic effects of mixtures of different inhibitors incorporated in sol-gel coatings on the protection of AA 2024-T3
EUROCORR 2009, September 06-10, 2009, Nice, France

M. Wittmar
Advanced environmental-friendly multifunctional corrosion protection by nanotechnology: Introduction part 2
MULTIPROTECT and MUST Dissemination Workshop, January 21-22, 2009, München

M. Wittmar
Results of the last project period, deliverables and milestones
Final Review Meeting of the EU-Project MULTIPROTECT, May 8, 2009, Saarbrücken

## Lehrveranstaltungen / Lectures

**Wintersemester 2008/09**

E. Arzt
INM-Kolloquium
Universität des Saarlandes, Saarbrücken

D. Strauss
Grundlagen der Medizinischen Messtechnik (Bachelor)
Vorlesung
Hochschule für Technik und Wirtschaft (HTW), Saarbrücken

D. Strauss
Einführung in das Neural Engineering (Bachelor)
Vorlesung
Hochschule für Technik und Wirtschaft (HTW), Saarbrücken

D. Strauss
Neural signal analysis and modeling (Master)
Vorlesung
Hochschule für Technik und Wirtschaft (HTW), Saarbrücken

D. Strauss
Audiologie (Master)
Vorlesung
Hochschule für Technik und Wirtschaft (HTW), Saarbrücken

M. Veith
Anorganisches Kolloquium
Kolloquium
Universität des Saarlandes, Saarbrücken

M. Veith
Chemische Fachdidaktik, Kurs A (FD1)
Kurs
Universität des Saarlandes, Saarbrücken

M. Veith
Anorganisches Praktikum für Fortgeschrittene (ACF)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Chemisches Praktikum für Studierende der Physik, Werkstoffwissenschaften, der Biologie und der Metalltechnik (Lehramt an beruflichen Schulen)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Chemisches Praktikum mit Seminar für Studierende der Biologie, der Physik, der Werkstoffwissenschaften und der Metalltechnik
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Einführung in das Fortgeschrittenenpraktikum für Lehramtsstudierende (FGLa1)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Einführung zum Praktikum für Studierende der Biologie, der Physik, der Werkstoffwissenschaften und der Metalltechnik
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Fortgeschrittenenpraktikum für Lehramtsstudierende (FGLa2)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Chemische Fachdidaktik inklusive Seminar zum Schulpraktikum, Kurs B (Fd1+FD2)
Seminar
Universität des Saarlandes, Saarbrücken

M. Veith

Seminar für eigene Mitarbeiter
Seminar
Universität des Saarlandes, Saarbrücken

M. Veith

Seminar zum fachdidaktischen Schulpraktikum (FD2)
Seminar
Universität des Saarlandes, Saarbrücken

M. Veith

Übungen zu Grundlagen der Hauptgruppenchemie (AC01Ü)
Übung
Universität des Saarlandes, Saarbrücken

M. Veith

Übungen zur Allgemeinen Chemie (AC00Ü)
Übung
Universität des Saarlandes, Saarbrücken

M. Veith

Allgemeine Chemie (AC00)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith

Grundlagen der Hauptgruppenchemie (AC01)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith u.a.

Anorganische und Organometallische Chemie
Vorlesung
Université Straßbourg / Ecole Européene de Chimie, Polymères et Matériaux, Strasbourg, France

I. Weiss

Biochemisches Großpraktikum I / Teil B (Bioinformatik und Enzymologie) (Bachelor) Studiengang Biochemie
Universität Regensburg, Regensburg

I. Weiss

Seminar im Rahmen des Praktikums „Wechselwirkungen von Zelloberflächenstrukturen mit funktionellen Oberflächen“ für Aleksandra Markova
Seminar am 13.01.2009
Universität des Saarlandes, Saarbrücken / Lehrstuhl für Pharmazeutische Biologie (Prof. Kiemer)

**Sommersemester 2009**

E. Arzt

INM-Kolloquium
Kolloquium
Universität des Saarlandes / INM, Saarbrücken

C. Fink-Straube, M. Koch

Chemische und physikalische Analytik im schulbegleitenden Praktikum
Laborpraktikum für Schüler
Laborpraktikum vom 21.09.2009 bis 13.11.2009

M. Veith u.a.

Vorlesungen im Rahmen des ERASMUS-Programms
Vorlesung
Ecole Polytechnique Paris Palaiseau, Paris, France
15.+18.05.2009

M. Veith

Metallorganische Chemie (AC6)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith

Molekülchemie der Hauptgruppenelemente (AC7)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith u.a.

Anorganisches Praktikum für Fortgeschrittene (ACF)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Materialien aus molekularen Vorstufen (AC9)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith u.a.

Spezielle Kapitel der Anorganischen Chemie (ACII)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith

Molekülchemie der Hauptgruppenelemente II (AC12)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith

Vertiefungspraktikum Anorganische Chemie (ACV)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Einführungspraktikum in das Fortgeschrittenenpraktikum für Lehramtsstudierende (FGla1)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Fortgeschrittenenpraktikum für Lehramtsstudierende (FGLa2)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Fachdidaktisches Seminar für Lehramtsstudierende (FD1)
Seminar
Universität des Saarlandes, Saarbrücken

M. Veith

Fachdidaktisches Praktikum für Lehramtsstudierende (FD2)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith u.a.

Einführung und Seminar zum chemischen Praktikum für Naturwissenschaftler
Seminar
Universität des Saarlandes, Saarbrücken
(SS 09)

M. Veith u.a.

Chemisches Praktikum für Studierende der Physik, Werkstoffwissenschaften, der Biologie und der Metalltechnik (Lehramt an beruflichen Schulen)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Seminar für eigene Mitarbeiter
Seminar
Universität des Saarlandes, Saarbrücken

I. Weiss

Sporenbildung von Dictyostelium auf mikrostrukturierten Oberflächen : Titel: Testing various sterilization methods for dictyostelium discoideum growth on gecko-inspired PDMS surfaces
(für Judith Strauch)
Praktikum 08.06.2009 – 26.06.2009 / Seminar
Universität des Saarlandes, Saarbrücken / Lehrstuhl für Pharmazeutische Biologie (Prof. Kiemer)

I. Weiss

Sporulation of slime molds on „Gecko-Surfaces“
Laborpraktikum für Natalie Concors
University of California, Santa Barbara, USA
Laborpraktikum vom 27.06. bis 04.09.2009

### Wintersemester 2009/10

C. Aktas

Chemische Nanotechnologie
Vorlesung
Fachhochschule Kaiserslautern / Campus Zweibrücken

E. Arzt und MitarbeiterInnen

„Nano/Biomaterialien“
Vorlesung und Übung
Universität des Saarlandes, Saarbrücken

E. Arzt

INM-Kolloquium
Kolloquium
Universität des Saarlandes / INM, Saarbrücken

R. Bennewitz

Experimentalphysik IVa (Festkörperphysik I) (EP IV)
Vorlesung und Übung
Universität des Saarlandes, Saarbrücken

T. Müller

Superparamagnetische Nanopartikel – Synthese und Einsatz
Vorlesung für Studierende Maschinenbau im 5.+6. Semester – Fachrichtung
Produtionstechnik mit Wahlpflichfach Nanotechnologie
ASW Berufsakademie Saarland, St. Ingbert
Vorlesung am 06.10.2009

T. Müller

Selbstreinigende Oberflächen – Immer sauber durch Photokatalyse
Vorlesung für Studierende Maschinenbau im 5.+6. Semester – Fachrichtung
Produtionstechnik mit Wahlpflichfach Nanotechnologie
ASW Berufsakademie Saarland, St. Ingbert
Vorlesung am 06.10.2009

D. Strauss

Querschnittsfach 11 – Seminar Radiologie
Seminar
Universität des Saarlandes, Saarbrücken

M. Veith u.a

Anorganische und Organometallische Chemie
Vorlesung
Université Straßbourg / Ecole Européene de Chimie, Polymères et Matériaux, Strasbourg, France

M. Veith

Allgemeine Chemie (AC00)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith

Anorganisches Kolloquium
Kolloquium
Universität des Saarlandes, Saarbrücken

M. Veith

Anorganisches Praktikum für Fortgeschrittene (ACF)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith

Chemische Fachdidaktik inklusive Seminar zum Schulpraktikum, Kurs B (Fd1+Fd2)
Seminar
Universität des Saarlandes, Saarbrücken

M. Veith
Chemische Fachdidaktik, Kurs A (FD1)
Kurs
Universität des Saarlandes, Saarbrücken

M. Veith
Chemische Fachdidaktik, Kurs A (FD1)
Kurs
Universität des Saarlandes, Saarbrücken

M. Veith
Chemisches Praktikum für Studierende der Physik, Werkstoffwissenschaften, der Biologie und der Metalltechnik (Lehramt an beruflichen Schulen)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Chemisches Praktikum für Studierende der Physik, Werkstoffwissenschaften, der Biologie und der Metalltechnik (Lehramt an beruflichen Schulen)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Chemisches Praktikum für Studierende der Physik, Werkstoffwissenschaften, der Biologie und der Metalltechnik (Lehramt an beruflichen Schulen)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Chemisches Praktikum mit Seminar für Studierende der Biologie, der Physik, der Werkstoffwissenschaften und der Metalltechnik
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Einführung in das Fortgeschrittenenpraktikum für Lehramtsstudierende (FGLa1)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Einführung zum Praktikum für Studierende der Biologie, der Physik, der Werkstoffwissenschaften und der Metalltechnik
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Fortgeschrittenenpraktikum für Lehramtsstudierende (FGLa2)
Praktikum
Universität des Saarlandes, Saarbrücken

M. Veith
Grundlagen der Hauptgruppenchemie (AC01)
Vorlesung
Universität des Saarlandes, Saarbrücken

M. Veith
Seminar für eigene Mitarbeiter
Seminar
Universität des Saarlandes, Saarbrücken

M. Veith
Seminar zum fachdidaktischen Schulpraktikum (FD2)
Seminar
Universität des Saarlandes, Saarbrücken

M. Veith
Übungen zu Grundlagen der Hauptgruppenchemie (AC01Ü)
Übung
Universität des Saarlandes, Saarbrücken

M. Veith
Übungen zur Allgemeinen Chemie (AC00Ü)
Übung
Universität des Saarlandes, Saarbrücken

M. Veith
Chemische Nanotechnologie
Vorlesung
Fachhochschule Kaiserslautern / Campus Zweibrücken

I. Weiss, M. Eder
Botanik – Baupläne und Systematik der Pflanzen
Vorlesung für Studierende des Bachelor-Studienganges Biologie
Universität des Saarlandes, Saarbrücken / Lehrstuhl für Botanik (Prof. Mues) und Lehrstuhl für Pflanzenbiologie (Prof. Bauer)
13.10.-22.10.2009 (Weiss)
27.10.-29.10.2009 (Eder)

I. Weiss
Biochemisches Großpraktikum I, Teil D (Protein- und Enzymreinigung)
Kurs und Seminar
Universität Regensburg, Regensburg

### Weitere Lehrveranstaltungen / Other courses

M. Schubert
NanoBioNet e.V. und cc-NanoChem e.V.
Nanotechnologie als Seminarfach
Lehrerseminar
02.04.2009, Saarbrücken

M. Schubert
NanoBioNet e.V. und cc-NanoChem e.V.
Experimentierkoffer Nanotechnoloige – Umgang und Einsatz
Lehrerseminar
10.09.2009, Saarbrücken

M. Veith, M. Quilitz u.a.
GDCh-Kurs “Chemische Nanotechnologie”
16. – 17.06.2009, Saarbrücken

## Patente / Patents

Im Jahr 2009 wurden acht neue Patentanmeldungen hinterlegt, die noch nicht offengelegt worden sind. Es wurden zehn Patente erteilt, davon drei innerhalb von Europa und sieben auf internationaler Ebene. Das INM - Leibniz-Institut für Neue Materialien unterhält somit rund 105 aktive Patentfamilien.

In 2009, INM has filed eight new patent applications which are not yet published and ten patents have been granted. Three of these patents are granted in Europe and seven in foreign countries. The INM – Leibniz Institute for New Materials had 105 active patent families.

### Erteilte europäische Patente

EP 1278582 B1

Titel: "Verfahren zur Abtrennung von Komponenten aus flüssigen und gasförmigen Medien mit Nanokompositen"
Erfinder: Thomas Schiestel, Thomas Müller, Hermann Schirra, Helmut Schmidt

EP 1525338 B1

Titel: „Substrat mit photokatalytischer $TiO_2$-Schicht"

Erfinder: Murat Akarsu, Ertugrul Arpac, Helmut Schmidt

EP 1681370 B1

Titel: „Verfahren zur Herstellung von photokatalytisch aktiven $TiO_2$-Teilchen und von Substraten mit photokatalytischer $TiO_2$-Schicht"
Erfinder: Murat Akarsu, Ertugrul Arpac, Helmut Schmidt

### Erteilte internationale Patente

Chinesisches Patent Nr. ZL03816327.6

Stammanmeldungstitel: „Substrat mit photokatalytischer $TiO_2$-Schicht"
Erfinder: Murat Akarsu, Ertugrul Arpac, Helmut Schmidt

Chinesisches Patent Nr.
ZL200480016387.4

Stammanmeldungstitel: „Antiadhäsive Hochtemperaturschichten"
Erfinder: Mesut Aslan, Robert Drumm, Klaus Endres, Hareesh Nair, Bernd Reinhard, Helmut Schmidt

Japanisches Patent Nr. 4320456

Stammanmeldungstitel: „Optische Bauteile mit Gradientenstruktur und Verfahren zu deren Herstellung"
Erfinder: Herbert Krug, Peter William de Oliveira, Helmut Schmidt, Stefan Sepeur

Japanisches Patent Nr. 4310602

Stammanmeldungstitel: „Verfahren zur Herstellung optischer Mehrschichtsysteme"
Erfinder: Martin Mennig, Peter William de Oliveira, Helmut Schmidt

Japanisches Patent Nr. 4318096

Stammanmeldungstitel: „Kunststofffolie mit Mehrschicht-Interferenzbeschichtung"
Erfinder: Anette Berni, Martin Mennig, Peter William de Oliveira, Helmut Schmidt

Japanisches Patent Nr. 4296431

Stammanmeldungstitel: „Substrate mit Biofilm hemmender Beschichtung"
Erfinder: Carsten Becker-Willinger, Helmut Schmidt

Japanisches Patent Nr. 4419167

Stammanmeldungstitel: „Verfahren zur Herstellung optischer Elemente mit Gradientenstruktur"
Erfinder: Ulrike Dellwo, Martin Mennig. Peter William de Oliveira, Helmut Schmidt, Heike Schneider

## Kooperationen / Cooperations

Al Azhar University / Gaza, Palestine
Assiut University / Assiut, Egypt

Austrian Research Centers GmbH ARC / Seibersdorf, Austria

Bilkent Üniversitesi / Bilkent, Turkey

Bogazici Üniversitesi / Istanbul, Turkey

Bundesanstalt für Materialprüfung / Berlin

cc-NanoChem e.V. / Saarbrücken

Centre National de la Recherche Scientifique – Institut des Matériaux Jean Rouxel (CNRS-IMN) / Nantes, France

Centre Suisse d'Electronique et de Microtechniques SA (CSEM) / Zurich, Switzerland

Centro per L'Assistenza Scientifica e Tecnologica alle Imprese (CASTI) / L'Aquila, Italy

Centro Sviluppo Materiali S.p.A. / Rome, Italy

Christian-Albrechts-Universität zu Kiel

CNRS Laboratoire de Chimie de Coordination (LCC) / Toulouse, France

Consejo Superior de Investigaciones Científicas / Madrid, Spain

Deutsche Gesellschaft für Holzforschung e.V. / München

Deutsches Zentrum für Luft- und Raumfahrt / Köln

DOE Joint Genome Institute / Los Alamos, NM, USA

Ecole Européene d'Ingénieurs en Génie des Matériaux (EEIGM) / Nancy, France

Ecole Polytechnique / Montreal, Canada

Ecole Polytechnique Fédérale de Lausanne (EPFL) / Lausanne, Switzerland

Ecole Supérieure de Physique et de Chimie Industrielles (ESPCI) / Paris, France

Eidgenössisch Technische Hochschule (ETH) Zürich / Zurich, Switzerland

Fachhochschule Kaiserslautern / Kaiserslautern

Fachinformationszentrum Karlsruhe (FIZ) / Eggenstein-Leopoldshafen

Forschungsgesellschaft für Verfahrenstechnik e.V. (GVT) / Frankfurt a.M.

Forschungsinstitut für Edelmetalle und Metallchemie / Schwäbisch Gmünd

Forschungszentrum Jülich

Fraunhofer Institut für Biomedizinische Technik (IBMT) / St. Ingbert

Fraunhofer Institut für Elektronenstrahl- und Plasmatechnik (IEP) / Dresden

Fraunhofer Institut für Silicatforschung (ISC) / Würzburg

Fraunhofer Institut für Solare Energiesysteme (ISE) / Freiburg i.Br.

Fraunhofer Institut für Werkstoffmechanik (IWM) / Freiburg i.Br.

Fraunhofer Institut für Zerstörungsfreie Prüfverfahren (IZFP) / Saarbrücken

Friedrich-Alexander-Universität / Erlangen, Nürnberg

Fritz-Haber-Institut / Berlin

Georg-August-Universität / Göttingen

Helsinki University of Technology / Helsinki, Finland

Hochschule für Technik und Wirtschaft des Saarlandes (HTW) / Saarbrücken

Illinois Institute of Technology / Chicago, IL, USA

Indian Institute of Science / Bangalore, India

Institut für Fenstertechnik (IFT) / Rosenheim

Institut für Solartechnik / Rapperswil, Switzerland

Institut National Polytechnique de Lorraine / Nancy, France

Institute of Materials Research and Engineering (IMRE) / Singapore, Singapore

Institute of Physical Chemistry of the Romanian Academy / Bucharest, Romania

Institute of Science and Technology for Ceramics / Rome, Italy

Instituto de Catalisis y Petroleoquimica (ICP) / Madrid, Spain

Instituto de Ceramica y Vidrio / Madrid, Spain

Instituto de Optica Daza de Valdes / Madrid, Spain

Instituto de Soldadura e Qualidade / Porto Salvo, Portugal

Jacobs University Bremen GmbH / Bremen

Joanneum Research Forschungsgesellschaft mbH / Graz, Austria

Julius-Maximilians-Universität / Würzburg

Karlsruhe Institute of Technology / Eggenstein-Leopoldshafen

Kocaeli Üniversitesi / Kocaeli, Turkey

Korea Institute of Industrial Technology (KITECH) / Seoul, Republic of Korea

Korea Institute of Science and Technology (KIST) / Seoul, Republic of Korea

Korea Research Institute of Chemical Technology (KRICT) / Seoul, Republic of Korea

Lawrence Berkeley National Laboratory / Berkeley, CA, USA

Leopold-Franzens-Universiät Innsbruck / Innsbruck, Austria

Los Alamos National Laboratory / Los Alamos, NM, USA

Ludwig-Maximilians-Universität / München

Max-Planck-Institut für Chemische Physik Fester Stoffe / Dresden

Max-Planck-Institut für Dynamik und Selbstorganisation / Göttingen

Max-Planck-Institut für Metallforschung / Stuttgart

Max-Planck-Institut für Mikrostrukturphysik / Halle

Max-Planck-Institut für molekulare Physiologie / Dortmund

Max-Planck-Institut für Polymerforschung / Mainz

McGill University / Montreal, Canada

Mid Sweden University / Sweden

NanoCat Nano-Center for Advanced Technologies / L'Aquila, Italy

Nanoscience Centre / Cambridge, UK

National Institute of Materials Physics (NIMP) / Bucharest, Romania

National University of Singapore (NUS) / Singapore, Singapore

Oak Ridge National Laboratory / Oak Ridge, TN, USA

Ohio State University / Columbus, OH, USA

Paul Scherrer Institut (PSI) / Villigen, Switzerland

Rheinische Friedrich-Wilhelms-Universität / Bonn

Rudjer-Boskovic-Institute / Zagreb, Croatia

Ruprecht-Karls-Universität / Heidelberg

Sandia National Laboratories / Albuquerque, NM, USA

Scuola Internazionale Superiore di Studi Avanzati di Trieste (SISSA) / Trieste, Italy

Technical Research Center Finland / Oulu, Finland

Technical University of Istanbul / Istanbul, Turkey

Technical University of Szczecin / Szczecin, Poland

Technion-Israel Institute of Technology / Haifa, Israel

Technische Universität Berlin

Technische Universität Darmstadt

Technische Universität Kaiserslautern

TNO – Netherlands Organisation for Applied Scientific Research / Eindhoven, Netherlands

Trinity College / Dublin, Ireland

Universidad Iberoamericana / Mexico City, Mexico

Universidad de Santiage de Chile / Santiago, Chile

Universidade de Aveiro / Aveiro, Portugal

Universidade Federal de Minas Gerais (UFMG) / Belo Horizonte, Brasil

Università degli Studi dell'Aquila / L Áquila, Italy

Università degli Studi "Magna Graecia" / Catanzaro, Italy

Università degli Studi di Udine / Udine, Italy

Universität Hamburg

Universität Regensburg

Universität des Saarlandes, Saarbrücken

Universität Siegen

Universität Stuttgart

Universitätsklinikum des Saarlandes / Homburg

Université d'Angers / Angers, France

Université de Franche-Comté / Besançon, France

Université Louis Pasteur / Strasbourg, France

Université du Luxembourg, Luxemburg

Université de Metz / Metz, France

Université de Mons-Hainaut / Mons, Belgium

Université Pierre et Marie Curie (UPMC) / Paris, France

Université de Toulouse / Toulouse, France

University of Arizona / Tucson, AZ, USA

University of Basel / Basel, Switzerland

University of California / Berkeley, CA, USA

University of California / Santa Barbara, CA, USA

University of Cambridge / Cambridge, UK

University of Chemical Technology and Metallurgy / Sofia, Bulgaria

University of Kansas / Kansas City, KS, USA

University of Kentucky / Lexington, KN, USA

University of Leoben / Leoben, Austria

University of Madrid / Madrid, Spain

University of Massachusetts / Amherst, MA, USA

University of Michigan / Ann Arbor, MI, USA

University of Nevada / Las Vegas, NV, USA

University of New South Wales / Sydney, Australia

University of Oklahoma / Oklahoma City, OK, USA

University of Pennsylvania / Philadelphia, PA, USA

University of Southern California / Los Angeles, CA, USA

University of Technology of Malaysia / Skudai, Kuala Lumpur, Malaysia

University of Washington D.C. / Washington D.C., USA

University of Wyoming / Laramie, WY, USA

Weizmann Institute of Science / Rehovot, Israel

Westfälische Wilhelms-Universität / Münster

Xian Jiaotong University / Xian, China

Zentralinstitut für seelische Gesundheit / Mannheim

Zentrum für Solarenergie- und Wasserstoff-Forschung Baden-Württemberg / Stuttgart

## Veranstaltungen / Events

Dissemination Workshop MULTIPROTECT: Advanced concepts in corrosion protection for light weight alloys and steel using Cr(IV) free nanostructured hybrid coatings, Organisation & Beiträge
M. Veith, M. Wittmar / EADS
January 21-22, 2009, NH Munich Airport, Schwaig

NanoMed – 6th International Conference on Biomedical Applications of Nanomedicine, Organisation & Beiträge
M. Veith, M. Schubert / cc-NanoChem e.V.
March 4-6, 2009, Berlin

Lehrerseminar: Nanotechnologie als Seminarfach, Organisation & Beiträge
M. Schubert / cc-NanoChem e.V. / NanoBioNet e.V.
April 2, 2009, Saarbrücken

Hannover Messe 2009, Stand
H. Bolz, M. Jochum, P. Kalmes, Th. S. Müller, M. Quilitz, A. Ullrich
April 20-24, 2009, Hannover

Korea-Germany Seminar on Materials and Components Technology, Beiträge
M. Veith, C. Becker-Willinger, M. Quilitz / KITECH
April 22-23, 2009, Hannover

Saarland Technology Corporation, Eröffnung Chicago Büro
J. Flackus, E. Arzt / gwSaar
April 20-25, 2009, Illinois Institute of Technology, Chicago, IL, USA

Nanotechnology-Workshop beim Illinois Institute of Technology (IIT) Sustainable Innovation: Nano Buildings, Beiträge
J. Flackus, P. W. de Oliveira / IIT
April 24, 2009, Chicago, IL, USA

Girlsday am INM, „Wie wird man Professorin", Organisation & Beiträge
M. Koch, C. Wühr, C. Fink-Straube, A. Koch, S. Schumacher, S. Siegrist, A. Jung, H. Rimbach-Nguyen, G. Heppe, A. Weber, E. Bubel
April 23, 2009, Saarbrücken

Nacht der Innovationen – Empower Deutschland, Stand
M. Veith, A. Ullrich, M. Quilitz, I. Weiss / Min. für Wirtschaft und Wissenschaft des Saarlandes
May 4, 2009, Saarbrücken

Workshop mit Teilnehmern des ISC, Würzburg, Beiträge
M. Veith, E. Arzt, J. Flackus, P. W. de Oliveira, C. Becker-Willinger, C. Aktas, R. Bennewitz, I, Weiss, T. Kraus, M. Geerkens / ISC Würzburg
May 14, 2009, Saarbrücken

Nano Road Show und Teilnahme an Automotive Engineering Exposition, Stand
J. Flackus, M. Quilitz
May 18-22, 2009, Yokohama, Japan

IDEC-Seminar „Nanotechnology made in Saarland", Beiträge
J. Flackus, M. Quilitz
May 21, 2009, Yokohama, Japan

Besuch Brasilianische Delegation, Organisation & Beiträge
J. Flackus, P. W. de Oliveira
June 8, 2009, Saarbrücken

GDCh-Seminar Chemische Nanotechnologie, Organisation & Beiträge
M. Veith, M. Quilitz, J. Adam, K. P. Schmitt, Th. S. Müller, S. Schmitz-Stöwe, C. Kasper, S. Heusing
June 16-17, 2009, Saarbrücken

Size Matters 2009, Organisation
J. Flackus / Nanobionet e.V. / u.a.
June 17-18, 2009, Saarbrücken

Wissenschaftszug „Expedition Zukunft", Exponat
M. Schubert, C. Sauer / Max-Planck-Gesellschaft
June 20-22, 2009, Saarbrücken

Teilnahme am Wissenschaftssommer 2009, Ausstellung
M. Schubert, C. Sauer, M. Koch, S. Schübbe, C. Schumann, M. Quilitz, H. Bolz, Th. S. Müller, M. Bender, D. Beckelmann, P. Born, T. Kraus, F. Wählisch, G. Guidoni, S. Schmitz-Stöwe, E. Weber, H. Smail, D. Bentz, F. Hausen, K. Brörmann / Wissenschaft im Dialog gGmbH
June 20-26, 2009, Saarbrücken

Editors meeting „Progress in Material Science"
E. Arzt, INM / Elsevier-Verlag
June 21-23, 2009, INM / Saarbrücken

Gefährdung durch Nanopartikel - Arbeitsmedizinisches Symposium, Organisation & Beiträge
A. Kraegeloh / Uniklinik Homburg
June 27, 2009, Saarbrücken

Sommerdialog, Automotive-Ausstellung, Stand
M. Schubert / BMWi
August, 17, 2009, Saarbrücken

Lehrerseminar: Experimentierkoffer Nanotechnoloige – Umgang und Einsatz, Organisation & Beiträge
M. Schubert / cc-NanoChem e.V. / NanoBioNet e.V.
September 10, 2009, Saarbrücken

EduNetwork 09, Stand
I. Weiss
Science on Stage Deutschland e.V.
September 25, 2009, Saarbrücken

Nanotech Europe, Stand bei AGeNT-D
M. Schubert / Spinverse
September 28-30, 2009, Berlin

EDINAM09: Energy Dissipation in Nanocontacts and Molecular Bonds
R. Bennewitz
September 28-October 1, 2009, Dresden

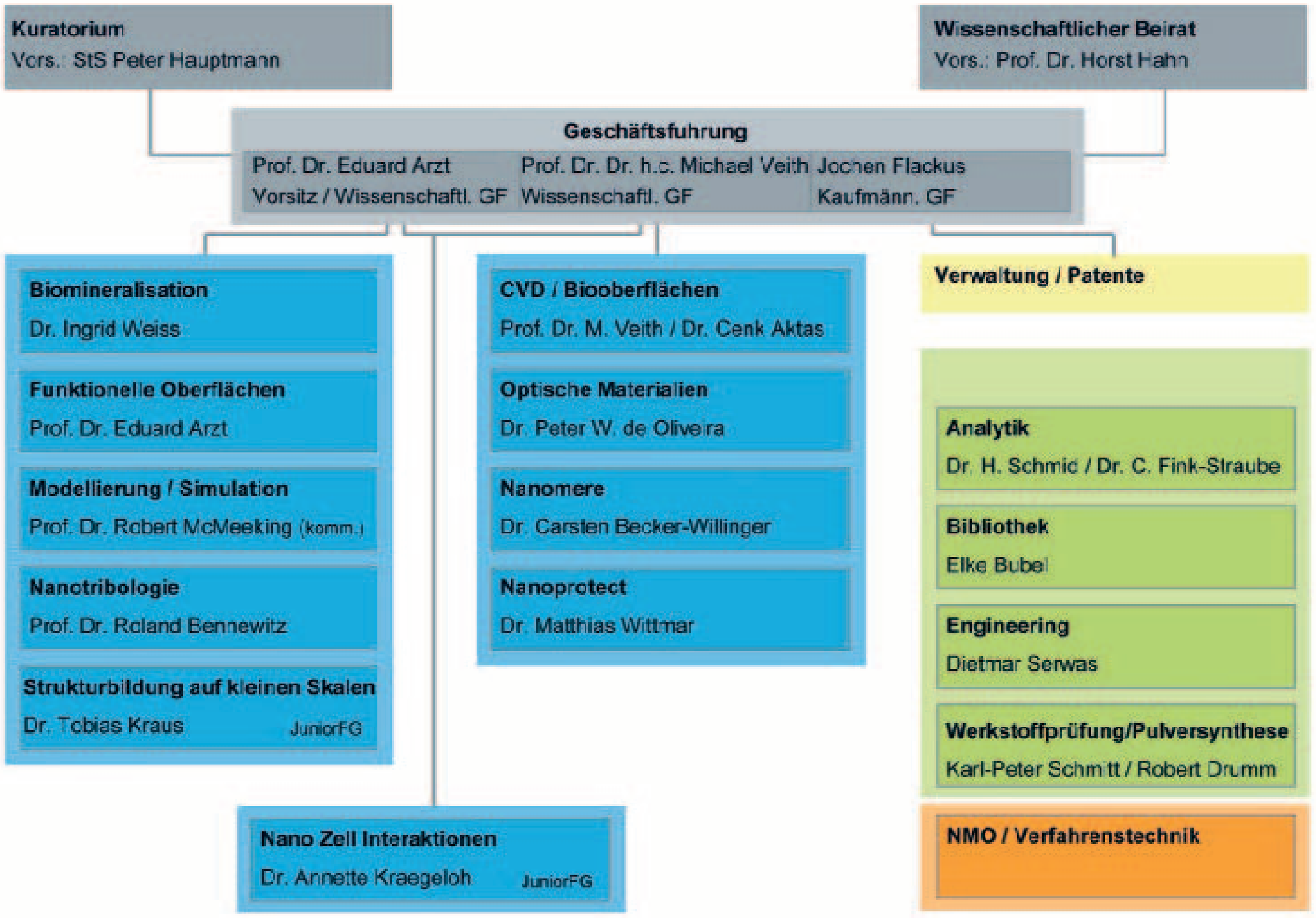
Ausstellung beim Bürgerfest anlässlich Tag der Deutschen Einheit, Stand
J. Flackus / NanoBioNet e. V.
October 2-3, 2009, Saarbrücken

Brazilian-German Workshop on Nanotechnology and Applications, Organisation & Beiträge
P. de Oliveira, M. Quilitz / CETEC
October 7-8, 2009, Belo Horizonte, Brazil

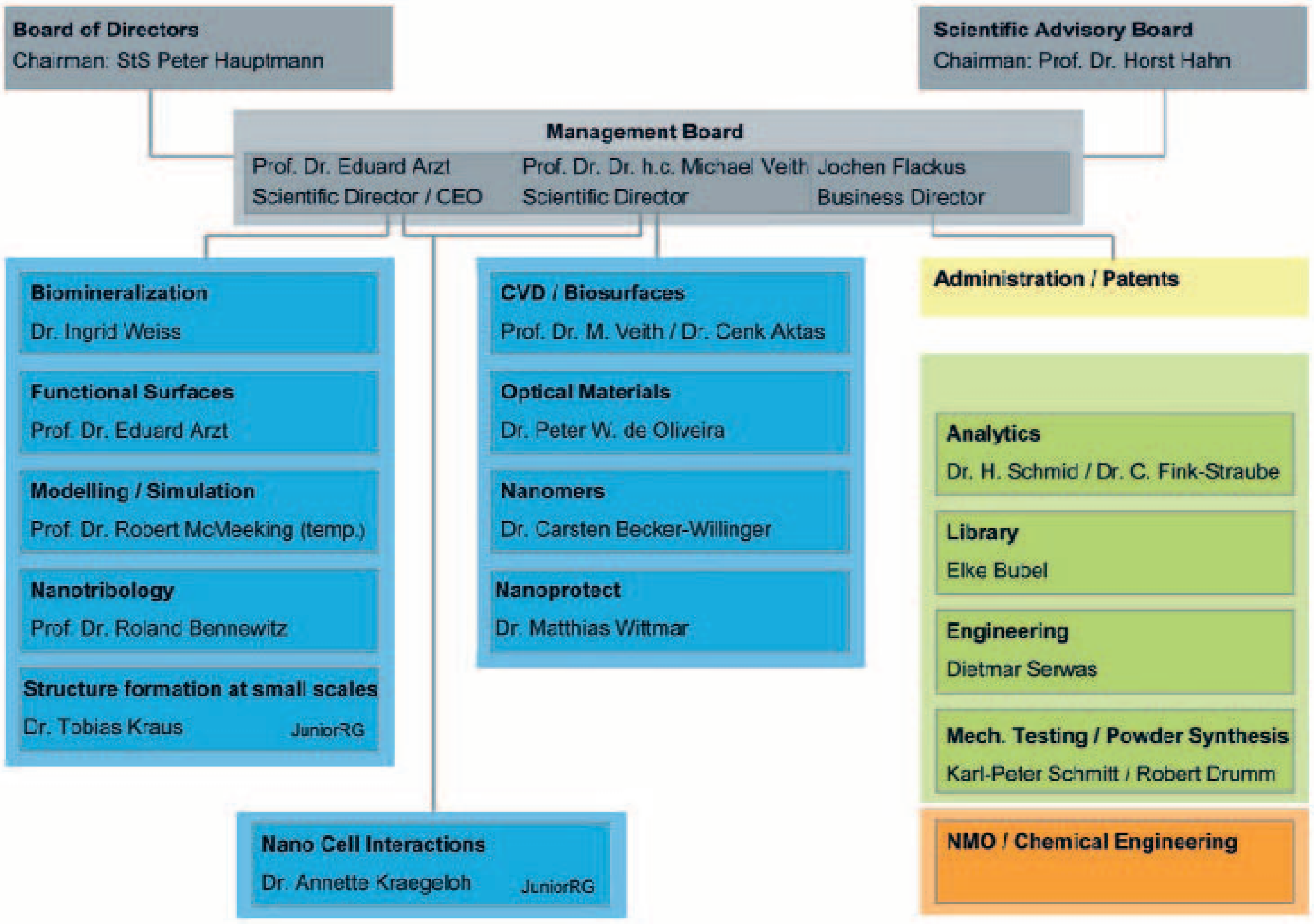
Symposium des International Institute for Nanotechnology (IIN), Stand
J. Flackus, C. Becker-Willinger / STC
October 27-31, 2009, Chicago, IL, USA

# Buntes INM 2009 / INM in 2009

# Organigramm / Organigram



Stand: 31. Dezember 2009



as of December 31, 2009

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Dr. S. Schübbe, Dr. C. Schumann

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INM - Leibniz-Institut
für Neue Materialien gGmbH

Campus D2 2
66123 Saarbrücken
www.inm-gmbh.de

Telefon: 0681/9300–0
Telefax: 0681/9300–223
E-mail: contact@inm-gmbh.de

Wissenschaftliche Geschäftsführer:
Prof. Dr. Eduard Arzt (Vorsitz)
Prof. Dr. Dr. h. c. Michael Veith

Kaufmännischer Geschäftsführer:
Jochen Flackus

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INM
Leibniz-Institut für
Neue Materialien