Annual Report

Jahresbericht

2006

Leibniz Institut für Neue Materialien

Ein Institut der Leibniz-Gemeinschaft

Saarbrücken

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Vorwort

Wie das letzte Berichtsjahr, war das Jahr 2006 ein Jahr der Veränderungen, aber auch zugleich ein Jahr der Konsolidierung. Viele der im Jahr 2005 eingeleiteten Prozesse wurden auch im Jahr 2006 konsequent fortgeführt.

Ein herausragendes Ereignis des Jahres war die Vorlage des Evaluationsberichtes der Leibniz-Gemeinschaft, in dem die wichtige Stellung des Institutes bei speziellen Arbeitsergebnissen, Ausstattung, Einwerbung von Industriemitteln, Erfolgen beim Technologietransfer und der internationalen Zusammenarbeit betont, jedoch ebenso auf die Notwendigkeit struktureller Veränderungen und wichtiger Akzentverlagerungen hingewiesen wurde. In der Folge sprach sich der Senat der Leibniz-Gemeinschaft für die weitere, vierjährige Förderung des Instituts aus.

Das Jahr 2006 brachte auch personelle Veränderungen:

Prof. Dr. Michel A. Aegerter, der seit 1995 Direktor der Abteilung Schichttechnologie war, wurde im Oktober in den Ruhestand verabschiedet. Prof. Aegerter verlässt das INM nach 12 Jahren erfolgreicher Arbeit, in der er die Forschung am INM mitbestimmte und vor allem auf dem Gebiet der Schichttechnologie, der transparenten leitfähigen Oxide und der elektrochromen Elemente entscheidend prägte.

Prof. Dr. Sanjay Mathur, der seit 2002 am INM in der Abteilung CVD forschte und sich 2004 an der Universität des Saarlandes habilitierte, erhielt einen Ruf auf eine W2-Professur an der Universität Würzburg, dem er Mitte des Jahres folgte. Er bleibt uns vorerst jedoch weiter in Doppelfunktion im Bereich der Programmbeauftragten erhalten.

Neben den Veränderungen bleibt Altbewährtes bestehen:

Die Fokussierung auf chemische Routen der Materialsynthese, die auch von der Evaluierungskommission positiv bewertet wurde, war in den vergangenen Jahren bestimmend und wird es auch weiter bleiben, da die chemische Nanotechnologie nach wie vor ein enormes Potenzial für die Entwicklung und die industrielle Herstellung neuer Materialien bietet. Ebenso spielt die chemische Strukturierung von Oberflächen eine große Rolle und ist speziell im Grundlagenbereich vertreten.

Das Hauptaugenmerk der Arbeit lag daher 2006 wiederum in der Synthese, Verarbeitung und Anwendung von nanoskaligen Partikeln, teilweise in Kombination mit unterschiedlichen Stoffsystemen. Die gezielte Modifizierung der Partikeloberflächen mittels unterschiedlichster funktioneller Gruppen dient der Herstellung maßgeschneiderter Materialeigenschaften und ist in fast allen Arbeitsgruppen als Thema präsent. Die interdisziplinäre Zusammenarbeit zwischen den Gruppen konnte dabei weiterhin verbessert werden, was sich nicht zuletzt auch bei der Teilnahme an zahlreichen BMBF- und EU-Förderprogrammen zeigt.

Für das am INM beheimatete Kompetenzzentrum „CC-NanoChem – Chemische Nanotechnologie für Neue Materialien“ endete im September 2006 die institutionelle Förderung durch das BMBF. Daraufhin wurde das Kompetenzzentrum in einen gemeinnützigen Verein überführt, dessen Vorsitz von mir übernommen wurde. Die Geschäftsstelle des cc-NanoChem e. V. bleibt auch künftig am INM und fungiert als Schnittstelle zwischen Institut, Öffentlichkeit, Herstellern und Anwendern von Nanomaterialien. In dieser Funktion wurden eine ganze Reihe von Veranstaltungen durchgeführt, zu denen die NanoMed 2006, drei Seminare der Reihe „Innovationen durch Nanotechnologie“ für die Branchen Automotive, Maschinenbau, sowie Architektur und Bauwesen und die Summer School für Chemische Nanotechnologie gehörten.

Um die Zusammenarbeit der Institute innerhalb der Wissenschaftsgemeinschaft Gottfried Wilhelm Leibniz (WGL) auf dem Gebiet der Nanotechnologie zu stärken und gemeinsame Stellungnahmen abgeben zu können, wurde am INM die Koordinierungsstelle Nanotechnologien der Leibniz-Gemeinschaft eingerichtet. Damit wird die zentrale Rolle des Institutes als kompetenter und aktiver Netzwerkpartner für die nationale und internationale Nanotechnologieszene unterstrichen.

Die jährliche Information über die Aktivitäten des INM (wie im vorliegenden Bericht) wird periodisch ergänzt in Form der seit 2006 dreimal pro Jahr erscheinenden INM-Zeitung „nanonews“. Dieses Medium für kurze und prägnante Information fand regen Zuspruch.

Wenn Sie nun dieses Heft in Händen halten, wird Ihnen zunächst der veränderte Aufbau des diesjährigen Jahresberichtes auffallen. Nach Einführung des neuen Logos im Jahre 2005 ist auch dies ein Zeichen, dass sich das Institut einer neuen Öffentlichkeitsarbeit verpflichtet sieht. Bei stark erhöhter Auflage, die es uns ermöglicht, einen größeren Kreis von

Interessenten zu erreichen, wurde der Inhalt des Bandes stärker verdichtet. Die Gliederung wurde aktualisiert. Der stärkeren Internationalisierung trägt die Abfassung der Artikel in Englisch Rechnung. Anstelle von Einzelberichten zu allen Themen stehen Berichte über die wissenschaftliche Arbeit der Gruppen stärker im Mittelpunkt. Zusätzliche längere Artikel informieren ausführlich zu ausgewählten Schwerpunktthemen. Natürlich ist es aufgrund zahlreicher Verpflichtungen aus Geheimhaltungsvereinbarungen wie früher nicht möglich, die Arbeiten des Institutes in ihrer gesamten Breite wiederzugeben.

Wie immer jedoch erwartet Sie auf den folgenden Seiten ein möglichst umfassender Einblick in die Tätigkeit unseres Instituts.

Dafür sei den Mitarbeiterinnen und Mitarbeitern des Instituts, den Zuwendungsgebern, den Partnern aus Wirtschaft und Forschung und nicht zuletzt auch den Mitgliedern von Kuratorium und Wissenschaftlichem Beirat gedankt.

M. Veith

Prof. Dr. Michael Veith
(Wissenschaftlicher Geschäftsführer)

Preface

As the previous year, 2006 was a year of changes but also of consolidation for our institute. Many of the processes initiated in 2005 were continued consequently.

An outstanding occurence of this year was the presentation of the evaluation report by the Leibniz association, in which the prominent position of the institute with regard to work output, resources, acquisition of industrial grants and success in technology transfer as well as in international cooperation was stressed. On the other hand the necessity of structural changes and of a relocation of priorities were underlined. In the following the senate of the Leibniz association approved the financial support of the institute for the following four year term.

The year 2006 also brought staff changes.

Prof. Dr. Michel A. Aegerter, being director of Coating Technology Department since 1995 retired in October. Prof. Aegerter left the institute after 12 years of successful work, in which he co-determined and – especially in the fields of coating technology, transparent conductive oxides and electrochromics – shaped research in INM.

Prof. Dr. Sanjay Mathur, who did research at INM since 2002 and was habilitated in 2004 by the University of the Saarland, was offered a W2-Professorship at the University of Würzburg, which he took up in August 2006. Furthermore he currently stays with us in his dual function as a program group leader.

The special strengths of the institute will continue to be distinctive. The focussing on chemical routes of materials synthesis – which was also positively evaluated - has been decisive in the past years and it will continue, as chemical nanotechnology offers an enormous potential for the development and the industrial production of new materials. The same holds for the chemical structuring of surfaces which plays an important role and is represented especially in basic research.

Therefore our work in 2006 again was mainly focussed on synthesis, processing and application of nanoscaled particles partly combined with varied material systems. The systematic modification of the particle surfaces with quite different functional groups is utilized for the production of customized material properties and thus is a central theme in almost all work groups. The interdisciplinary cooperation between the groups was improved furthermore, which is demonstrated last but not least in the participation of the INM in various BMBF and EU support programmes.

Institutional funding for the INM based national competence center for chemical nanotechnology (CC-NanoChem – Chemische Nanotechnologie für Neue Materialien) phased out in September 2006. In the following the competence center was transformed into a non-profit association with me as a chairman. The competence center thus remains at the INM and is acting as an interface between institute, publicity, procucers and users of nanoscaled materials. In this function lots of activities were performed among those were: the conference NanoMed 2006, three seminars in the series "Innovation by Nanotechnology" for the industrial sectors automotive, construction and architecture as well as the Summer School for Chemical Nanotechnology.

To strengthen cooperation of institutes within Leibniz association especially working in the area of nanotechnology and to enable coordinated statements a coordination bureau for nanotechnology in the Leibniz association was installed at INM. This again underlines the central role of the institute as a competent and active partner in the national and international nanotechnology network scene.

The annual spread of information on the activities of the INM – as in this report – will be periodically supplemented by the INM newsletter “nanonews” which is supposed to be released three times a year. This medium for short and concise information was widely appreciated by the target audience.

Currently having this annual report in your hands you will notice the altered structure of it compared to previous editions. Following the implementation of the new institutes logo as a first step in the year 2005 this is also demonstrating that the institute has committed itself to a new marketing strategy.

An increased print run of this years report will help us to reach a larger circle of interested readers. At the same time the content of the report was concentrated and its structure was revised. The formulation of the articles in English allows for an enhanced internationality. Reports of the scientific groups replace the reports to singular topics. Additional extended articles provide information on various selected focus topics. As before the entire research work cannot be reported here due to the fulfilment of obligations from non-disclosure agreements.

Nevertheless, once again an impressive insight in the activities of our institute is compiled on the following pages. Special thanks to our employees, our sponsors, the partners from industry and research and, last but not least, to the members of the Board of Directors and the Scientific Board.

M. Veith

Prof. Dr. Michael Veith
(CEO / Scientific Director)

Statusbericht

Stausbericht

Finanz- und Ertragslage der Gesellschaft

Als Forschungseinrichtung der Leibniz-Gemeinschaft hat das INM auch im Haushaltsjahr 2006 eine gemeinsame Förderung durch Bund und Länder erhalten. Diese belief sich auf 11.273 T€; hiervon 8.750 T€ zur Finanzierung von Personal- und Sachaufwendungen, 2.078 T€ für erforderliche Neu- und Ersatzinvestitionen, sowie 445 T€ für Sanierungsmaßnahmen am Institutsgebäude.

Insgesamt erfolgte somit im Haushaltsjahr 2006 eine um 309 T€ höhere Zuwendung als im Vorjahr 2005.

Das INM – Leibniz-Institut für Neue Materialien gGmbH – erreichte im Geschäftsjahr 2006 einen Gesamtumsatz in Höhe von 14.352 T€. Die Erträge aus der vorgenannten Zuwendung im Rahmen der Grundfinanzierung entsprechen somit rund 74% des Gesamtbudgets.

Im Geschäftsjahr 2006 erzielte das INM eigene Erlöse aus Forschung und Entwicklung sowie sonstige betriebliche Erträge in Höhe von 3.627 T€ (Vorjahr: 3.982 T€). Die Industrieerlöse aus Forschung und Entwicklung sowie aus Lizenzvereinbarungen beliefen sich hierbei auf 1.717 T€ (Vorjahr: 1.681 T€). Im Rahmen öffentlicher Projektfinanzierungen erzielte das INM im Jahr 2006 Erträge in Höhe von 1.346 (Vorjahr: 1.184 T€). Im EU-Projekt „Multiprotect“ ist das Leibniz-Institut für Neue Materialien Projektkoordinator und hat in dieser Funktion weitere 863 T€ Fördermittel der Europäischen Union vereinnahmt und an die entsprechenden Projektpartner weitergeleitet.

Wie bereits 2005 ist auch in 2006 positiv festzustellen, dass der Anteil der öffentlichen Projektförderungen an der Gesamtfinanzierung des Institutes weiterhin zugenommen hat. Beides – Industrieaufträge und öffentliche Projektförderungen – darf nicht gegeneinander konkurrieren, sondern muss auch künftig in einem vernünftigen Verhältnis zueinander stehen.

Personalentwicklung

Die Beschäftigtenanzahl ging 2006 gegenüber dem Jahr 2005 leicht zurück. So waren Ende 2006 156 Mitarbeiter (130 Vollzeitäquivalente) gegenüber 170 Mitarbeiter (145 Vollzeitäquivalente) Ende 2005 beschäftigt. Hiervon waren 27 Mitarbeiterinnen und Mitarbeiter (dies

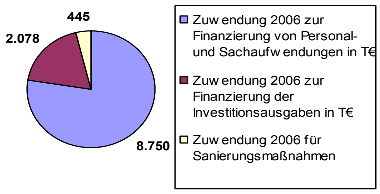

Fig. 1: Zuwendungen 2006.

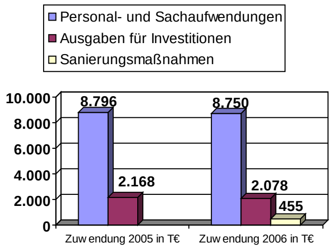

Fig. 2: Vergleich der Zuwendungen 2005 und 2006

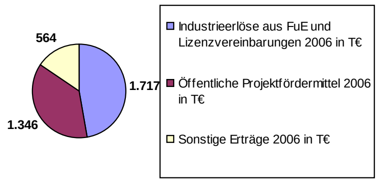

Fig. 3: Verteilung der Drittmittel 2006

entspricht 24 Vollzeitäquivalenten) im Drittmittelbereich beschäftigt. Während die Anzahl der Auszubildenden bei sechs gehalten werden konnte, reduzierte sich der Anteil der Mitarbeiter im Verwaltungsbereich und den Sekretariaten um 1,2 Prozentpunkte von 15,3 Prozent auf 14,1 Prozent und der Anteil der Doktoranden /Diplomanden um 3,1 Prozentpunkte von 15,9 Prozent auf 12,8 Prozent. Der Anteil der wissenschaftlichen und graduierten Mitarbeiter nahm gegenüber dem Vorjahr um 2,5 Prozentpunkte von 34,7 Prozent auf 37,2 Prozent zu; der Anteil der Werkstättenmitarbeiter und der Mitarbeiter im technischen Bereich konnte um 3,2 Prozentpunkte von 21,2 Prozent auf 24,4 Prozent erhöht werden. Für das Jahr 2007 wird eine deutliche Erhöhung der Beschäftigtenzahl angestrebt.

Status Report

Financial and income situation of the company

As a research institution of the Leibniz Association, the INM obtained a common delivery by our federation and countries also in the financial year 2006. These amounted to 11.273 T€, from that 8.750 T€ were used for financing personal and material expenses, 2.078 T€ for necessary new- and substitute investments as well as 445 T€ for reconstruction measures.

In consequence in the financial year 2006 there was a about 309 T€ higher allowance compared to the previous year 2005.

In 2006 the INM – Leibniz-Institute for New Materials – realized a total turnover amounting to 14.352 T€. The funds of the above named basic and special financing thus come up to approx. 74% of the total turnover.

In 2006 INM gained own funds from research and development, from patents/licenses as well as from other third-party funds amounting to 3.627 T€ (previous year: 3.982 €). At this the industrial funds and the incomes for licences reached 1.717 T€ (previous year: 1.681 T€). In line with public project financing the INM realized funds amounting to 1.346 T€ (previous year: 1.184 T€).

The INM is the project coordinator of an EU-project named “Multiprotect” and in this function the company collected another subsidies amounting to 863 T€ from the European Union. These subsidies were

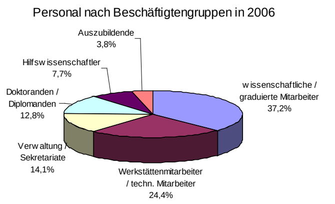

Fig. 4: Personal nach Beschäftigtengruppen 2006

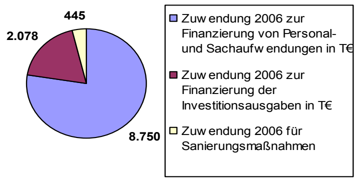

Fig. 5: Aufkommen in 2006

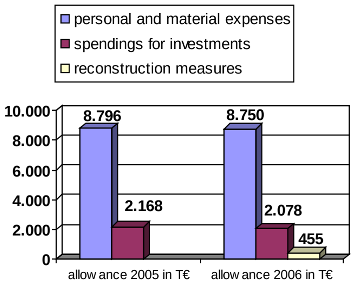

Fig. 6: Compared allowance for 2005 and 2006

transferred to the corresponding project partners.

Like in 2005 the INM could register positively in 2006 too an increase of public project subsidies to finance the Institute. Both – industrial orders and public project subsidies – must not compete against each other but has to be in a reasonable relationship to each other in the future.

Development of personnel

In comparison to 2005 INM had a moderate decrease of the number of employees.

At the end of 2006 156 employees (130 full-time equivalents) worked at INM, compared to the previous year with 170 employees (145 full-time equivalents). 27 employees (24 full-time equivalents) were financed by the third-party funds.

While the number of apprentices could be hold at six, the share of the numbers of the administration and the secretariats was shortened about 1,6 percentage points from 15,3% to 14,1% and the share of the PhD candidates and graduates reduced about 3,1 percentage points from 15,9% to 12,8%. The share of scientific and graduated employees raised about 2,5 percentage points from 34,7% to 37,2% and the share of the crafts people and the workers in the technical services increased about 3,2 percentage points from 21,2% to 24,4%.

In 2007 INM strives to raise the numbers of employees clearly.

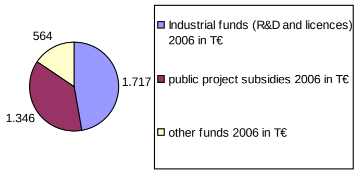

Fig. 7: Distribution of third party funds in 2006

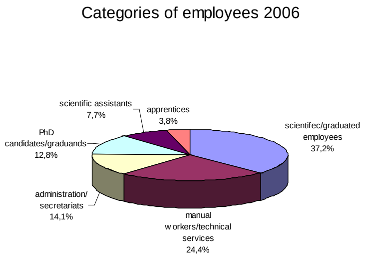

Fig. 8: Categories of exployees in 2006

Dem Kuratorium des INM gehören folgende Mitglieder an: (Stand: Ende 2006)

Staatssekretär Dr. Christian Ege

Ministerium für Wirtschaft und Arbeit des Saarlandes
- Vorsitzender -

MR Klaus Gerstner

Leiter der Abteilung C – Mittelstand, Wirtschaftsförderung, Innovation – im Ministerium für Wirtschaft und Arbeit des Saarlandes
- Stellvertr. Vorsitzender -

Prof. Dr. Volker Linneweber

Präsident der Universität des Saarlandes

Dr. Gisela Helbig

Regierungsdirektorin, Referat 511 Nanomaterialien, Neue Werkstoffe
Bundesministerium für Bildung und-Forschung, Berlin

Prof. Dr. Frank Pobell

Hochfeldlabor Dresden,

Beirat

Dem Beirat des INM gehören folgende Mitglieder an: (Stand Ende 2006)

Forschungszentrum
Rossendorf e.V.

Prof. Dr. Wulff Possart

Lehrstuhl für Thermodynamik der Werkstoffe
Universität des Saarlandes

Prof. Dr. Frank Mücklich

Lehrstuhl für Funktionswerkstoffe
Universität des Saarlandes

Prof. Dr. Sanjay Mathur

Institut für Anorganische Chemie der Universität Würzburg und Leiter Arbeitsgruppe CVD-Technologie der INM gGmbH, Saarbrücken

Prof. Dr. Hans-Joachim Güntherodt

Leiter des Instituts für Physik
Universität Basel

Dr. Wolf-Dieter Haecker

Direktor a. D.
Robert Bosch GmbH, Stuttgart

Dr. Max Häring

Vorsitzender des Vorstandes
Landesbank Saar Girozentrale, Saarbrücken

Prof. Dr. Hans-Heinrich Moretto

Direktor a. D.
Bayer Industry Services GmbH & Co. OHG, Leverkusen

Prof. Dr. Frank Pobell

Hochfeldlabor Dresden,
Forschungszentrum Rossendorf e.V.
- *Vorsitzender* –

Dr. Franz Josef Eckle

Hydac Electronic GmbH, Saarbrücken

Prof. Dr. Alfred K. Louis

Institut für Angewandte Mathematik
Universität des Saarlandes

Prof. Dr. Rolf Mülhaupt

Institut für Makromolekulare Chemie
Albert-Ludwigs-Universität, Freiburg

Prof. Dr. Ludwig Schultz

Institut für Metallische Werkstoffe
Leibniz-Institut für Festkörper- und Werkstoffforschung, Dresden

Dr. Klaus Harste

Saarstahl AG, Völklingen

Prof. Dr. Horst Hahn

Institut für Nanotechnologie
Forschungszentrum Karlsruhe

Prof. Dr. Ludwig Gauckler

Institut für Nichtmetallische Werkstoffe
ETH, Zürich

Prof. Dr. Martin Möller

Lehrstuhl für Textilchemie und Makromolekulare Chemie RWTH, Aachen

Ralf Becker

Villeroy & Boch AG, Mettlach

Group Nanomers

Head: Dr. C. Becker-Willinger

Group Nanomers

Die Forschungs- und Entwicklungsarbeiten der Abteilung Nanomere liegen schwerpunktmäßig auf der Synthese, Oberflächenmodifikation und Verwendung von Nanopartikeln in polymerartigen bzw. organisch-anorganischen Matrices zur Herstellung von Nanokompositsystemen, den so genannten Nanomeren. Diese Materialklasse besitzt eine hohe werkstofftechnische Variabilität und bietet die Möglichkeit, maßgeschneiderte Eigenschaftsprofile für ganz spezifische Anwendungen einzustellen. Die Aktivitäten der Abteilung Nanomere, bestehend aus 15 Mitarbeitern, beschränkten sich dabei im Jahre 2006 nicht nur auf Basisentwicklungen für neue Werkstoffkonzepte, sondern in großem Maße auch auf industrielle Forschungsprojekte (z.T. öffentlich gefördert über BMBF bzw. AiF/ DECHEMA) zur angepassten Materialentwicklung. Schwerpunktmäßig wurden dabei transparente Kratzfest-Beschichtungen, tribologische Beschichtungen mit hoher Verschleißbeständigkeit sowie Niedrigenergie-Beschichtungen mit hoher Dauerhaftigkeit und elektrischen Isolationseigenschaften und kompakte optische Materialien bearbeitet. Weiterhin wurde in den meisten Industrieprojekten zusätzlich zur Materialoptimierung auch eine Technologie-Entwicklung durchgeführt. Hierzu gab es eine enge Zusammenarbeit mit der Applikationsabteilung NMO, um die Resultate vom Labormaßstab in die praktische Anwendung zu überführen. Zusätzlich wurden die Entwicklungen der Abteilung Nanomere auch weltweit auf entsprechenden Ausstellungen und Industriemessen präsentiert. Aufgrund der Resonanz dieser Präsentationen kann auf ein nach wie vor großes Potential der Nanomer®-Technologie im Sinne einer breiten industriellen Anwendung gesetzt werden.

The research and development activities in the department Nanomers are focused on the synthesis, surface modification and dispersion of nanoparticles as well as their transfer into polymeric and organic/ inorganic matrices in order to form nanocomposite systems, the so called Nanomers. This class of materials has a high chemical variability and opens the possibility to achieve even difficult combinations of specific requirements. The wet chemical synthesis approach enables to process the materials using technically relevant and cost saving methods as well as to develop and optimize materials with tailored properties with regard to a broad variety of possible applications. In the year 2006 many activities on the creation of basic knowledge and also on industrial research project activities have been performed in the department Nanomers consisting of 15 co-workers. Most of the industrial projects have been dealing with coating applications mainly in the fields of transparent scratch resistant coatings, tribological coatings with high wear resistance as well as low surface free energy coatings with high durability and special electrical insulation properties. The use of nanoparticles with their intrinsic solid state physical properties enables to add various features with new interesting functionalities to the Nanomer systems.

Another sector of the research activities was the use of nanoparticles for the modification of compact materials such as polyurethane or epoxy resins in order to change e.g. their thermo - mechanical and electrical properties. In comparison to the year 2005 the activities on coatings and compact materials have been almost balanced on a comparable level.

In particular in the field of Nanomer coatings basic, investigations have turned out that the use of special nanoparticles in the size range below 20 nm even in a small amount can improve dramatically the long term electrical insulation properties of commercially available organic lacquer systems. Nanoparticles with special electronic structure could be successfully incorporated into insulation materials showing 100 times higher insulation capability compared to conventional coating systems (figure 1).

This principle could be protected with respect to the intellectual property and has been successfully used in R&D projects to develop new material solutions for the electronic industry. It also has been found out that nanoparticles can be of interest to improve the stress relaxation behaviour in nanocomposite systems. As a result new coating systems with specifically surface tailored nanoparticles could be developed, which are applied as reactive curable coating systems, showing extremely low intrinsic stress after curing. By this approach also nanocomposite systems with high loading levels of nanoparticles could be created, which show after only UV curing a very high elastic modulus. These materials can be patterned in a very fine structure (figure 2), which is of interest for many areas in the electronic and optoelectronic industry. Also this approach has been protected by an appropriate patent application and now serves as a basis for new industrial projects in the future.

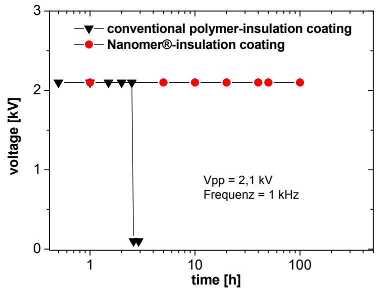

Fig. 1: Voltage-time-diagram of conventional Polymer-insulationcoating (2.5 h) and new Nanomer®-insulation coating (>100 h)

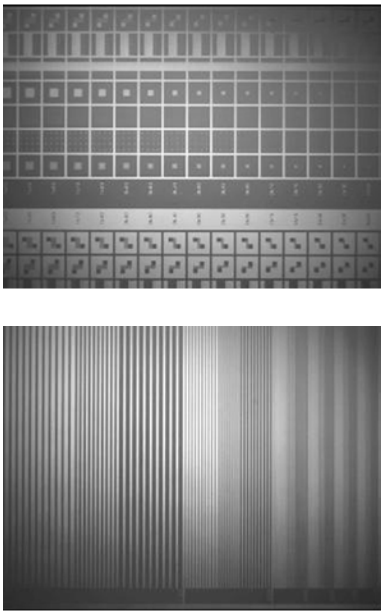

Fig. 2: Interferometer micrographs of various patterns generated by photolithography

In the area of anti-adhesive coatings a project supported by the AiF/ Dechema (AiF Nr. 14228 N/2) concerning the development of adhesion minimizing coatings for wet processes in the food production industry has been continued as a basic research and development work. New compositions for coating materials, useful for the application on already existing equipment in the food production industry with interesting new surface properties, could be developed in a tailored way (figure 3).

The structure - property relationships with respect to adhesion mechanisms of specific adhering substances and food products could be investigated more in detail together with the R&D cooperation partner in the project. The results could be used to optimize the materials with respect to the substrate surface, the surface morphology and the surface free energy in order to find a tailored solution for specific problems in the relevant industrial applications favoured in this project.

In addition to this more basic development work, anti-adhesive surfaces with long lasting properties have been investigated for the use as semi-permanent mould release agents in polyurethane foam applications in automotive industry (figure 4).

Special variations of these types of systems have shown that this application requires specific design of the anti-adhesive coating material in order to fulfil the complete requirement profile. The approaches followed still show great potential for future developments.

A highly innovative field with big potential for the future is the area of tribological low friction coatings. In addition to 2005, where low friction coating systems containing solid state lubricants have been developed, which combine a low coefficient of friction with excellent adhesion and corrosion protection on low alloyed steel (figure 5), also new Nanomer® compositions with low friction and high wear resistance could be developed for the use on plastic parts for the automotive industry.

New material combinations and processing technologies enabled to approach the region of coefficient of friction which is normally covered by hydrodynamic lubrication only. This is an important milestone which shows the great potential of the Nanomer systems.

A lot of investigation effort has also been set on the use of nanoparticulate additives for conventional coatings and lacquer systems with respect to

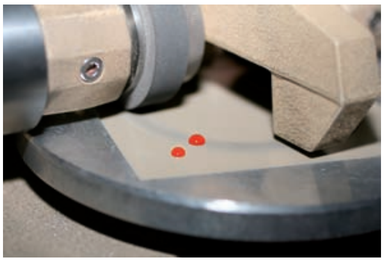

Fig. 3: Taber abraser test – even after 1000 cycles taber abraser test no wetting by water (contact angle against water higher than 90°)

Fig. 4: PU-foam in an aluminium mould, left side with an durable Nanomer® mould release coating

polymerisation catalysing properties. In a project supported by the BMBF (FKz.: 13N9119) the investigations have been focused on the effect of nanoparticles catalysing especially photo polymerisation reactions in organic coating systems. This intrinsic property of the nanoparticles has high industrial demand and can be a useful alternative for conventional approaches using organic molecules as photo initiators.

In the area of polymer matrix nanocomposites, nanoparticles have been used in transparent or non transparent matrices to tailor optical, thermal and mechanical properties of compact bulk materials. Reactive curable resins such as epoxies and polyurethanes have been equipped with nanoparticulate fillers as well as thermoplastic matrices, which can be compounded, extruded or injection moulded. By this approach transparent temperature stable resins have been developed, which can be used for the fabrication of optical elements. These materials combine easy process ability with relatively low density compared to glass and tailor ability of optical properties such as refractive index. Investments have been made for the future with respect to the equipment, to enable to process not only reactive curable systems but also thermoplastic materials for refractive optical and foil applications (figure 6).

A big part of the know-how in the group can be ascribed to the specific surface modification and compatibilisation of nanoparticles with polymer type matrices, which is important to obtain nanocomposite systems with almost perfectly dispersed nanoparticles. This know-how concentration in the group is an important tool to develop tailored materials within a short time. During the year 2006 a lot of projects with industrial partners have been performed in the group where many of them cannot be mentioned because of specific non disclosure agreements. Furthermore it is important to note that for most of the cooperation projects a technology development in addition to the pure materials optimisation was of high importance in order to transfer the results from the lab scale to the practical application. This step has been performed together with the application centre NMO. Furthermore also many expositions on fairs ranging from Germany to Japan and Korea have been performed. From the results of these fair activities it could be derived that the Nanomer technology still has a big potential for a broad range of industrial appli-

Fig. 5: Windmill with an Nanomer® coated (right side) and an uncoated (left side) transmission shaft

Fig. 6: INM-Equipment for film extrusion

cations especially – but not only - for e.g. the electronic and automotive industry. In this sense it is expected that the chemical nanotechnology approach has not tapped its full potential up to now and still should be able to open completely new solutions in the future.

Group Glass and Optics

2006 war ein erfolgreiches Jahr für die Industrieprojekte im Bereich Glas und Optik. Ein erheblicher Teil dieser Projekte war in den Gebieten Entwicklung, Optimierung und Upscaling optischer Materialien, optische Beschichtungen und Produktion diffraktiver Elemente angesiedelt. Sowohl spezielle Beschichtungen für den Korrosionsschutz von Metallen, funktionelle Film auf Glas und Plastik, als auch dekorative Beschichtungen spielten im Jahr 2006 eine große Rolle bei der Entwicklung neuer Produkte. Im Übrigen war die Arbeit des Bereiches Glas und Optik besonders mit der Entwicklung und Optimierung neuer optischer Kompositmaterialien befasst, deren Herstellung und besonders deren Feineinstellung der optischen Eigenschaften massgeblich auf der chemischen Kontrolle der anorganisch-organischen Netzwerkbildung basiert. So war ein Schwerpunktgebiet die Entwicklung neuer GRIN-Materialien (Graded Refractive Index).

Weitere wichtige Arbeiten wurden im Rahmen der EU-Projekte ROLLED und NOVACOAT durchgeführt, wobei ROLLED die Arbeiten an transparenten Filmen für die Produktion von OLEDs auf flexiblen Substraten, NOVACOAT dagegen den Einsatz haltbarer Niedrigtemperaturhybridschichten zum Ersatz von Glasierungen in der Fliesenherstellung avisiert. Das nationale Projekt FlexNet startete in 2006. Es hat die Abscheidung von Dünnfilmsolarzellen auf flexiblen Substraten zum Ziel.

Weitere Aktivitäten umfassten unter anderem Synthese und Charakterisierung neuer Metall-Metalloxid-Kernschale Partikel zur Anwendung in Katalyse und Photokatalyse, transparente leitfähige Ersatzmaterialien für Indiumzinnoxid (ITO), sowie Optimierung der Herstellung des ITO, geprägte TiO2-Schichten, und schliesslich neue Aktivitäten auf den Gebieten Elektrochromie und Supraleitung.

The work of the Glass and Optics department in 2006 was mainly focused on the research, development and optimisation of new optical composite materials based on the chemical control of the organic and inorganic network formation for the fine tuning of the optical properties. Following the market tendency, special emphasis has been placed on the development of new photosensitive GRIN-materials (Graded Refractive Index) and optical set up supported by quality control program for the continuous production of optical elements in large scale. Basic research as a combination between photochemistry and optics has been initiated to achieve materials with higher stability and higher holographic sensitivity.

The work on transparent flexible barrier films was continued as part of the EU funded collaborative research project ROLLED [1], which targets the production of organic light emitting diodes (OLEDs) on flexible substrates. Due to the high sensitivity of OLEDs to moisture and oxygen, an encapsulation having very good barrier properties is required. The demands could be met with a barrier film consisting of a gas-tight glass layer of approximately 0.5 µm thickness on a much thicker polymeric carrier substrate. A novel process for producing such a barrier film was developed on lab scale and is currently being transferred into pilot scale.

Barrier films with a different scope are being developed in the nationally funded collaborative research project FlexNet [2] started in 2006. This project deals with the deposition of thin film solar cells on flexible low-cost substrates such as metal foils. Since a contamination of the solar cell by the substrate metal reduces the photovoltaic conversion efficiency, the substrates have to be covered with barrier films in order to prevent the migration of metal ions during processing. The development of the barrier films is based on glass-like coatings as developed earlier for anti-stain and anti-corrosion purposes.

Further work was executed for the EU Craft Project NOVACOAT [3] where novel hybrid coatings were studied in order to deliver a durable, low temperature curable coating with a potential to replace traditional glaze in tile manufacturing and provide new decoration opportunities that can not be applied with the traditional high temperature glaze coatings (e.g true trichromatic colours) (figure 1). The coating systems further developed in the project are based on several different hybrid coating compositions of INM and were aimed at meeting specific requirements of the tile manufacturers and end users. The coating systems

Fig. 1: Project Novacoat – Development of novel coatings for ceramic tiles introduction of opalescence piments

were developed and tested for chemical durability and application behaviour as well as their potential to incorporate colour and functional effects. Much of the work executed in 2006 was targeted on development of a water based hybrid coating system starting from organic solvent based systems to meet the H&S regulations in the tile production environment. The developed coating materials have been optimised to be applied using conventional ceramic coating methods (in particular curtain coating and spraying).

Tiles coated with this technique are not as yet commercially acceptable due to the low alkali resistance and further research to improve the properties is needed.

Another field of activity deals with synthesis and characterization of novel metal @ metaloxide core-shell particles with a potential use in e.g. catalytic especially in photocatalytic applications. The work in 2006 focused on the development of new high yield wet-chemical synthesis routes for the metallic core particles based on binary intermetallic chemical compounds such as FePt (figure 2). The difficulty lies in the development of an easy strippable intermediate surface modification. This surface modification must be stable enough to stabilise the freshly prepared core particles during processing, but must be removable in order to allow a growth of the desired metal oxide shell in the next step. Furthermore it must be compatible with the synthesis process.

Within a cooperation program between Prof. H. Schmidt (Universität des Saarlandes, Material Department and INM) transparent conductive coatings on glass and plastic substrates as a possible replacement for indium tin oxide (ITO) have been developed. The alternative material of choice were carbon nanotubes (CNTs) which have - especially due to their high aspect ratio - a high electrical conductivity. Very thin functionalized, purified multi-walled carbon nanotubes (MWNTs, Nanocyl S.A.) were investigated, both as networks as well as embedded in conductive and insulating matrixes. The conductive matrix studied was antimony doped tin oxide (ATO), which is already well known in the literature as a transparent conductive oxide with high transparency in the visible range showing, however, inferior electrical properties i.e. lower electrical conductivity than those presented by ITO systems. The MWNTs were investigated as possible additional conductive elements

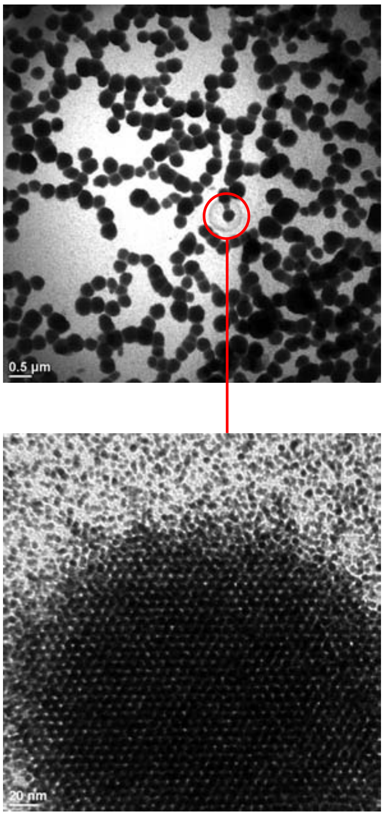

Fig. 2: TEM-micrograph of a (FePt-nano-particle / Ti-chelate complex) compound. Within the chain-like ordered drop-lets (200–700 nm in diam-eter) the particles ($d \approx 4$ nm) are self-assembled in a multilayer ($n \geq 3$) hcp ordering (see inset).

in this matrix. The results showed that the sheet resistance of the ATO/MWNT composite decreased 16 times in comparison with pure ATO matrix. The insulating system studied was a TiO2 –based one, normally used in applications where a high refractive index is required. MWNTs have provided electrical conductivity to the system, and resistivity in the order of 10^{-1}-10^{-2} Ωcm were obtained. The structural, optical, mechanical and electrical properties of all coatings were studied using different techniques. For the optimization of the films, different parameters have been changed, i.e. concentration of the MWNTs in the composites, temperature of sintering of the coatings, number of layers, among others. At the end, a comparison of the films obtained in this work with others found in the literature is given, considering transparency of the films, conductivity values obtained as well as cost benefits.

The surface of multi-walled carbon nanotube (MWNT) networks deposited on borosilicate glass and sintered at 300°C was examined by scanning electron microscopy (SEM) and is shown in Figure 3. The MWNTs are randomly oriented forming a continuous network of carbon nanotubes, which allows electrical conduction across the coating.

For special application on diffractive and refractive optics, ITO nanoparticles play a very big role. To improve their optical properties INM has developed a synthesis for ITO, which allows to produce agglomerate-free nanoparticles with a particle size of about 5 to 20 nm. The nanoparticles can be redispersed in different solvents after surface modification and can be incorporated into different alkoxysilanes and several polymers like acrylates. The coating can be applied by different coating techniques like spin coating, dip coating, flooding, casting methods, foil coating etc. and cured by both UV and thermal treatment.

During these investigations, INM has optimized the influence of Sn content, oxygen voids and calcination conditions on the optical properties and the crystallinity of ITO nanoparticles. It could be shown, that these variations have a great influence on the optical properties; it is therefore possible to adjust the desired optical properties by these methods.

For the Integrated Project Cell-PROM Project, micro and submicron structures have been replicated

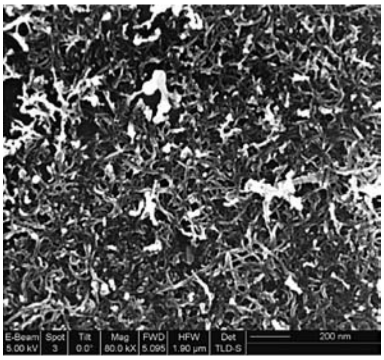

Fig. 3: SEM image of MWNT networks deposited on bo-rosilicate substrate

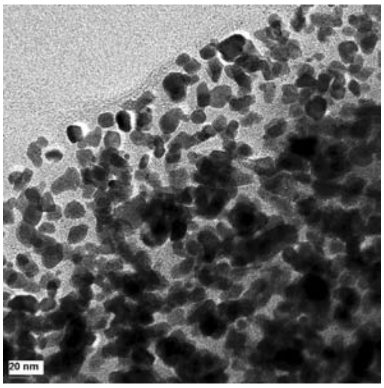

Fig. 4 : HR-TEM picture of ITO powder in a solvent free acrylate polymer after UV curing; particle size 10-20 nm

by embossing in a TiO_2 coating to study the stem cells behaviour in dependence of the morphology and the topology of the surfaces.

The TiO_2 coating consist of about 85 % TiO_2 the rest being mostly SiO_2 but also a certain amount of organic residues. Since the cured coating was becoming turbid by time, we focused on establishing a pure TiO_2-coating. Layers made from this material are stable against hydrolysis and remain unclouded.

In the field of superconductive materials the work was focussed on two main topics:

For the optimization of the electrical properties of MgB_2 superconductors, nanoscaled dopant particles were used to influence the properties especially at the grain boundaries leading to higher J_c and better J_c – H – T- relations. Other activities will investigate the use of nanoscaled materials for the synthesis of MgB_2 and the respective precursors for ex-situ- and in-situ-synthesis routes aiming at improved microstructures and homogeneities.

The Glass & Optics Section has participated in a research program between DAAD-FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo –Brasilien) and INM, which has been initiated by Prof. Aegerter. During 2006 a single-phase hybrid organic-inorganic polymer was applied in a electrochromic device using WO_3 (electrochromic) and an optimized CeO_2 -TiO_2 (counter-electrode – ion storage) electrode. The electrochromic device exhibited excellent colour and bleach reversibility, high coloration efficiency from the first cycle up to more than 60000 CA cycles. Its remarkable behaviour and high stability render this material an excellent candidate for application in electrochromic devices.

The year 2006 has been a success year for the industrial projects at Glass & Optics department. A big part of the industrial projects have been done in the area of development, optimization and up scaling of optical material, optical coatings and diffractive devices production. Special coatings for corrosion protection for metal, functional films for glasses and plastics, as well as decorative coatings played a big role in the development of new products in 2006.

[1] Project ROLLED - Roll-to-roll manufacturing technology for flexible OLED devices and arbitrary size and shape displays; funded by the EU under priority FP6-2003-IST-2, contract no. 4315; duration: 01.08.2004 – 31.07.2008. The consortium includes three research organizations, a chemical company and three end user partners from Finland, Switzerland and Germany

Group Life Science

Head: Dr. S. Gerbes

[2] Project FlexNet - Funktionsschichten für flexible, kostengünstige CIGS-Dünnschichtsolarzellen; funded by the BMBF; contract no. 03SF0321B; duration: 01.08.2006 – 31.07.2009. Collaboration of six German research institutions

[3] Project NovaCoat - Replacement of CONVENTIONAL GLAZE on Tiles and Other High Temperature Processes with Novel Hybrid Coating CONTRACT N°: COOP-CT-2005-005799 - The consortium included four tile producers from 4 different European countries together with an Italian equipment supplier, a German SME coating supplier and RTD performers from UK, Finland and Germany (INM).

Group Life Science

In der Life- Science Gruppe werden nanopartikuläre Systeme für medizinische sowie für bio- und lebensmitteltechnische Anwendungen entwikkelt. Zur Zeit wird stark grundlagenorientiert in öffentlich geförderten Projekten gearbeitet, jedoch mit einem starken Anwendungsbezug. Im Folgenden wird ein kurzer Überblick über die Arbeit der Life- Science Gruppe in 2006 gegeben.

Zunächst sind da Arbeiten an nanopartikulären Suspensionen für die Magnetofluid-Hyperthermie, eine neuartige Krebstherapie, die auf magnetischen Nanopartikeln mit einer spezifischen Aufnahme in Tumorzellen basiert. Für die Untersuchung von Aufnahmewegen und –mechanismen dieser Partikel in Tumorzellen wurden markierte Modellpartikel entwickelt. Dabei sollten auch verschiedene Anbindungswege für die Fluoreszenzmarker evaluiert werden, die dann auch an den Magnetpartikeln nachvollzogen werden sollen.

Im Bereich Beschichtungsmaterialien wird über den Fortschritt bei der Entwicklung einer dauerhaft adhäsiven Beschichtung für Zähne berichtet, der Effekt konnte unter in vitro- Bedingungen auf beschichteten Zahnproben gezeigt werden. Für das EU-Projekt CellPROM wurde neben chemisch und topologisch nanostrukturierten Oberflächen auch eine biokompatible magnetische Beschichtung entwickelt, diese hat eine Sättigungsmagnetisierung vergleichbar zu der von Nickel und erwies sich als sehr biokompatibel.

Für mikrobizide Oberflächenmaterialien wurde ein neues Testsystem zum Nachweis und zur Visualisierung der keimtötenden Wirkung entwickelt.

Based on chemical nanotechnology, the group Life Science focuses upon development of inorganic-organic materials for applications in medical science, bio- or food-technology. In the following some highlights of our research and development work done in 2006 are shortly presented.

Marked Particles for Investigations of Uptake -Pathways and -Mechanisms for Magnetic Nanoparticles

Within a project supported by the German ministry of education and research (BMBF), we develop nanoparticles, which carry drugs into cancer cells and set them free by thermal activation.

Therefore drugs should be attached to iron oxide-nanoparticles by different methods. These iron oxide-nanoparticles were designed for a magnetofluid hyperthermia therapy for cancer. They were injected into the tumor-tissue and afterwards heated up by means of an alternating magnetic field. Since these particles are strongly absorbing light, our objective was to make model-particles having approximately the same size and surface as the original particles and to attach ligands by using different methods. For this we employed commercially available silica particles (IPA-ST, Nissan Chemicals, USA). Around these particles we build up a monolayer of aminosilane-molecules, changing their surface charge from negative at neutral pH to cationic. To this amino-groups ligands as e.g. fluorescence dyes or drugs can be coupled by establishing connections like amide-, shiff-base-, thiourea-, disulfide or other bridges. By doing this, it was important to maintain the positive surface charge needed for the colloidal stability of the suspensions. These particles were given to medical partners for investigating the uptake pathways an mechanisms of the iron oxide particles, which cannot be labelled by fluorescence dyes due to their strong absorption by the tumour cells.

Development of a Dental Coating

Another activity was related to the development of a new dental material. A coating for sensitive teeth was to be developed. The idea was to establish a permanent anti- adhesive surface on the tooth. This surface should ensure that under in vivo conditions occurring plaque can easily be removed by shearing forces present in the oral cavity. If this succeeds, the risk of formation of dental calculus, caries and of paradonthosis will be reduced drastically.

INMs part in this project is to develop the nanocomposite material having the antiadhesive properties, which is supposed to be also stable under in vivo conditions and is itself as well as all its components nontoxic.

Fig. 1: Coated dental enamel sample, the water droplet demonstrates the low energy surface.

On coated and UV-light cured samples a enamel an easy to clean effect could be demonstrated in vitro by a clinical partner (fig. 1). The good adhesion of the coating to the enamel could also be shown.

A great challenge was also the adjustment to blue light (400- 500 nm) curing, particularly to avoid effects of oxygen- inhibition. For this monomers freshly developed by project partners were employed.

Participating in CellPROM

The objective of the EU- Project CellPROM is to develop a device for automated cell-handling in order to differentiate adult stem- cells.

INMs part is to develop chemical and topological structured surfaces for this cell-handling device.

Beside the work on these patterned surfaces a magnetisable coating stable under cell-culture conditions was developed. We obtained layers with magnetic moments comparable to that of cobalt (161. emu/g) and higher than that of nickel (54.5 emu/g). Figure 2 shows the hysteresis curve for these coatings. The coating is an epoxide based two component system. The resin- component contains two types of particles; iron-microparticles and iron oxide-nanoparticles. The coating is applicable to surfaces of glass, metals or polymers like PE. The magnetic momentum was measured with bulk probes made from the coating material.

The magnetic momentum at saturation was determined to be 158 emu/g, the coercitive force was found to be 54.43 Oe. The coating can be printed by the sieve technique, the biocompatibility was successfully tested.

Visualisation of Microbicidal Effect of Coatings

The development of microbicidal coating materials has been another topic of the work done by the group Life Science. The effectiveness of such materials is tested by use of a standardised system (ASTM E2180), which is based on the determination of the number of viable cells and therefore is suited to quantify the microbicidal activity of such materials. Disadvantages of this test system are the high effort and the long test duration. For these reasons, a system was established, which indicates the metabolic activity of bacterial cells by a blue coloration (fig. 3) and is suited for qualitative determinations on the effects of coating materials. The coloration is based on the activity of

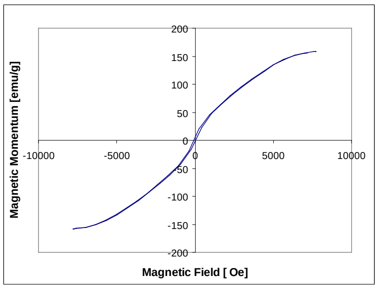

Fig. 2: Hysteretic curves measured for bulk samples of the magnetisable coating.

Fig. 3: Coated substrates in the β-galactosidase-assay: The blue colouration is caused by metabolically active bacterial cells on top of a coating without microbicidal activity (left); a colouration does not appear, when the cells are layered on top of a microbicidal coating (right).

the bacterial enzyme β-galactosidase, which takes part in the generation of a blue indigo-derivative. With a detection limit of less than 10 cells ml^{-1}, the system exhibits a high sensitivity. The system was initially used for the characterisation of silver based coatings, but it turned out to be also applicable for materials, which are based on a distinct active principle. Because of the relatively low effort, the procedure is similarly suited for the quality control of known systems as well as for an assessment of the effectivity of unknown materials. Beyond the material characterisation, the enzyme reaction was also used to investigate the mode of silver ion action on bacterial cells, which is still under discussion. This is important, because silver ions mediate the action of silver based microbicidal materials. Our investigations indicate that silver ions affect different targets within the bacterial metabolism. For example, instantaneously after contact, they inhibit protein biosynthesis. In conjunction with subsequent effects, this finally causes loss of cellular viability.

Group Ceramics

Die Arbeiten der Keramik-Gruppe lassen sich den Gebieten „Herstellung deagglomerierter und oberflächenmodifizierter Nanopartikel“ und „Herstellung keramischer Bauteile und Strukturen unter Verwendung von Nanopartikeln“ zuordnen.

Neben umfangreichen Arbeiten für die Industrie auf dem ersten Feld, wurden auf beiden Gebieten neue Aktivitäten gestartet. Dies waren seitens der Synthese von Nanopartikeln unter anderem die Systeme $CePO_4$ und Cermolybdat. Als keramische Strukturen wurden ZrO_2-Schichten und PZT-Ultraschall-Linsen über innovative, nanopatikelbasierte Prozesse erfolgreich hergestellt (figur 1).

Since a longer period of several years the work of the ceramics group can be divided in two main activities, to be named as

- preparation of de-agglomerated and surfacemodified nanoparticles, and
- use of nanoparticles in the preparation of ceramic parts and structures.

In 2006 the ceramics group worked for the most part for industrial clients and achieved a respectable budget in relation to the number of its members. Because of confidentiality

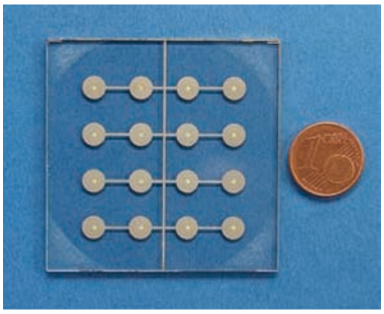

Fig. 1: Array of piezoelectric dots (on Pt electrode structure / sapphire substrate) obtained from mechanochemical synthesis of PZT and its electrophoretic deposition. Cooperation with Fraunhofer IBMT aiming at the application of acoustic lenses / microscopes.

these works can not be published. It can be mentioned that they all can be ascribed to the de-agglomeration and surface modification of different nanoparticle types and their colloidal processing in various liquids.

The group was involved in the EU FP6 project “MULTIPROTECT” in the last quarter of 2006 with the development of nanoparticle syntheses for $CePO_4$ and cerium molybdate. A wet chemical synthesis route was developed which is based on pressureless and near room temperature processing. It delivers crystalline, easy to de-agglomerate $CePO_4$ nanorods. Having this new synthesis in the portfolio is also interesting because $CePO_4$ is a known functional ceramic material.

The cerium molybdate system is more variable in the reaction products. Nanoscaled amorphous cerium molybdate and crystalline $Ce_2(MoO_4)_3·4,5H_2O$ as well as $Na_{0,5}Ce_{0,5}(MoO_4)$ occurred in the experiments. Finally we succeeded to synthesise pure nanoscaled $Ce_2(MoO_4)_3·4,5H_2O$ (crystalline) which seems to be an interesting inhibitor for the corrosion protection of aluminium and can also serve to obtain anhydrous $Ce_2(MoO_4)_3·$by calcination. Cerium molybdate is also known and used as catalytically active substance. A directed preparation of $Na_{0,5}Ce_{0,5}(MoO_4)$ would also be possible, but it didn’t show good inhibiting properties.

A further contribution to MULTIPROTECT was to charge nanostructured carriers with inhibitors and to deliver them for the incorporation in anti corrosive coatings.

As own research activity beyond the frame of a project the group started to work on special ceramic coatings in 2006. They are based on wet coating methods using particle suspensions as starting material. After the application of the suspension (for example by spraying) and its drying on a substrate it is possible to obtain porous ceramic coatings after thermal treatment at 500°C, for example. Considering that this temperature is far below usual sintering temperatures the coatings undergo a remarkable mechanical consolidation due to bonding caused by nanoparticles.

Group Corrosion Protection

Head: Dr. M. Wittmar

2006 we attended the practical aspects of a diploma thesis. The candidate very successfully covered a complete particle processing route from powder synthesis to a functional ceramic structure. To produce acoustic lenses consisting of PZT he applied the mechanochemical (dry milling) synthesis of the PZT, its chemomechanical dispersion in the near nanosized range and its shaping by electrophoretic deposition. Further, the optimization of the sintering step was carried out as well as the application of electrodes, the poling and the characterization of the piezo ceramic.

On the basis of former work on the synthesis of $BaTiO_3$ and $BaSnO_3$ nanoparticles some papers have been prepared and submitted to journals. In 2007 two of them have been published and three more have been accepted for publication in journals. These basic works offer a basis of knowledge to enter the field of functional ceramics with our nanoparticle experience.

Group Corrosion Protection

Der Schwerpunkt der Forschungsaktivitäten der Korrosionsschutzgruppe lag in der Entwicklung von Cr-freien, multifunktionalen Korrosionsschutzschichten mit „Self-Healing-Effekt“ auf Stahl- und Aluminiumlegierungen, die gleichzeitig Zielsetzung eines vom INM koordinierten europäischen Verbundprojektes namens „Multiprotect“ ist. Die Entwicklung von neuen Korrosionsschutzschichten mit so genannten „dritten Eigenschaften“ durch Einbettung von metallorganischen Nanopartikeln konnte hierbei ebenso erfolgreich angegangen werden wie die Erforschung neuer Inhibitoren zur Erzeugung von Selbstheilungs-Eigenschaften. Für die Charakterisierung dieser neuartigen Korrosionsschutzschichten stehen der Korrosionsschutzgruppe neben herkömmlichen Prüfverfahren wie Salzsprühnebel- und CASS-Tests auch modernste Korrosionsprüfverfahren wie zum Beispiel SVET, SKP und Elektrochemische Impedanzspektroskopie zur Verfügung.

Research activities

Due to the increasingly restrictive legislation concerning chromium containing corrosion protection schemes, great effort is made to find environmentally friendly alternatives. This was also the incitement for the corrosion protection group of the INM to initiate a European Integrated Project named “Multiprotect”

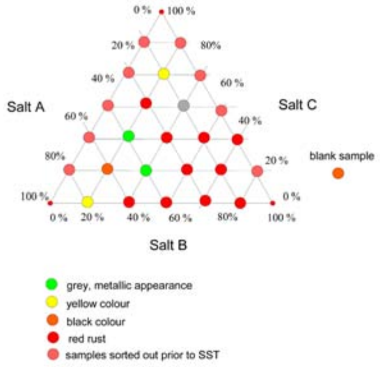

Fig. 1: Ternary mixtures of corrosion inhibitors determined via combinatorial chemistry.

in which now 30 partners from 13 countries under the coordination of the INM are involved. The aim of this project is the development of multifunctional chromium-free corrosion protection coatings with self-healing properties on steel- and aluminium alloys. In this context a multitude of new corrosion inhibitors were determined with regard to their corrosion protection abilities on aluminium alloys and steel. Figure 1 shows the results of a combinatorial chemistry test series in which several combinations of corrosion inhibitors on steel substrates were tested.

In collaboration with the analytical department the leaching behaviour of different corrosion inhibitors doped corrosion protection coatings were analysed. The leaching of cerium and benzotriazole out of the coatings in aqueous media was proved by means of High Performance Liquid Chromatography (HPLC) and Inductively Coupled Plasma - Optical Emission Spectrometry (ICP/OES) respectively. The contents of benzotriazole (BZT) in aqueous samples after specific immersion time durations of four different corrosion protection coatings were determined via HPLC (figure 2).

Beside the classical corrosion testing methods like saltspray and CASS tests the corrosion protection group employs state-of-the-art electrochemical measuring methods and devices to detect corrosion causing weak points in corrosion protection systems on different types of metals and environments. Changes in the corrosion protective coating and the phase interface are measured by means of EIS (Electrochemical Impedance Spectroscopy; in the range of 10 µHz – 1 MHz). In contrast to the solely visual sample evaluation by saltspray- and CASS-test, modern corrosion test techniques like SVET (Scanning Vibrating Electrode Technique) and SKP (Scanning Kelvin Probe) allow to resolve local corrosion defects in the microscopic scale. Figure 3 shows the results of a SVET determination in a salt solution of a CeO_2 nanoparticle filled coating, which was provided with a cross cut, on unalloyed mild steel immersed in a sodium chloride salt solution. The two blue funnels stand here for local anodic areas in the cross cut with a high corrosion activity.

A further emphasis of the research was the development of coatings filled with metal-oxide nanoparticles, e. g. ZrO_2, ZnO or TiO_2 to improve the corrosion protection as well as to yield new material properties like scratch resistance, hydrophilicity, hy-

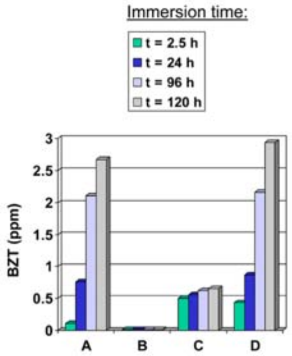

Fig. 2: Contents of BZT in dependen ceon the immersion time of four different BTZ doped coatingsys tems on aluminium alloy 2024 in aqueous media measured by means of Optical Emission Spectrometry.

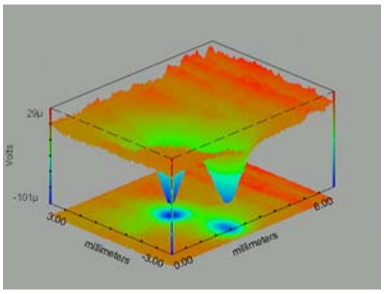

Fig. 3: SVET measured potential distri bution of a CeO_2 doped corrosion inhibited coating system on unalloyed mild steel after an artificial scratch. The red areas stand for cathodic, the blue ones represent anodic activities. The left side of the figure shows the original substrate.

drophobicity, etc. Embedding of various contents of CeO_2 nanoparticles in the coatings yielded for example in the insight that the corrosion in an artificial scratch is blocked most efficiently by high CeO_2-concentrations, while the general corrosion is inhibited effectively by comparatively low CeO_2-contents. The coatings show exposure times in a salt spray test of more than 3500 h without general corrosion, and reduced corrosion at an artificial scratch.

Group Combinatorial material development

Wie bereits in den zurückliegenden Jahren lag das Hauptaugenmerk in der Kombinatorischen Werkstoffentwicklung in der Entwicklung neuer Methoden zur Beschleunigung der am Institut durchgeführten Arbeiten durch z. B. Automatisierung von Syntheseschritten sowie in der Unterstützung der Forschungsgruppen bei der Optimierung ihrer Materialssysteme. In diesem Zusammenhang wurde die bereits im letzten Berichtszeitraum begonnene Zusammenarbeit mit der Gruppe Korrosionsschutz fortgesetzt. Dadurch konnte eine weitere Optimierung der für Aluminium eingesetzten Lacksysteme erreicht werden. Neue Methoden wie etwa ein heiz- und kühlbarer Schüttler für Multiwellplatten konnten in das System integriert werden. Dadurch konnte eine deutliche Reduktion des für Synthesen benötigten Ansatzvolumens bei gleichzeitiger Erhöhung der Ansatzanzahl erreicht werden.

As in the years before the combinatorial material development has mainly concentrated on the development of new methods and in the support of other groups in the development and optimization of syntheses and coating systems. Therefore, the cooperation with the corrosion group was continued within the EU-project “MULTIPROTECT”. After starting this work in 2005 the corrosion protection system for aluminium could be clearly advanced to better performance in the salt spray test. The optimization of the corrosion protection system for aluminium was done according a simplex matrix. Three components of the lacquer system were varied to find the most promising system. It was found that binary systems without the component silicon dioxide showed the best results in salt spray test. In these studies the integration of a heat- and coolable shaker could further reduce the complexity of the work (figure 1).

Fig. 1: Shaker “Thermoshake” H&P Labortechnik

Fig. 2: µ-Litre dosage pump, Micro MechatronicTechnologies

Group Process Engineering

Head: Dr. A. Altherr

Due to the shaker system 96 different syntheses could be prepared in parallel under permanent mixing and temperature control. A volume of up to 2 ml solution per experiment can be prepared within short times. In comparison to the 13 ml tube reactor system the reduction of reaction volume can further accelerate the screening and optimisation tests in material development.

Beside the work in optimisation of corrosion protection systems experiments with regard to the EU-project CellPROM were carried out.

After reduction of the reaction volume it was also necessary to reduce the doseable volume of the robot. Therefore a micro litre pump was purchased (Figure 2). The integration of this pump is currently underway. It will enable the combinatorial material development to mimic the normal laboratory syntheses in small volumes, because even small amounts of catalysts will be doseable.

Group Process Engineering

Die Arbeitsgruppe Chemische Verfahrenstechnik bearbeitete im Jahr 2006 überwiegend Themenstellungen aus dem Bereich der Grundlagenforschung mit dem Fokus auf zwei Arbeitsgebieten. Zum einen wurden die begonnen Arbeiten zur elektrochemischen Abscheidung von oxidischen Materialien (ITO, ZnO) im Rahmen einer Diplomarbeit weitergeführt und vertieft, zum anderen erfolgten unabhängig hierzu in einem zweiten Themengebiet im Rahmen der Dissertation von Mark Klook Studien zur Herstellung neuer temperaturstabiler Cellulose-Siloxan-Komposite.

As described in the abstract about NMO the linking of both groups is very close. While NMO is more specialized on industrialisation of lab results, the process engineering group develops new methods in synthesis of nano-materials or new application methods for those materials. This allows to focus on new synthesis techniques – maybe more risky projects - without a direct relation to industry financed projects.

Typical for this basic research is the diploma thesis of Benjamin Rabung. The cause of the examinations was to improve and examine a procedure to synthesize nano scaled (mixed) metal oxide particles by an electrochemical deposition process and the characterisation of the obtained materials. The synthesis route starts with metal or alloy electrodes with

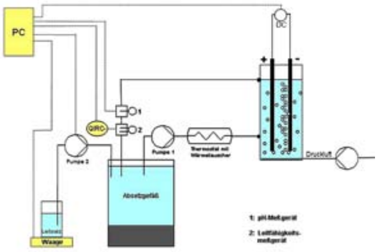

Fig. 1: Schematic description of the computer controlled electrochemical deposition cell

the desired composition in a water based electrolyte. Using this method it was possible to synthesize pure metal oxides like Al_2O_3, ZnO or mixed metal oxides like ATO or ITO. Adding conductor salts controlled during the electrolysis, it was possible to use acids like acetic acid instead of ionic substances without shifting the pH-value. In the process the deposited materials were surface modified by conducting materials (salts or acids). After the deposition process the solids were separated and dried at atmospheric conditions in a furnace. Compound oxides like ITO or ATO were obtained by further calcinations and reduction processes. The studies were focused on the automation of the electrochemical deposition process including the continuous addition of conducting materials and the characterisation of the obtained materials by physicochemical and chemical analysis. Structural analysis of the resulting materials were carried out by EDS, SEM, TEM, XRD, XPS and Mößbauer spectroscopy. First results demonstrated that the electrochemical deposition process allows the synthesis of ITO-materials and nano scaled ZnO particles.

To get more information about the quality of the products more detailed studies are necessary. The diploma thesis was still running at the end of 2006 and should be finished in May 2007.

A second topic in the process engineering group in 2006 was the development of new materials based on renewable materials for new production technologies. This examinations were performed since 2004 by Mark Klook as part of his doctoral thesis. The dissertation should be finished in 2007.

The new composite materials should be synthesised with the main focus on the relation between mechanical strength and temperature resistance. The resulting compound material was formed in a moulding press and dried to get tension rods for mechanical examinations.

The thermomechanical examinations of the material were performed at a dynamic mechanical thermal analysis instrument (DMTA V manufactured by Rheometric Scientific). In this experiment the compound was tested in a two point bending test with a certain frequency and elongation. The resulting E-Moduli were measured and recorded for increasing temperatures.

The analysis of the experiments demonstrated that it is possible to create new compounds based on renewable

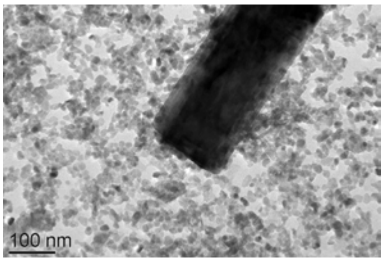

Fig. 2: TEM-picture of a nano-scaled ZnO-synthesized by electrochemical deposition with a bimodal size distribution.

Fig. 3: Tension rods (cellulose-siloxane compound) before/after mechanical test

materials. Looking to the data of the dynamic mechanical investigations it can be shown that the new material has an interesting thermal stability with a glass transition temperature of approximately >100 °C.

In 2007 the dissertation will be finished, whereas during the last months a special focus should be layed on the structural analysis of the compound material.

Additional to the basic research, in an industry project nano scaled oxide materials were synthesized in small amounts using the electrochemical deposition process.

As a part of INM the members of the process engineering group support the other departments of INM with their know-how.

Group Binder and insulation materials

Die Arbeiten in der Forschungsgruppe Binder und Isolationswerkstoffe konzentrierten sich im Jahre 2006 auf die Entwicklung und Optimierung der drei Materialklassen nanokompositäre Binder, Brandschutzgele und anorganische Funktionsschichten.

Im Rahmen eines Industrieprojektes gelang es, ein neuartiges Bindemittel zu entwickeln, welches für den Einsatz bei der Erdölförderung geeignet ist. In künstlichen Formationsspalten kann es hier zur Verfestigung sogenannter Proppants zur Steigerung der Förderleistung eingesetzt werden.

In 2006 konnte ein öffentlich gefördertes Projekt gestartet werden, welches auf die Langlebigkeit einheimischer Nadelhölzer in der Außenbewitterung abzielt. Zum Erreichen dieser anspruchsvollen Zielstellung soll zunächst mittels einer Imprägnierung die Dimensionsstabilität der Hölzer unter wechselnden klimatischen Bedingungen optimiert werden. Über überwiegend anorganische, hydrophobierende Beschichtungskompositionen wird eine Verbesserung der Hölzer gegen Bewitterung und UV-Bestrahlung angestrebt.

The work in the research group binder and insulation materials was directed to three different fields of application of nano-technology. In a first objective the work was focused to the development of nano composite based binders and to the use of these materials in challenging applications with high performance characteristics. Basic investigations were performed in the adjustability of the reactivity of these systems on a broad profile of requirements. Analytical investigations with dynamic mechanical thermoanalysis, HP-rheometry, HP-DSC, DSC/TG/FTIR/MS and NMR were useful methods in the characterisation of such binder formulations. Different methods for aimed transesterifications on sol-gel-binder systems with a high condensation degree could be established. In an industrial project the group has worked on the development of a novel proppant bridging technology for improving the productivity in oil and gas wells.

A second field of activitiy was the optimisation of effective nano composites for fire protecting systems. These systems featured a very effective energy absorption mechanism. For extending the application spectrum the nanocomposite material has to be improved related to the hygroscopic behaviour and the flexibility of the nanocomposite after hardening. Different additives were investigated in relation to their effects on fire protecting characteristics. By using a self-reconstructed muffle furnace with a sample holder in the front door the materials were characterised by detection of specific temperature-time-profiles.

The third objective in the group was the development of thin inorganic sol-gel coatings for applications on different substrates with function as electrical and thermal insulation, as barrier layer for photocatalytically active coatings on photosensitive substrates and as weathering, pollution- and UV-stable coating for wooden and cement stone based substrates.

In 2006 a public founded project was started with the aim to improve domestic wood against the effects of weathering and UV-irradiation. By impregnation with nanocomposites the dimensional stability of the wooden substrates under changing climate conditions has to be optimised. The protection of the modified wood against the destructive effects of weathering should be realised by predominant inorganic compounds in the sol-gel-based coating composition. The coated wooden substrates were characterised by artificial weathering and outdoor exposure according to the protecting effects.

Application Centre New Materials for Coating Technology (NMO)

Head: Dr. A. Altherr

Application Centre New Materials for Coating Technology (NMO)

Seit der Gründung des Anwendungszentrums ist dieses das zentrale Instrument des INM für den Technologietransfer aus dem Labor in die industrielle Anwendung. Wie in den vergangenen Jahren hat sich die NMO 2006 auch nach dem Wechsel in der NMO-Führung diesen Aufgaben gestellt. So wurden in dem Zeitraum insgesamt 22 Kleinprojekte/Bemusterungen und 6 Großprojekte zur industriellen Umsetzung von Laborentwicklungen durchgeführt. Diese Projekte beinhalteten das Up-Scaling von Lackrezepturen, die nasschemische Applikation auf unterschiedlichsten Substraten einschließlich deren Härtung sowie die Pilotserienfertigung von Beschichtungen.

Since the foundation in 1996 the Application Centre New Materials for Coating Technology represents the central instrument at the INM concerning the transfer of lab scaled developments to industrial application. To reach this an intensive interaction is needed between the research groups and NMO. Especially the linking to the process engineering is very close because of the process engineering represents one of the biggest work packages during the industrialization of laboratory results. As in the last years the topics of NMO work were focused on the industrial application of results obtained during the investigations in the research and development groups of INM.

Staff:

The projects at NMO were executed by five employees (chemists, process engineer, physical-technical-assistant, varnisher).

After 7 years Dr. K. Endres - head of NMO since 1999 - left NMO/INM to the end of August 2006. Since September 2006 Dr. A. Altherr - scientist at INM since 1999 – leads the application centre.

In 2006 22 small scale projects and 6 large scaled projects were performed.

In the small scaled projects – typically provision of samples - the services varied in a wide range:

NMO synthesized in a project ETC-lacquers in small amounts (up to batches of 5 l) for pilot productions in the industries.

Nanomer coatings with ETC properties were applied in 12 industry projects by spray coating/dip-coating techniques and curing by thermal treatment/UV-radiation. The substrate materials coated in this projects were made of steel or aluminium.

As a special public financed project the coating of a concrete wall in Dudweiler was done, to test the anti-post-bill and anti-graffiti behaviour of an INM developed easy- to-clean-coating.

In three industry projects lacquers for glass like coatings were applied on metal and ceramic substrates by spray coating, doctor blade techniques or dip-coating. The lacquers were densified in a high temperature process to glass like coatings.

As support for small and medium sized enterprises NMO executed analysis services (calorimetric measurements of reaction heat and measurement of flash point of lacquers, …) and rented technical equipment for materials synthesis and lacquers applications.

Large scaled projects dealt with the synthesis of sol-gel lacquers and the application of these materials on various substrate materials.

In one large project a pilot line was transferred to production scale. This include the complete production steps beginning with the synthesis of the lacquers based on monomers, the application of the lacquers on substrates via flat spray coating, the curing in a furnace and the quality control.

After the technology transfer the company was ready to produce the coating by there own, renting the needed equipment and services at NMO/INM.

In two projects lacquers for optical applications were synthesised in batch synthesis with a maximum batch size of 100 l. This work was done in cooperation with the department Glass and Optics.

Application tests with various lacquers (sol-gel lacquer developed in the Nanomer-department and lacquers of a customer) were performed on the automated spray coaters of NMO (flat spray coater and automatic spray unit with rotating sample holder).

Additionally to this practical work NMO in 2006 carried out several consulting services for small and medium sized enterprises.

Department of Coating Technology

Für die Abteilung Schichttechnologie war das wohl wichtigste Ereignis des Jahres 2006 die Pensionierung von Prof. M.A. Aegerter. Prof. Aegerter, der im Oktober in den Ruhestand

Fig. 1: Process controlled reactors for sol-gel lacquers synthesis

Fig. 2: NMO roller passage kiln for temperatures up to 600 °C

Fig. 3: NMO flat spray coater

ging, verliess das INM nach 12 Jahren erfolgreicher Forschungsarbeit und Lehrtätigkeit an der Universität des Saarlandes.

Die Abteilung Schichttechnologie war vor allem im Bereich nasschemischer Prozesse zur Fabrikation optischer Schichten und Geräte tätig. Folgende Themengebiete wurden schwerpunktmäßig bearbeitet:

Die Entwicklung von funktionellen optischen Beschichtungen auf Glas- und Polymer-Substraten (z.B. Folien) auf der Basis der Sol-Gel-Technologie wurde vorangetrieben.

Ein weiterer Fokus lag auf nasschemischen Beschichtungstechniken für die oben erwähnten Materialien.

Schliesslich war die Abteilung auch auf dem Gebiet der passiven und aktiven Beschichtungssysteme z. B. bei den „Smart windows'“ und bei Displaykomponenten aktiv.

A major change for the Department of Coating Technology was the retirement of Prof. M.A. Aegerter as the Director in October 2006. Prof. Aegerter left INM after 12 years of successful research work at the INM and teaching activities at the University of Saarland. The contributions that Prof. Aegerter made to the fields of transparent conducting oxides coatings and electrochromic devices will now be built upon.

Thin film technology represents a key technology in materials development. By application of thin functional coatings with thicknesses of less than 1 µm (a thousandth part of a millimetre), the properties of surfaces and components can be tailored without losing fundamental properties of the bulk substrate. By combining different properties, thus often new applications can be realized.

The department of coating technology is mainly engaged in wet chemical processes for the fabrication of optical coatings and devices. The main areas of focus include the development of

- functional optical coatings on glass and plastics (e. g. foils) on the base of the sol-gel technique also including nanoparticles,
- wet coating techniques for the above mentioned materials,
- passive and active coating systems (e.g. 'smart windows', display components).

Major advantages of wet coating techniques over vacuum deposition are the higher flexibility of production and, above all, the comparably low investment and operation costs.

Depending on the substrate shape and the coating requirements, various wet coating techniques from the laboratory to pilot-scale are available even under clean-room conditions (figure 1).

In addition to the deposition of the wet film, the sintering or curing of the coating materials play an important role in wet coatingtechnology. For this purpose, a variety of techniques can be used ranging from conventional thermal drying and sintering, rapid thermal laser firing (CO_2 laser) to curing by irradiation (IR, UV), which is particularly interesting for polymer substrates.

Functional coatings

The developed optical coatings on the basis of sol-gel hybrid materials cover a broad field of active and passive functions and properties. Examples of such coatings include decorative or optical coatings with, for example, anti-reflective or anti-glare functionality. The focus of recent activities, however, was directed on transparent conducting oxide coatings and coatings for electrochromic devices.

Functional coatings are also addressed by the EU FP6 project EFONGA - European Forum on New Glass Applications (CA 013983, www.efonga.org) which was initiated in 2005 by several leading glass research institutions and glass manufacturers. Under the chair of Prof. Aegerter, the project's work package 2.1 entitled "Coatings made by sol-gel and chemical nanotechnology" is aiming at advancing and fostering applications of wet coatings on glass substrates. In this context, a database with applications of sol-gel hybrid coatings was compiled and round-robin tests will be performed to investigate the glass/coating interface.

TCO coatings

Transparent conducting oxides (TCO) find wide application, for example, as electrodes in displays and thin film solar cells, due to the combination of high electrical conductivity with a high optical transmission. In addition to the electrical conductivity of these materials, the closely related IR reflectivity is particularly of high interest for heat insulating windows (low-E, solar control). The materials involved mostly are doped n-type semiconducting oxides with a wide band gap (> 3 eV) including materials such as In_2O_3, SnO_2 and ZnO. The wet-chemical processing of such TCO materials offers two principal routes, namely the classical sol-gel process based on

Fig. 1: Dip coating equipment for the inside coating of glass tubes.

soluble metal salts and the nanoparticle approach using discrete crystalline TCO nanoparticles.

The sol-gel process is a cost-efficient alternative for depositing TCO coatings on temperature-resistant substrates such as glasses and ceramics. Examples of such TCO materials include ATO – SnO_2:Sb (alternatively: Ta, Nb, W), ITO – In_2O_3:Sn, AZO – ZnO:Al and ternary oxides such as Zn_2SnO_4. For their deposition, not only large-area coating techniques such as dip coating can be used but also, for example, spin coating and the more flexible spray coating process. In addition, special coating techniques were developed for a deposition inside glass tubes (figure 1,2) and on thin display glasses (≤ 0.7 mm) to take account of the substrate requirements. The achieved sheet resistance values (single coatings) are in the lower kΩ/sq region (ATO) or 300 Ω/sq (ITO), respectively, with a transmission of 85-90 % (400 to 750 nm).

In view of future display applications, novel sol-gel TCO materials with specific properties as, for example, high work functions were investigated in the frame of a PhD thesis.

New applications arise from the use of functional TCO nanoparticles. Such materials can be deposited as thin films or can be incorporated in polymers and lacquers to obtain electrical conductivity or IR reflective properties. In this way, UV curable ITO coatings can be deposited also on temperature sensitive polymer substrates (e.g. PC, PMMA, PET) with a sheet resistance < 1 kΩ/sq and a transmission > 88 %. Large-area coatings on flexible polymer films are also possible by using appropriate printing techniques such as gravure, offset or flexo printing. The additional opportunities of a direct patterning of TCO materials, moreover, are opening new applications especially in the field of printed electronics.

ROLLED – Roll-to-roll manufacturing of OLED devices

A corresponding gravure printing process of patterned ITO anodes for use in flexible OLED displays is being developed within the scope of the EU-funded ROLLED project (FP6-2003-IST-2-004315). The project is aiming at a cost-effective, volume-scale, roll-to-roll manufacturing technology for the realization of flexible OLED devices on web. To realize this ambitious goal, all components including the ITO anode, the emitter layer, the metal cathode

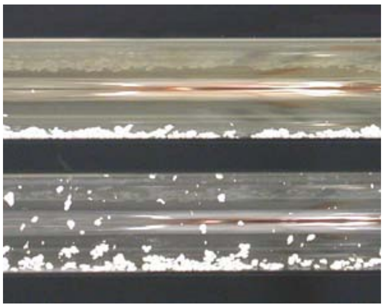

Fig. 2: Antistatic ATO coating inside a glass tube (upper) compared to an untreated tube (lower)

and the encapsulation layers have to be made printable in a roll-to-roll process. For the transparent conducting ITO anode patterns, this was achieved by gravure printing on PEN (polyethylene naphtalate) foil resulting in a sheet resistance of < 500 kΩ/sq and a transmission > 88 %.

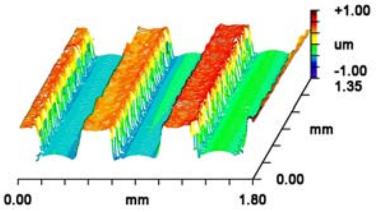

Fig. 3: WLI surface profile of a gravure printed ITO pattern on PEN foil.

Electrochromic windows

Electrochromic (EC) windows, also called “smart windows”, change their optical properties (transmittance or reflection) in a reversible manner when a voltage is applied and a current flows through them. They are of considerable interest for architectural and automotive applications in order to control the solar radiation entrance and to save costs for air conditioning. EC windows developed in the INM-Leibniz-Institut für Neue Materialien consist of a five layer system (figure 4): between two glass substrates, coated with a transparent electrically conducting layer (e.g. ITO or FTO), are an electrochromic (EC) coating, an ion-storage (IS) coating and in between a solid state composite lithium ion conducting electrolyte. The EC- and IS-coatings and the solid composite electrolyte have been developed at INM. Depending on the EC-layer the windows can color from transparent to blue (tungsten oxide, WO_3) or from transparent to grey (molybdenum doped niobium oxide, Nb_2O_5:Mo). By applying a small voltage (up to 3 V) the transmission in the visible range can be changed continuously from 70 % down to about 25 % (T_L values) with g-value (DIN EN 410) varying from 42 % to 17 % so that the energy entrance into the buildings can be varied in a wide range. The switching time depends on the size of the window and lies between 3 and 5 min. The voltage is only necessary to change the transmission of the window so that the energy consumption is small (0.1 Wh/m^2). The long-term switching stability has been tested up to > 60000 cycles and the windows have withstood UV-suntest for 1000 hours without change of the switching behaviour.

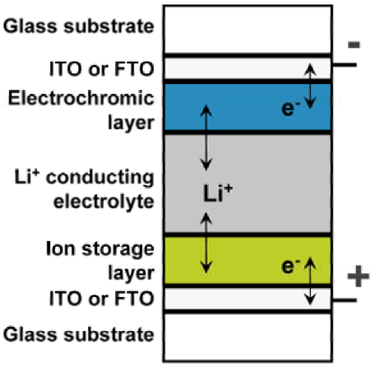

Fig. 4: Configuration of the EC-windows

In 2006 research and development was done and continued to develop a brown coloring EC layer using nickel oxide titanium oxide. Using this EC-layer EC windows with a transmission change from 70 % to 25 % were fabricated, whereby the long term stability was about 7000 cycles. Furthermore an ion-storage layer was developed which can be hardened at low temperature by UV treatment. This is advantageous, because the normally used CeO_2-TiO_2

IS-layer has to be heat treated at high temperatures (450 to 550 °C), which leads to a high energy consumption during the fabrication process and makes the layer not useful for the deposition on plastic substrates. The low temperature deposition was realized by development of CeO_2-TiO_2 nanoparticles, which can be redispersed in a solvent and after mixture with a binder and a UV initiator the dispersion could be deposited by dip-coating and hardened by UV-treatment. Windows using this IS-layer showed a transmission change from 70 % to 30 % after 13 min, which shows that the kinetics is not as fast as for the standard heat treated CeO_2-TiO_2 layer, but a first step to fabricate EC-windows on plastic substrates has been done. In cooperation with the university of Sao Carlos, Brasil (PROBRAL) the development of new cost-efficient electrolytes for EC-windows based on renewable primary products were done, whereby gelatine, starch and agar-agar were used for gelification and $LiClO_4$, $LiClO_3$ or acetic acid were used for ion conduction. First results showed that a small transmission change (from about 60 % to 40 %) could be obtained. Further work has to be done to improve these results.

Using the standard EC system of the INM, depending on heat treated sol-gel layers as EC- and ion storage layers (tungsten oxide and cerium oxide titanium oxide respectively) a patterned EC-window of 5 x 5 pixels has been fabricated. The coloration and bleaching of the pixels was controlled by a PC program and a switching unit developed in the INM. Each pixel could be colored and bleached individually, but also different patterns as 4 different pixels together, horizontal or vertical stripes or the whole area could be colored and bleached together (figure 5). A structured EC-window could be used to show information as e.g. prizes in a shop window or a company logo in an office building. Because only for the change of the transmission energy is necessary, the information could be shown for a long time with low energy consumption.

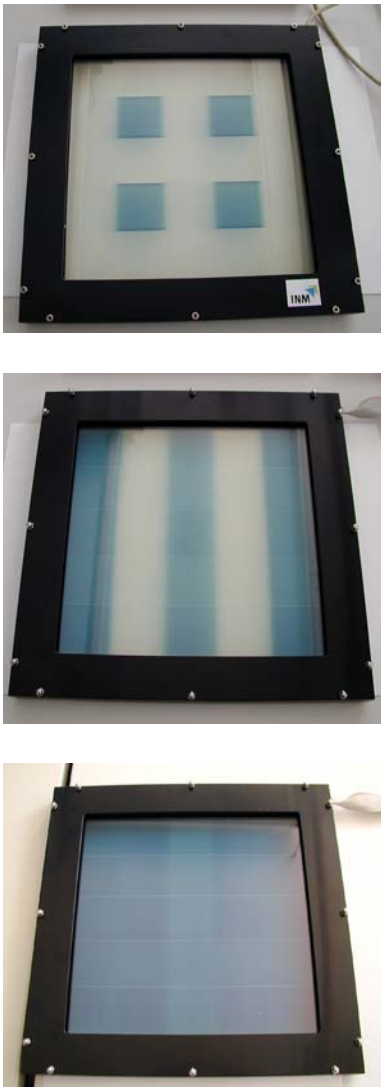

Fig. 5: Patterned electrochromic window with 5 x 5 pixels, whereby each pixel can be colored and bleached individually and different structures can be colored and bleached. Shown: four pixels, three stripes and whole area colored.

Department CVD and PVD Technology

Head: Prof. Dr. S. Mathur

Department CVD and PVD Technology

(i) One-Dimensional Inorganic Nanostructures: Growth, Applications and Devices

Due to their unique structural features and interesting functional properties one dimensional (1D) inorganic materials are gaining high attention. These nanostructures show promising application potential in vacuum and oxidizing atmospheres, which makes them competitive for device fabrication. We have developed a generic approach for size-selective and site-specific growth of nanowires by combination of chemical precursor design and a catalyst assisted growth mechanism. For instance, high-yield synthesis of NWs of tin, vanadium and iron oxides was performed by the chemical vapor deposition of appropriate metal-organic precursors. Axial and radial dimensions of the NWs were varied in the ranges 30-1000 nm and 25-40 µm, respectively by adjusting the precursor feedstock, deposition temperature, and catalyst size. In addition, SnO_2 / V_2O_5 heterostructures and oriented tin oxide NW arrays were grown by control of gas phase saturation and substrate materials. We have investigated the device potential of these building blocks as photo- and gas sensors and obtained electrical characterisation of materials is performed. Illuminating tin oxide NWs with UV photons triggers interesting photo-conductance, which can be modulated by tuning the wire diameter as demonstrated for samples possessing radial dimensions in the range 50–1000 nm. The stable photo-response over several on-off cycles demonstrated their potential for applications in UV detectors or optical switches, where the NWs can act as resistive elements whose conductance changes by charge-transfer processes. In addition, tin oxide NWs were grown on sensor platforms and their response towards different gaseous species was recorded. Besides multiwire devices, individual SnO_2 nanowires were contacted by FIB nanolithography and their intrinsic properties were investigated in close collaboration with the University of Barcelona (Research Group: Prof. Romano-Rodriguez) to obtain precise information about their electrical and sensing behaviour in different atmospheres (Nanotechnology, 2007; Phys. Rev. B, 2007)

This work was supported by the priority programme – SFB 277 “Grenzflächenbestimmte Materialien” – of German Science Foundation (DFG),

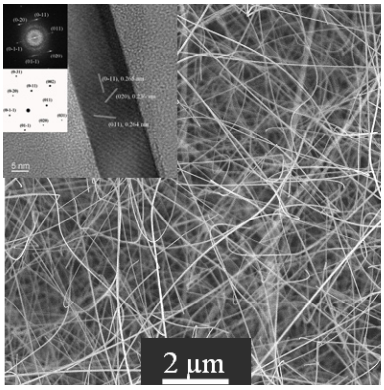

Fig. 1: Tin oxide nanowires grown by molecule-based CVD process Small 2005, 1, 713.

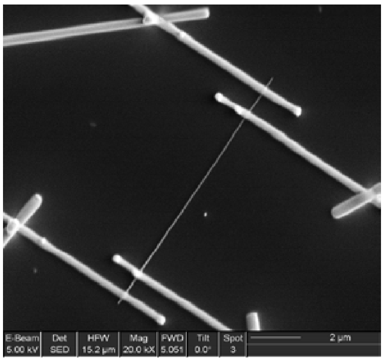

Fig. 2: Electrical circuits based on single nanowires for gas sensing applica tions
Nanotechnology 2006, 17, 5577.

which has led to the doctoral thesis of Dipl. Chem. Sven Barth who will defend the same in 2008. In addition, the fundamental knowledge developed in this work has paved the way to a research project financed by BMBF in the framework of call *NanoFutur*, which is led by Dr. Hao Shen. The major aim of this project is to develop strategies for controlled growth of one dimensional nanostructures followed by their integration into devices for sensing applications.

In another effort, iron oxide nanotubes were synthesized, in collaboration with Max Planck Institute of Microstructure Physics, Halle (Profs. Gösele and Nielsch), by using single molecular precursor $[Fe(OBu^t)_3]_2$ in an atomic layer deposition (ALD) process (*J. Am. Chem. Soc.* 2007). For this purpose, the molecular precursor was decomposed in anodic alumina membranes to produce iron oxide nanotubes of different wall thickness followed by investigations on their magnetization. The results obtained are highly relevant for engineering future high-density data storage systems.

(ii) Transparent Hard Coatings and Barrier Films by Plasma Enhanced Chemical Vapor Deposition

The Plasma Enhanced Chemical Vapor Deposition (PE-CVD) process is based on the decomposition of gaseous precursors by the use of electrically charged particles (plasma), at relatively lower temperatures. The PE-CVD technique is a very flexible coating process, appropriate for the deposition of a variety of materials such as oxides, nitrides or carbides, relevant for applications in microelectronics, optical coatings or hard and protective thin films. The plasma-assisted processes are gaining attention due to the increasing need to minimize the high temperature processing steps for fabrication of devices with sub-micrometer features as well as intrinsic advantages of the process that include high growth rates, high plasma density, and reduced damage due to low temperature at the substrate.

Deposition of transparent scratch resistant silicon oxide (SiO_2) films onto polycarbonate has been investigated in RF plasma using hexamethyldisiloxane HMDSO ($(CH_3)_3SiOSi(CH_3)_3$), as precursor in combination with oxygen (O_2). The coatings were characterized with respect to their optical properties, microstructure, chemical composition and mechanical properties. Furthermore profilometry has been carried out to study the

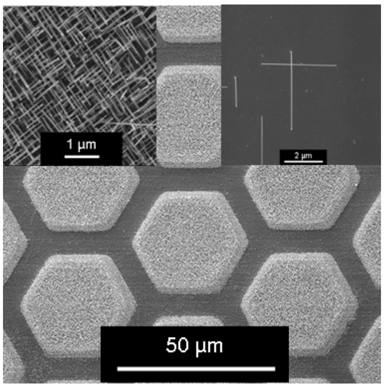

Fig. 3: Site-selective growth of tin oxide nanowires. Small 2007, accepted.

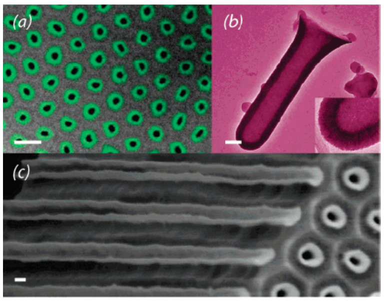

Fig. 4: Scanning and transmission electronmicrographs of iron oxide nanotubes

deposition rates. To achieve coatings with optimal combination of desired film properties (transparency, scratch resistance, adhesion and high deposition rate), different variation of O_2/HMDSO ratio, RF-power and bias voltage by changing size of electrode in asymmetric capacitively coupled plasma system has been utilised.

By adjusting the precursor flux, we could achieve high deposition rates (1.5 nm / sec) which lead to short coating durations and thus high throughput. The RF-power had to be adjusted very carefully when using high precursor concentrations in order to suppress any undesirable homogenous gas phase reactions which could result in the particle formation and decreased transmission of the visible light due to enhanced surface roughness. The precursor fragmentation was found to reach an optimum window in the range of 200 W. All deposited films showed smooth morphology, very dense and homogenous microstructure.

A precisely tuned O_2/HMDSO ratio produced carbon-free layers, which however did not show the best scratch resistance. Furthermore, these films were poorly adherent indicating high residual stress. Films containing low amount of carbon (2-4 atom-%) show the best performance in terms of adhesion indicated by the scratch tests and SEM images of the scratch profiles.

The bias voltage was found to be one of the key parameters, beside carbon content, to obtain suitable hardness in the coating, which is directly correlated to ion bombardment caused by negative bias voltage. Optimum parameters for hard transparent coatings depended on O_2/HMDSO ratio, RF-power and bias voltage. The results obtained were supported by Taber test according to DIN 52 347 (load: 2,7 N; cycles: 500; wheels: CS-10F) with scattered light fraction of 2 % which is similar to that of float glass.

Our PECVD deposited SiO_x films also exhibit high barrier properties and can be used for instance to reduce the permeation of atmospheric moisture. (Collaboration with IBMT)

Analytics: Microscopy and X-ray Analysis

Die herausragenden Eigenschaften neuer Materialien basieren in wachsendem Maße auf einem definierten chemischen, morphologischen und kristallinen Aufbau in nanoskaligen und atomaren Dimensionen. Zur

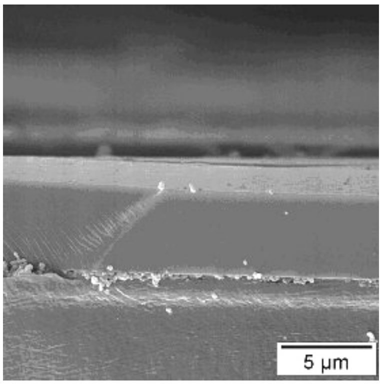

Fig. 5: Cross-section SEM micrograph of a glassy PECVD film on polycarbonate.

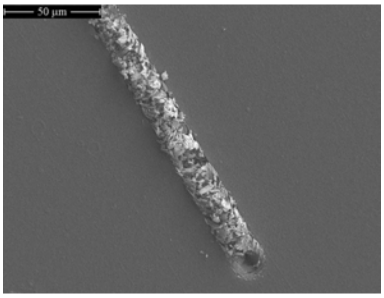

Fig. 6: SEM image of a nano-scratch test performed on SiO_x films

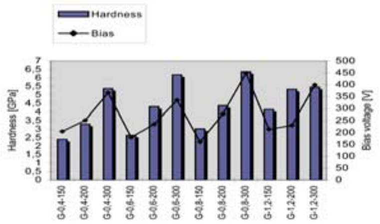

Fig. 7: Dependence of hardness values of the SiO_x films on the bias voltage

Charakterisierung der synthetisierten Materialien sind daher Methoden einzusetzen, die sowohl statistische Aussagen über Materialparameter, als auch Aussagen über individuelle Strukturen über einen großen Skalenbereich bis hinab auf die atomare Skala liefern. Hierfür steht im INM ein Verbund aus Elektronen-, Rastersonden- und konfokaler Laser-Scanning-Mikroskopie sowie Röntgen-Diffraktometrie zur Verfügung, der aufgrund der unterschiedlichen Signalträger (Elektronen, Photonen und mechanische Sonden) ein breites Spektrum an Informationen über den strukturellen Aufbau der Materialien liefert.

Tiefe Einblicke in die Struktur individueller kristalliner nanoskaliger Objekte übermittelt das Transmissions-Elektronenmikroskop. Aufgrund der im Institut anwachsenden Forschung auf dem Gebiet nanokristalliner Strukturen – wie der Synthese von Nanodrähten – sind diese Einblicke von besonderer Bedeutung. Eine umfassende transmissions-elektronenmikroskopische Charakterisierung von Nanodrähten erfordert neben der Abbildung ihrer Struktur auch den Einsatz mikroanalytischer Methodik wie beispielsweise der Elektronenbeugung. Erst der durch die Elektronenbeugung eröffnete Einblick in den reziproken Objektraum liefert die zur Erfassung der Kristallstruktur der Nanoobjekte notwendigen Informationen (siehe 1. Beitrag).

Zur Oberflächen-Analytik steht dem INM seit 2005 ein mit einer Feldemissions-Kathode ausgerüstetes Raster-Elektronenmikroskop zur Verfügung, dessen besondere Stärke durch zwei Vakuum-Moden gegeben ist, die eine Untersuchung bei höheren Drücken erlauben („Low Vacuum Mode“: bis 1,5 torr und „ESEM-Mode“: bis 20 torr). Das Gerät erschließt damit die Möglichkeit, sowohl stark gasende als auch feuchte Proben zu untersuchen. Eine Untersuchungs-Richtung, die diese Eigenschaft ausnutzt, ist die Charakterisierung des Benetzungs-Verhaltens von Oberflächen in Abhängigkeit von ihrer Chemie und Topographie (siehe 2. Beitrag).

Die auf der Basis von EDXS betriebene Elektronenstrahl-Mikroanalyse wird in vielen Fällen im TEM und SEM eingesetzt, um Auskunft über die chemische Zusammensetzung von Proben in lokalen Bereichen zu erhalten. Die Exaktheit der Resultate wird hierbei stark von dem Umstand beeinflußt, inwieweit die sich einstellende Elektronen-Target-Wechselwirkung mit den Voraussetzungen der

EDX-Korrekturrechnung übereinstimmt. Um durch eine Abschätzung der sich einstellenden Fehler größere Sicherheit bei der chemischen Analyse zu erlangen, wurden in einer Untersuchungsreihe zertifizierte Materialien einer EDX-Analyse unterzogen (siehe 3. Beitrag).

Eine deutliche Steigerung der Aussagekraft analytischer Untersuchungen gelingt durch Kombination von Methoden, die auf unterschiedlichen Wechselwirkungen basieren. So können durch Kombination von Röntgen-Diffraktometrie und Raman-Spektrometrie zum einen mittels Röntgenbeugung statistische Aussagen zur Kristallstruktur und zum anderen mittels Photonen-Phononen-Wechselwirkung Aussagen zur Kristallstruktur und zu nichtkristallinen organischen Bestandteilen gewonnen werden. Auf diese Weise wurden wertvolle Informationen über den Einfluss unterschiedlicher Synthesewege auf die Materialeigenschaften erhalten (siehe 4. Beitrag).

In the following, an overview is given about some analytical problems that were typical in the INM in the year 2006 and about their solutions by applying of TEM (Transmission Electron Microscopy), SEM (Scanning Electron Microscopy), EDXS (Energy Dispersive X-ray Spectroscopy) and XRD (X-Ray Diffraction):

TEM Characterisation of Nanowires

The transmission electron microscopy yields information of local structures in micro- and nanoscaled dimensions. A local electron microscopical investigation becomes absolutely essential if morphology, chemical composition and crystal structure vary within these dimensions as in case of nanowires. The combination of imaging and analytic methods provides in this case unique insights: For example, Fig. 1a shows a SnO_2 nanowire imaged by means of the bright-field diffraction contrast. The nanowire with a length of 165 nm and a uniform thickness of 16 nm carries at its upper end a gold nanoparticle as growth catalyst. Information about the crystal structure is given by the selected-area electron diffraction. A diffraction diagram made by this technique discloses in Fig. 1b an [100] orientation and a [011] growth direction of the monocrystalline wire. Furthermore, from the diagram can be extracted that the ideal smooth surface and the end face below the gold nanoparticle are limited by (011) lattice planes.

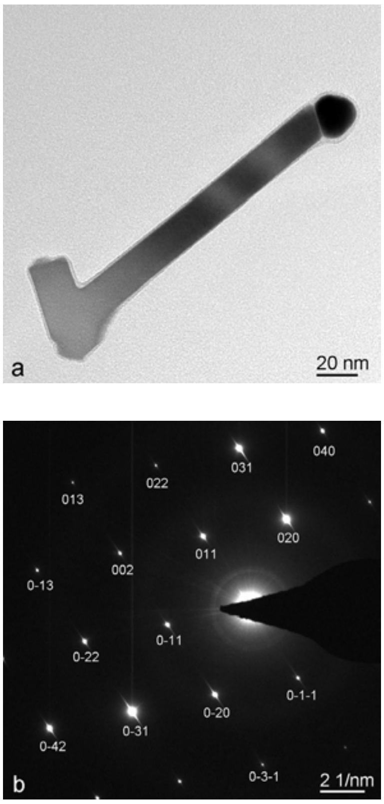

Fig. 1: SnO_2 nanowire with gold nanoparticle on the wire tip imaged by diffraction contrast in bright-field mode (a). Selected area diffraction diagram (spot pattern) of the [100] oriented tetragonal SnO_2 nanocrystal (b).

Additional possibilities arise from imaging of nanowires by using the high resolution transmission electron microscopy and evaluation of the Fourier spectra of the structure images. A detailed representation of this expressive method is given by the article “Evaluation of HR-TEM Images of Atomic Lattice Structures by Fourier Transformation”.

Wetting Phenomena on Nanowire Structures

An important role to control surface properties is wetting behaviour, which is influenced by two factors: structure and chemistry. For a flat surface the maximum contact angle Θ of water at the three phase boundary where the physical conditions solid, liquid and gas intersect, is 120° for the case of a CF_3-terminated surface. For a given material it is possible to enhance the contact angle by roughening the surface to get superhydrophobic character (Θ > 160°), if the contact angle Θ of water is >90° against a flat surface. In case of nanowire structures it is possible to get superhydrophobic character also for materials, which have contact angles less than 90°, e.g. SnO_2 or Al_2O_3. A very useful instrument to investigate wetting phenomena is ESEM® (Environmental Scanning Electron Microscopy). At a temperature of 276 K and a water vapour pressure of 800 Pa, wetting and dewetting of surfaces can be studied down to submicron resolution by changing the water vapour pressure. Water droplets with diameter greater than 3 µm are lying on the surface. Water droplets which are smaller than 1 µm can be found both inside the nanowire forest as well as on the surface (figure 2). There is no fakir state seen. The results can be used to optimise materials for biomedical applications.

Quantitative Spectrochemical Analysis of Certified Materials in Analytical Electron Microscopy (TEM & SEM)

X-ray spectrometric investigations of certified powder materials[1] using TEM and SEM attached with EDXS, are concerned with questions about the reliability of micro-analytical results in connection with the morphologic structural information of imaging in the electron microscope.

Regarding analytical investigations in the TEM the properties of the specimens (habit and size of particles) and the micro-geometry (roughness, porosity) of the excited area ranges can influence the generated radiation in

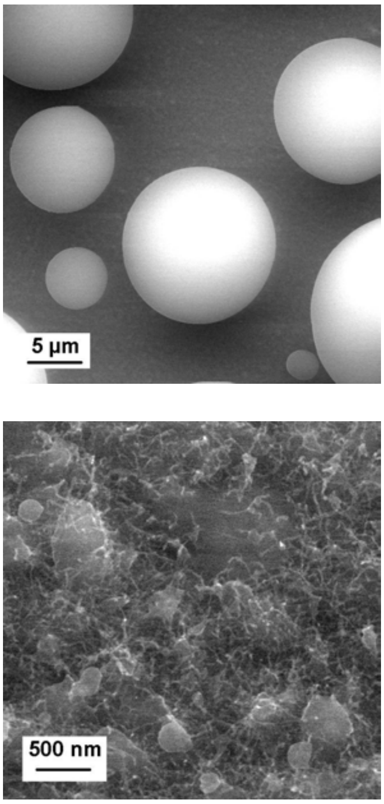

Fig. 2: Water droplets on a superhydrophobic nanowire structure seen by ESEM®. Big droplets (diameter > 3 µm) have round shape and are lying on the surface (left picture). Small droplets (diameter < 1 µm) are both on and inside the nanowire forest.

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[1] Reference Standards for TEM, registered Stand. No. 5998, Science Services München

such a way that lower energetic photons may suffer a stronger absorption on their way to the detector compared to higher energetic ones. Besides the influences of the geometrical parameters, the chemical composition – on the one hand the presence of light elements together with heavier ones (esp. oxides) or otherwise only small Z differences of the material – plays an important role for the certainty of the quantitative analytical results. Finally, the available software package determines the quality of handling and evaluation of the original spectral data. Therefore, a general valid specification of the accuracy of the quantification preferably should be replaced by assumption of an error budget associated with the special analytic problem.

Selected results of quantification of identical specimens analyzed as well in the TEM as in the SEM are summarized in the following table. It shows the data of a low Z material: Na Al Fluoride, which is a specimen prepared from natural mineralic powder (Cryolite). Using TEM/EDXS the application of an absorption correction results in good agreement with the data of SEM investigation; here, the minority constituents are not taken into account.

Table: Cryolite, Na-Al-Fluoride, Na_3AlF_6

	Major Constit.			Minor Constit.		
Spectr. Line	F K	Na K	Al K	Si K	Cl K	Ca K
Certif. Comp.	54,3	32,85	12,85	---	---	---
Weight % by Element, SEM						
Mean Value	55,8±1,9	31,6±1,6	12,6±0,5	---	---	---
Weight % by Element, Absorption t = 250 nm, TEM						
Mean Value	55,0±5,7	28,6±3,4	15,8±4,6	0,4±0,4	0,1±0,1	0,1±0,1

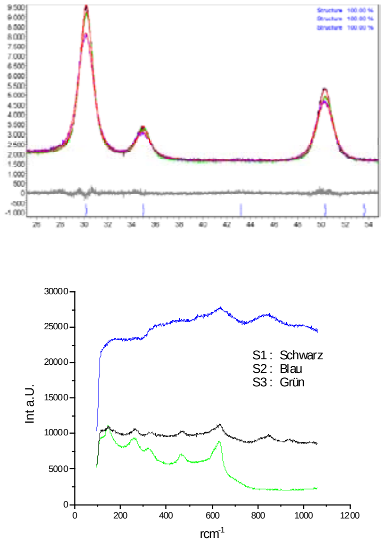

Fig. 3: XRD diffractograms (a) and Raman spectra (b) of 3 ZrO_2 samples.

More extensive comparative standardless TEM/EDXS and SEM/EDXS analytical procedures (s. detailed report) have shown that the resulting compositions agree within acceptable confidence ranges with certified data. The evaluations of selected materials consisting of lower and higher Z components reveal that the analytical strategy using the TEM is – related to the SEM – much more sensitive against different influences of excitation and propagation of X-radiation in the microscope.

Structural Investigation on ZrO_2 Using Raman Scattering and XRD.

ZrO_2 is a material of great technical importance. ZrO_2 at room temperature is monoclinic, but the high temperature phases (tetragonal, cubic) can be stabilised at room temperature also. A lot of different synthesis techniques are used to improve its properties. Hence the influence of each step during the synthesis on the structure of ZrO_2 is of great interest. So we took 3 samples to check whether there are remarkable differences and how they can be investigated. Here we present the first results of these investigations.

Sample number 1 was milled in an organic acid. After removing the or-

Analytics: Chemical analysis

Head: Dr. C. Fink-Straube

ganics with NaOH, the sample was milled a 2nd time in ethanol (sample number 2). Then the sample was heated to 500°C (sample number 3).

Some results of the XRD measurements are presented in Fig. 3a. All 3 samples can be well described using the cubic phase. No indication of an other phase or amorphous content was found. The particle sizes of the samples were 7.3 nm, 6.1 nm and 7.8 nm, respectively, were the strain was 0.25% in all three samples. In Fig. 3b the Raman spectra in the range from 150 to 1100 rcm^{-1} are shown. While sample 1 and 3 clearly show the lines of the tetragonal phase, the spectrum of sample 2 cannot be described by the zone centre modes of one of the 3 phases of ZrO_2. It seems that the number of structural defects in this samples is so high that modes are visible witch are normally forbidden in the Raman spectrum.

On the one hand the combination of Raman and XRD measurements can clarify the differences between the samples, on the other hand there are open questions for the future. For example: Why is the tetragonal content, detected by Raman scattering, not visible in the diffractograms? Is there really no amorphous content?

Analytics: Chemical analysis

Das Hauptaufgabenfeld des Servicebereichs chemische Analytik beinhaltet die Charakterisierung von Reaktionsabläufen bei der Materialherstellung und die Ermittlung der Zusammensetzung und des Aufbaus von im INM synthetisierten Materialien. Die analytischen Untersuchungen werden mittels Flüssig- und Festkörper-NMR-Spektroskopie, chromatographischer (HPLC, GC / MS) und atomspektrometrischer Methoden (ICP OES, AAS) durchgeführt.

Schwerpunkte der Arbeiten sind analytische Untersuchungen zu laufenden Projekten des INM. So wurden im letzten Jahr beispielsweise kommerziell erhältliche Nano-Produkte qualitativ analysiert, die unterschiedlichen Stufen der Waschwässer der Nano-ZrO_2-Synthese des Institutes auf Abfallprodukte untersucht, Precursor wie z. B. MPTS, FTS, MTEOS, PhTES und Lösemittel in Beschichtungssolen quantitativ bestimmt und Ausdünstungen von easy-to-clean-Schichten auf Edelstahl, die im Druckbereich angewendet werden, analysiert.

Für die quantitative Bestimmung des Ölgehaltes in Druckluft wurde ein neuer Gaschromatograph mit FID (Flammenionisationsdetektor) installiert und mit dem vorhandenen automatischen Thermodesorber (ATD) gekoppelt.

Außerdem wurden neue HPLC-Säulen für die Größenausschlusschromatographie (GPC, GFC) gekauft und entsprechende Kalibrationskurven erstellt, um Molekülgrößen von Polymeren und biologischen Proben zu bestimmen.

Die qualitative Analyse von in Parfüm ausgelaugten Beschichtungsbestandteilen mit GC / MS ist im Folgenden näher beschrieben.

The service group chemical analysis deals with the characterisation of reactions during the material development and the determination of compositions of the prepared new materials. It is well equipped with various instrumental methods:

- Liquid State and Solid State Nuclear Magnetic Resonance Spectroscopy (NMR) to investigate material structures and to study chemical reactions
- Gas Chromatography Mass Spectrometry (GC / MS) in combination with headspace, thermal desorption and pyrolysis for the determination and characterisation of volatile organic components of the developed materials, for the incoming products inspection and process control
- High Performance Liquid Chromatography (HPLC) equipped with different detectors (refractive index detector, diode array detector and mass spectrometry detector) for non-volatile organic substances
- Atomic spectrometric methods like atomic absorption spectrometry (AAS) and optical emission spectrometry with inductively coupled plasma (ICP OES) for the quantification of the element compositions of the new materials
- The determination of the total amount of organic components is followed by a CHN analyser

As every year, a vitally important task was the routine inspection of incoming goods such as solvents and precursors for the coating sol synthesis of the new materials, which are delivered in barrels. The reagent grade of these chemicals is proofed and the quantitative analysis of trace elements is performed continuously by methods of GC / MS and atomic spectrometry.

The second and most important area of activities is the suitable solution of analytical tasks for current projects. This focusses on the selection of the suitable method and the development and adaptation of the method parameters. Among others, the chemical analytics group has characterised commercial Nano products qualitatively, examined washing water of the Nano–ZrO_2 synthesis of INM, analysed precursors like MPTS, FTS, MTEOS, PhTES and solvents in coating sols of INM quantitatively and investigated effluvia of easy-to-clean coated stainless steel plates applied in printing units by GC / MS.

A new gas chromatograph with FID (flame ionisation detection) was installed and coupled with thermal desorption (ATD) in order to investigate the oil content in compressed air quantitatively.

Besides this, new columns for Size Exclusion Chromatography (GPC, GFC) were supplied for determination of molecular sizes of polymers and biological samples.

As one example, the qualitative determination of the migration of coating components into perfume by GC / MS is described.

Determination of migration of coating components into perfume by GC / MS

Im Rahmen eines Forschungsprojektes wurde am INM eine glasartige, dekorative Beschichtung für die Innenseite von Parfümflaschen entwickelt. Eine der Anforderungen an die Schicht war, dem Originalparfüm für 8 Wochen bei 42 °C ohne Beschädigung und Migration von Schichtbestandteilen standzuhalten. Dazu wurden die Analyse des Originalparfüms und der in den beschichteten Flakons ausgelagerten Parfüms mit GC / MS (Gaschromatographie gekoppelt mit Massenspektrometrie) durchgeführt. Bild 1 zeigt das Totalionenchromatogramm einer 1-%igen Lösung des Originalparfüms in Hexan und die mittels MS und Vergleich mit NIST-Datenbanken identifizierten 23 Duftstoffkomponenten. In Bild 2 sind die Chromatogramme von Parfümproben, die in beschichteten Flakons lagerten, im Vergleich mit dem Original dargestellt. Im oberen Teil wurde das Original mit einer Parfümprobe verglichen, die 24 h bei 42 °C in einem mit kommerziellem Hartlack beschichteten Flakon lagerte. Es wurden 4 zusätzliche Signale im Retentionsbereich 4,74 bis 5,5 min detektiert, die als 1,3,5-, 1,2,4- und 1,2,3-Trimethylbenzen

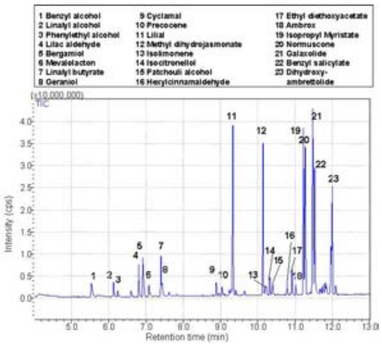

Fig. 1: Total ionic chromatogram of 0.2 µl of a 1 % solution of the given perfume into hexane and identified fragrance components

sowie 1-Ethyl-2-Methylbenzen analysiert wurden. Im unteren Teil ist das Chromatogramm einer 3 Monate bei 42 °C in einer mit INM-Lack beschichteten Flasche im Vergleich zum Original zu sehen. Es konnten mit GC / MS keine zusätzlichen Signale detektiert werden.

INM has developed a glass-like coating for perfume bottles using sol-gel technique as an inert interior decoration. One of the requirements was that the decorative coating should withstand exposure to the perfume for 8 weeks at 42 °C without damage or migration of coating elements into the perfume. The determination of original perfume and the migration of coating components into perfume was monitored by GC / MS (gas chromatography coupled with mass spectrometry) measurements, which were carried out on a GC / MS QP5050A connected with auto injector AOC 20i from Shimadzu. The components were separated on a 30 m long capillary column of 100 % of dimethylpolysiloxane, having 0.25 mm of inner diameter and 0.25 µm of film thickness. An optimum separation of the perfume components was achieved at an injector temperature of 250 °C, the initial temperature of the column being set as 40 °C and ramped at 20 K/min to 200 °C, held for 1 min and then ramped at 10 K/min to a final temperature of 250 °C. The carrier gas (helium) was set at a constant linear velocity of 43 cm/s. Injections of 0.2 µl were made using an auto sampler. The mass spectrometer was operated in the scan mode (35-500 m/z), and mass spectra were compared against the entire NIST Mass Spectral Library for matches of greater than 90 %. Using this approach, 23 distinct fragrance components of the given original perfume could be detected.

Figure 1 shows the total ion chromatogram of a 1 % solution of the given original perfume in hexane and the identification of the fragrance components.

Figure 2 shows the chromatograms of perfume solutions, which were stored in perfume bottles with different coatings. In the upper picture a part of the total ionic chromatogram of a perfume sample is displayed, which was stored for 24 hours at 42 °C into a bottle with a commercial hard coating. The right side shows a perfume sample, which was kept for 3 months at 42 °C in a perfume bottle with INM glasslike coating inside. The original perfume is presented in both graphs for comparison.

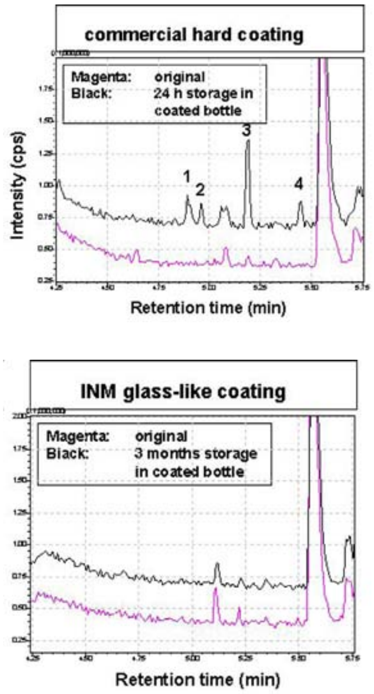

Fig. 2: Comparison of the total ionic chromatograms of the original perfume and the perfume, stored in coated perfume bottles

1: commercial hard coating, storage duration 24 h, 42 °C **1**: 1,3,5-tri methyl benzene **2**: 1-ethyl-2-me thyl benzene **3**: 1,2,4-trimethyl benzene **4**: 1,2,3-trimethyl ben zene

2: INM glass-like coating, storage duration 3 months, 42 °C

Modelling Group

Head: Prof. Dr. Dr. D. J. Strauss

For the commercial hard coating, 4 additional signals are visible, identified as different trimethylbenzenes (1,3,5-, 1,2,4- and 1,2,3-trimethyl benzene) and 1-ethyl-2-methyl benzene. The INM glasslike coating showed no leaching even after three months. It can be concluded, that the glasslike coating withstands the storage of perfume for 3 months without damages and migration of coating components.

Modelling Group

Vorrangiges Ziel der Gruppe Modelling in 2006 war die Unterstützung des EU-Projektes MULTIPROTECT in Bezug auf die computergestützte Charakterisierung und Optimierung von Korrosionsschutzschichten. Weiterhin wurden neue mathematische Werkzeuge zur Inklusion von chemischen Reaktionsgleichungen in Multiskalenmodelle entwickelt und zur Multiskalenmodellierung der chemischen Gasphasenabscheidung angewendet. In Kooperation mit der Arbeitsgruppe „Computerbasierte Diagnostik und Biokybernetik“ am Universitätsklinikum des Saarlandes und der Hochschule für Technik und Wirtschaft des Saarlandes, dem Zentrum zur Erforschung von medizinischen Kommunikationsstörungen am Universitätsklinikum des Saarlandes, mit der Klinik für diagnostische und interventionelle Neuroradiologie am Universitätsklinikum des Saarlandes sowie mit mehreren Partnern in Malaysia und den USA wurde ein neuer Forschungsschwerpunkt im Bereich „computational biomaterials science“ gebildet. Vorrangiges Ziel ist hier ist die Anwendung, Optimierung, und Anpassung von innovativen INM-Materialien für aktuelle Probleme in der Biomedizin – welche aus der klinischen Praxis stammen - in kooperativen Projekten mit anderen Gruppen am INM und den medizinischen Partnern, vorzugsweise unter Einbindung der medizinischen Industrie.

The main objective of the modelling group during 2006 has been primarily the support of the EU-Project MULTIPROTECT regarding the computational characterization and optimization of corrosion protection coatings. In addition to MULTIPROTECT, new computational tools for chemical reaction engineering, in a multiscale modelling framework, were developed and applied to the problem of multiscale modelling and simulation of chemical vapor deposition. In collaboration with the “Computational Diagnostics & Biocybernetics

Unit", Saarland University Hospital & Saarland University of Applied Sciences, the "Centre for Research in Medical Communication Disorders" at the Saarland University Hospital, the "Department of Diagnostic and Interventional Neuroradiology" at the Saarland University Hospital as well as partners in Malaysia and the USA, a research focal point "computational biomaterials science" has been established. The major objective here is the application, optimization, and adaptation of innovative INM materials for current problems in biomedicine – stemming from the clinical practice – in cooperative projects with other groups at the INM, the medical partners, and, preferably, with the medical industry.

In dem EU-Projekt „MULTIPROTECT -Advanced environmentally friendly multifunctional corrosion protection by nanotechnology" soll computergestützte Modellierung die Optimierung einen selbstheilenden aktiven Korrosionsschutzmateriales unterstützen und ein besseres Verständnis für den Selbstheilungseffekt an sich liefern. In diesem Jahr wurde der Fokus auf ein Modell von korrosionsinhibierenden Ionen in einer porösen Sol-Gel Matrix gelegt. Diese Modell, welches auf einem Nernst-Planck Ansatz mit Butler-Vollmer Dynamik und Maxwell-Garnett Theorie für ein 2-Phasen System basiert, lieferte sehr gute Ergebnisse in der in-silico Simulation sowie in experimentellen Untersuchungen, insbesondere in Bezug auf Zeitskalen der Inhibitionsdynamik.

Corrosion Inhibiting Ions in Porous Sol-Gel Systems: Inhibition Dynamics and Estimation of Time-Scales

During the present year, the mathematical modelling group at INM continued its activities within the EU-project MULTIPROTECT - Advanced environmentally friendly multifunctional corrosion protection by nanotechnology. The main activity focused on advancing the heterogeneous multiscale-model of the self-healing process by corrosion inhibitors, with a particular emphasis on providing deeper understanding of the underlying chemical and physical mechanisms as well as deriving optimization strategies for the material design at the chemical level. For instance, the optimal particle size and matrix structure, but also including characterizations at macroscale level, e.g., self healing time scale and determination of an upper bound for the thickness of nanocomposite coatings regarding their reservoir features.

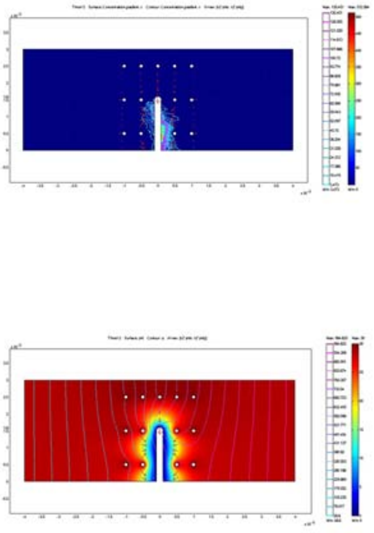

Fig. 1: Simulation of a Nernst-Planck System in porous media

In a first stage the basic mathematical framework, at the macroscale involved inhibitors mass transport by the diffusion equation with a time-dependent drain term representing the reservoir consumption, whereas at the microscale the chemical potential and solubility were described by the Gibbs-Thompson and Ostwald-Freundlich relations, respectively. Different boundary profiles were initially tested in order to tune the model and qualitatively simulate the mass transport experienced by the coating under presence of an artificial crack and aggressive environments.

In a second stage based on experimental results regarding testing of different coating systems, including salt spray and drop tests on sol-gel specimens, INM adopted a different modelling approach by supporting the hypothesis that ion corrosion inhibitors are released from a porous sol-gel matrix. In order to quantify the flux of such inhibiting ions a modified Nernst-Planck equation was considered so as to consider transport of species under both ionic concentration and electric potential gradients as the main driving forces for active components. In addition, the mass transport equation was preliminarily coupled to an ionic velocity vector equation which involves porous media parameters for the matrix, e.g., radius of pores, porosity, tortuosity, potential field and capillarity pressure. Figure 1 shows the first simulation of such mathematical scaffold on a 2D domain in which activity around corrosion crack and porous structures is incorporated in the inhibitor transport.

The study of inhibitors release timescales is of great interest as the system is subject to concentration and potential gradients as main driving forces with an additional contributing term provided by capillarity forces. In such respect, approximated inhibitor release times have been calculated by using a simplified 1D Nernst-Planck model which incorporates the effects of corrosion and the inhibitor fluxes by Butler-Vollmer like dynamics. The effective mobility of the porous sol-gel matrix was computed using the Maxwell-Garnett theory of a two phase material so as to provide a qualitative transport inhibitor profile around the crack. Figure 2 (above) shows a simulated transport inhibitor release profile after 1 week for a diffusivity value of order (-7), Figure 2 (below) shows the diagram of the simplified 1D model which represents the basic scheme of a corrosion system involving an anode and cathode elements

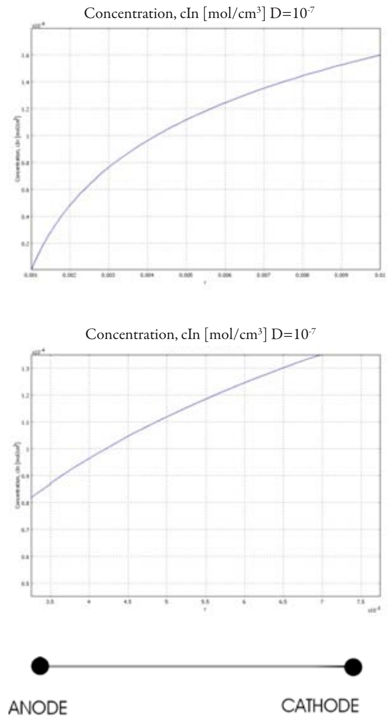

Fig. 2: (above) Transport inhibitor profile after 1 week with order diffusivity parameter (-7), (below) 1D scheme of the simplified corrosion model.

Library

Head: E. Galli

which represent sources of oxidant and inhibitor agents which are responsible for promoting and reducing the corrosion effects in the matrix.

Library

Die INM Bibliothek ist eine wissenschaftliche Spezialbibliothek mit naturwissenschaftlich-technischer Ausrichtung. Ihre Hauptaufgabe besteht in der Informations- und Literaturversorgung der wissenschaftlichen Mitarbeiterinnen und Mitarbeiter des INM. Ein Arbeitsschwerpunkt 2006 bestand darin, das elektronische Informationsangebot zu erweitern.

The INM library is responsible for supplying the staff of INM with a comprehensive and high-quality range of literature and information services. The library provides services in the fields of documentation, information research and document delivery. A survey of printed and electronic resources, books and journals is provided by the local Online Catalogue Libero as well as by the Online Public Access Catalogue of the University Library of Saarbruecken and by the Union Catalogue of Suedwestdeutscher Bibliotheksverbund (SWB)

The library is also open for students and members of Saarland University and external users. In 2006 the opening hours have been enlarged from 27 to 35 hours a week.

The INM library offers the following services: Information research in scientific databases worldwide, document delivery directly to customers working place, journal content alerting services and bibliometric analysis.

In 2006 a priority was the enlargement of the library offerings to electronic information sources worldwide. 6 computer workstations enable access to all of the library's electronic sources and licences free of charge.

Online versions of licensed journals can be found in the Electronic Journals Library of INM. In 2006 the INM library held electronic journal collections from Springer, Elsevier, American Chemical Society, Royal Society of Chemistry and also the national licences of the DFG (German Research Foundation).

Via the Database Informationsystem (DBIS) the INM library provides an overview about all available literature and information databases in science and technology. In 2006 Elsevier SCOPUS database has been licensed for use in INM. For individual in-

Facts and Figures in 2006	
New acquisitions (books, theses)	233
Journal subscriptions (print)	108
Lendings	996
Registered Library Users	323
Document delivery service	1429
Patent- and literature research	50

formation research in literature and patent databases the INM library has user licences for various information hosts worldwide, like STN, FIZ Karlsruhe, FIZ Technik, Genios.

The INM library is a member of Arbeitskreis Bibliotheken und Informationseinrichtungen der WGL and Arbeitsgemeinschaft der Spezialbibliotheken e.V.

Dr. M. Schubert, Managing director CC-NanoChem Chemical nanotechnology for new materials

Das INM hat seit dem Wechsel an der Institutsspitze einiges getan, um sich anderen Instituten und Unternehmen zu öffnen. Die Änderung der inneren Einstellung wurde in der Außendarstellung durch die Schaffung eines neuen Corporate Designs begleitet. Das neu geschaffene Logo, die neuen Imagebroschüren und der Newsletter sowie der völlig neu aufgebaute Internetauftritt erfuhren und erfahren intern wie extern große Zustimmung.

Beispiele für die neue Qualität der Zusammenarbeit mit den Ausgründungen sind die Einrichtung eines Alumni-Portals und die Schaffung der gemeinsamen Marketingplattform Saarland Empowering Nano.

Für das am INM beheimatete Kompetenzzentrum „CC-NanoChem – Chemische Nanotechnologie für Neue Materialien“ endete September 2006 die institutionelle Förderung durch das BMBF. Planmäßig erfolgte am Ende der Laufzeit die Überführung des Kompetenzzentrums in einen gemeinnützigen Verein, dessen Vorsitz von Prof. Veith übernommen wurde. Die Geschäftsstelle des cc-NanoChem e. V. bleibt auch künftig am INM und fungiert damit als Schnittstelle zwischen Institut, Öffentlichkeit, Herstellern und Anwendern von Nanomaterialien.

Von den Veranstaltungen des CC-NanoChem sind 2006 vor allem die NanoMed 2006 – 5th International Workshop on Biomedical Applications of Nanotechnology sowie drei Seminare der Reihe Innovationen durch Nanotechnologie für die Branchen Automotive, Maschinenbau sowie Architektur und Bauwesen hervorzuheben. Die Summer School für Chemische Nanotechnologie wurde aufgrund der großen Nachfrage in den vergangenen Jahren gleich zweimal durchgeführt.

Um die Zusammenarbeit der Institute innerhalb der Wissenschaftsgemeinschaft Gottfried Wilhelm Leibniz (WGL), die auf dem Gebiet der Nanotechnologie arbeiten, zu stärken und gemeinsame Stellungnahmen abgeben zu können, wurde schließlich am INM die Koordinierungsstelle Nanotechnologien der Leibniz-Gemeinschaft eingerichtet. Der Sitz der Koordinierungsstelle am INM in Saarbrücken unterstreicht die zentrale Rolle des Institutes als kompetenten und aktiven Netzwerkpartner für die nationale und internationale Nanotechnologieszene.

As most important criteria for the evaluation of economic and scientific success of a research institute the manner and the number of publications, the number of patent applications, the amount of available third-party funds and other comparably countable evaluation criteria can be mentioned. These strong parameters, verifiable with figures, allow the institute to be comparable, but they hardly permit any inference to the further development of the following years. There are some criteria that might be much more important and sustainable than any numerable values such as the support and the encouragement of motivated, open minded and creative employees.

The changes at the top of the institute and the results of the evaluation performed by the Leibniz-Association have caused a strong impulse in these soft factors. The openness towards public, companies and other institutes are actively promoted. The CEOs of spin-off companies now pay frequent visits to the INM; joint projects serve economic as well as scientific aims.

Another gratifying consequence of cooperations and commonly arranged presentations of several nano-companies at fairs as in Tokyo or Seoul, is the foundation of the label "Saarland empowering nano". Together with Nano-X GmbH, Nanogate AG, sarastro GmbH and the Saarland Economic Promotion Corporation, INM has originated this common marketing-platform at the end of 2006.

In the area of public relations we have improved a lot. To visualize the changes at the institute externally, a new corporate design has been created. The newly created logo as well as the new image-leaflets and the internet presentation received great internal and external approval. The consistently positive feed-back throughout the first year shows the changing perception of the institute. Many of those, who have sceptically prosecuted the work of the institute for the recent years, now realize INM as a competent and strong partner, with whom the transfer from top-research to commercializable products is guaranteed.

With the development of an alumni-portal, another junction in the network of scientists and entrepreneurs, who passed a pivotal part of their career at our institute throughout the past 20 years, was build up.

As a further module the first issue of INM-Nanonews has been transmitted to all friends and partners of the institute in November 2006. On four pages the reader is informed about news of the institute, such as new engagements, received honours and prizes, as well as information about participations in fairs and events, which were substantially influenced by contributions of INM-employees. Work groups are described in detail. With common comprehensibility as premise and the presentation of INM as a lively community, Nanonews stimulates the interest to learn more about the institute, its staff and its scientific results.

Apart from this, INM has specially engaged in two nano-networks in 2006: NanoBioNet e.V. and cc-NanoChem that reach – with different focuses of interest – the majority of the companies and scientists working in the field of chemical nanotechnology in Germany.

As a consequence of the end of institutional support through BMBF for the nanotechnology competence centres in autumn 2006, the organizational structure of both networks had to be changed. CC-NanoBioTech, Competence Centre with former headquarters at the TU Kaiserslautern, had been integrated into NanoBioNet e.V. By that INM is, as reference and mediating partner for requests, at disposal for a bigger circle of members of NanoBioNet e.V.; as a member INM participates in the events of the association and opens its doors for delegations and sightseeing tours.

Equally the phase of institutional support by the BMBF has ended for the competence-centre “CC-NanoChem chemical nanotechnology for new materials”. It was founded together with another five competence-centres in 1999 and has initially been conducted through INM and the University of Tübingen (later TU Kaiserslautern). Due to a great amount of members and the wide range of interest, the centre was split into two new competence-centres. The centre directed by INM continued its work under the name of CC-NanoChem, whereas the newly founded Centre in Kaiserslautern was named CC-NanoBioTech.

Until September 2003 CC-NanoChem was supported by three partners: INM, IBMT Fraunhofer-Institute for Biomedical Engineering and the chair of metallic materials of the Saarland University.

The main objectives were the national cross-linking of the actors in the field of chemical nanotechnology, the exchange of scientific experience, technology transfer from science to business, to assure a qualified and enthusiastic scientific offspring, and the intensification of regional, trans-border co-operations in Saarland-Lothringen-Luxembourg (Saar-Lor-Lux) in the scope of nanotechnology and new materials.

The number of network-members raised duplicative up to 310 persons from 220 companies and institutes.

One major field of activity of the centre was the organisation of events. Most substantial congress in the period of report surely was the "NanoMed 2006 – International Workshop on Biomedical Applications of Nanotechnology", that already took place for the fifth time. Over 200 participants from all over the world came to Berlin to get more information about latest scientific results (figure 1).

For CC-NanoChem members the thematic workshops always were of particular interest. These workshops were held at different places, combined with the visit of firms and laboratories, as for example at the locations of the members BASF AG (Ludwigshafen), Netzsch Feinmahltechnik GmbH (Selb), and Bayer Schering Pharma (Berlin). The events of CC-NanoChem, like the Summer School for chemical nanotechnology or one-day workshops allowed members to present latest scientific results and technological developments to a larger audience. This sequence of workshops is entitled "Innovation through Nanotechnology" and appeals to certain sectors with an adapted programme. In 2006 themes like automotive, engineering industry and architecture were offered.

In that year the Summer School (figure 2) took place even twice, where students, graduate students and postdocs were acquainted with all aspects of chemical nanotechnology. The assistance of numerous members to the second event in October was used to found the association of cc-NanoChem e.V., which should continue the successful network of the former CC-NanoChem at INM. The 13 founder-members designated Prof. Michael Veith as chairman,

Fig. 1: NanoMed 2006 in Berlin

Fig. 2: Participants of the Summer School chemical nanotechnology

Prof. Günter Fuhr, director of IBMT, and Prof. Matthias Hannig, director of the department of conservative dentistry, parodontology and preventive dentistry at the Saarland University hospital, as vice-chairmen. The management of the new association is directed by Dr. Martin Schubert, who was in charge of the coordination of the competence-centre in collaboration with Dr. Marius Kölbel before. Dr. Kölbel henceforth works free-lance for the association.

The support of teachers and pupils in the field of nanotechnology is of particular concern of the former and the new cc-NanoChem. For these purposes, the development of an experimental kit for chemical nanotechnology has been set on and co-operations with "Schulen ans Netz e.V." and "Nanotechnologie und Schule e.V." have been established (figure 3). Experiments and lesson-materials were discussed in a workshop for teachers. The feed-back of the practical use at school exerts influence on the melioration of instruction materials, which enables a distribution from October 2007.

The engagement in this area also results in the work packages, which cc-NanoChem e.V. will adopt in the working group of nanotechnology competence centres in Germany (AgeNT-D).

A totally different kind of network-building was proposed by Prof. Veith on a meeting of section D of the Leibniz-Association. To strengthen the collaboration between WGL-institutes working on nanotechnology and to enable common statements, a co-ordination-point for nanotechnologies of the Leibniz-Association has been created. Under the common logo "Leibniz-nano!" (figure 4) nine institutes from all parts of Germany have already signed in. The network is accessible for all institutions of WGL, working in the fields of nanoscience and nanotechnologies.

The co-ordination-point being based in INM Saarbrücken underlines the central role of the institute as competent and active network-partner for the national and international nanotechnology scene.

Fig. 3: Experimental-kit for chemical-nanotechnology, developed at INM

Fig. 4: Logo of the co-ordination-point nanotechnologies of the Leibniz-Association

Corrosion inhibiting cerium compounds for chromium-free corrosion protective coatings on AA 2024

Michael Schem, Thomas Schmidt, Hinka Caparrotti, Matthias Wittmar, Michael Veith

Summary

Due to the upcoming ban of chromium-containing corrosion protection coatings in the near future, there is a worldwide effort to find a replacement for chromium as a corrosion inhibitor that also exhibits self-healing properties in scratches but without the negative effects like health and environmental hazards. In the present study promising results to achieve this goal are shown by using cerium compounds incorporated into an organic-inorganic hybrid material produced by the sol-gel process. Cerium compounds like cerium nitrate, cerium nitrate plus acetylacetonate, cerium acetylacetonate, and cerium sulphate were incorporated in sol-gel coating systems. The corrosion protection properties of these coatings were determined by means of Electrochemical Impedance Spectroscopy (EIS) and in a conventional salt spray test. Furthermore, the leaching behaviour of the coatings was examined via Optical Emission Spectrometry (OES). Significant hints for self healing properties were obtained with a hybrid system doped with cerium nitrate in combination with acetylacetone.

Introduction

The AA 2024-T3 stands for a frequently used aluminium alloy in the aerospace industry. It combines relative high tensile strength (11 times higher than pure aluminium) with low density. The alloy consists of up to 4.9 wt% copper, 0.9 wt% manganese, 1.8 wt% magnesium, 0.5 wt% silicon, 0.5 wt% iron, and aluminium [1]. The high copper content makes the material very sensitive to corrosion attack since the copper-rich intermetallics act as local cathodes which promote the anodic dissolution of the surrounding aluminium [2]. State of the art in the corrosion protection of aluminium alloys is the use of chromium (VI)-containing coatings. Due to the toxicity and carcinogenity of chromium (VI) alternative corrosion protection coatings have to be develop.

According to the work of several groups [3-6] the use of cerium compounds appears to be a feasible alternative for the replacement of chromium. Mansfeld et, al. proposed the treatment of aluminium in cerium nitrate solutions [7], in which the substrates are kept for several hours at temperatures close to the boiling point of the solution. The long process duration appears to be impractical for industrial use, therefore in this study the use of cerium compounds in a sol-gel derived hybrid organic-inorganic coating will be discussed.

Experimental Setup

Synthesis of coating material

An inorganic-organic hybrid sol was synthesized according to reference [8]. In summary, the sol was synthesized by mixing and hydrolysing three solutions that had been prepared separately. Firstly, tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) and SiO_2 nanoparticles, as components of the inorganic network, were mixed and hydrolysed by concentrated hydrochloric acid (HCl). Secondly, for creation of the organic substructure and crosslinking with the inorganic network, 3-glycidoxypropyltrimethoxysilane (GPTS) was used. To assist hydrolysis, 0.1 M hydrochloric acid was added as a catalyst. At this stage the cerium compounds were added to the solution at cerium concentrations of 2.5 wt% and 4 wt%, calculated with respect to the solid material. Thirdly, the organic substructure of the hybrid material, consisting of 2,2'-bis-(4-hydroxyphenyl)-propane (BPA), was dissolved in an organic solvent. Finally, after completing the hydrolysis, the three solutions were mixed together. Prior to coating, the organic crosslinking was started by adding 1-methylimidazole to start the organic polymerisation.

The cerium compounds used for these experiments were cerium acetylacetonate ($Ce[acac]_3$), cerium nitrate, and cerium sulphate. Additionally cerium nitrate was dissolved in ethanol and mixed with an equimolar amount of acetylacetone (Hacac). This mixture was also added to the coating material. The samples of this material were labelled cerium nitrate plus acetylacetonate. These compounds were added to the coatings in order to achieve a cerium concentration of 2.5 wt% related to the solid coating material. Only the cerium nitrate plus acetylacetonate doped coating system had a higher solid content of 4 wt%.

Substrates and Pre-treatments

Aluminium alloy 2024-T3 was used for deposition of single layer sol-gel coatings. The aluminium samples were degreased with acetone, cleaned with Metaclean T2001 (Chemie

Vertrieb Hannover, Germany), and afterwards etched in an alkaline cleaner (Turco Liquid Aluminetch Nr. 2 from Turco Chemie, Germany). Subsequently the substrates were desmutted with Turco Liquid Smutgo NC. The coatings were applied by dip-coating with a coating velocity of 9 mm/s and cured at 120 °C for 4 h.

Characterization of the coated samples

The corrosion protection performance of the samples was characterized by means of the neutral salt spray test according to DIN 50021. The backside and the edges of the samples were covered with adhesive tape and beeswax respectively. An artificial scratch was applied in the corrosion protection coating according to Van Laar [9] in order to examine the delamination behaviour. The samples were taken out of the test once a week in order to take photos with a digital camera with a resolution of 0.07 Pixel per millimeter. These images were then used to evaluate the corrosion protection by measuring the time in the salt spray test until the first occurrence of corrosion marks

The long-term barrier performance of the coated samples were tested in a 3.5 wt% sodium chloride solution via Electrochemical Impedance Spectroscopy (EIS) using a potentiostat 2273 (AMETEK Princeton Applied Research, Tennessee, US). A three-electrode electrochemical cell with a platinum sheet and a saturated calomel electrode as counter and reference electrode, respectively, was used for the measurements. The sample testing area exposed to the electrolyte was 6.6 cm^2 and the signal amplitude was 10 mV with a frequency range between 5 mHz and 485 kHz. Electrochemical impedance spectra were recorded regularly from each coated sample. The impedance values from the low frequency range can provide information about the self-healing properties of a coating-system [10]. For this reason in particular the impedance values at 0.01 Hz were considered in this work and were plotted against the immersion time.

Following the EIS measurements, Tafel plots (± 20 mV from the open circuit potential (OCP)) were carried out for determining the corrosion current density of these coated samples.

The possibility that an inhibitor is released from a coating and migrates to a scratched area is a basic requirement for self-healing properties of a

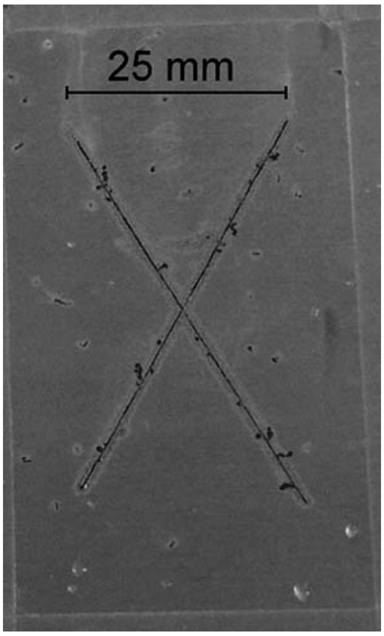

Fig. 1: Coating material without cerium compounds after 330 h salt spray test

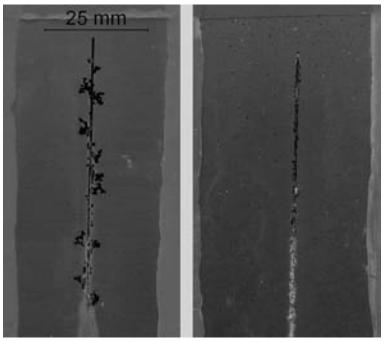

Fig. 2: Cerium sulphate (left) and cerium acetylacetonate (right) filled coatings after 336 hours salt spray test

coating. For this reason the leaching of cerium out of the coatings after certain periods of time (2.5, 24, 96, and 120 h) in aqueous media was determined via Inductively Coupled Plasma / Optical Emission Spectrometer (ICP/OES) ULTIMA 2 (HORIBA Jobin Yvon GmbH, Munich, Germany). Each double-sided coated sample with a total coating area between 44 cm^2 (cerium nitrate plus acac) and 50 cm^2 (Ce[acac]$_3$) was cut in four pieces and was immersed in 100 ml bidest water. To avoid a direct contact of the sample pieces in the immersion medium, the edges were coated with beeswax. After a certain time (2.5, 24, 96, 120h), a water sample of 10 ml was taken out of the immersion medium and subsequently analysed via ICP/OES. The coating thicknesses were measured by means of a magnetic induction method with a PERMASCOPE (Helmut Fischer GmbH & Co, Sindelfingen, Germany).

Results

The coating system without cerium compounds showed first corrosion marks after 170 hours. After 336 hours of neutral salt spray test corrosion in the general area as well as sub-surface migration at the artificial scratch is clearly detectable (figure 1).

While the cerium sulphate containing coatings showed creepage at the artificial scratch after 336 h of salt spray testing, the cerium acetylacetonate filled coatings exhibited pitting all over the substrate after the same time. A comparison of the cerium sulphate, and cerium acetylacetonate filled coatings after 336 hours salt spray test is displayed in figure 2. Comparing cerium sulphate and cerium acetylacetonate filled coatings with unfilled ones demonstrates a slightly reduced amount of pitting (figure 1 and figure 2). In the case of cerium nitrate the substrate remained without traces of corrosion for 700 hours (figure 3).

The coating filled with cerium nitrate plus acetylacetone showed no corrosion marks for 1800 hours of neutral salt spray testing. A comparison of images of this coating system after 336 h and 1800 h respectively is shown in figure 4.

The coating thickness is in the range of 10 µm for all samples (table 1). Therefore the influence of the coating thickness on the corrosion protection properties is negligible.

Sample name	Coating thickness
• Unfilled coating	9 µm
• Cerium nitrate	13 µm

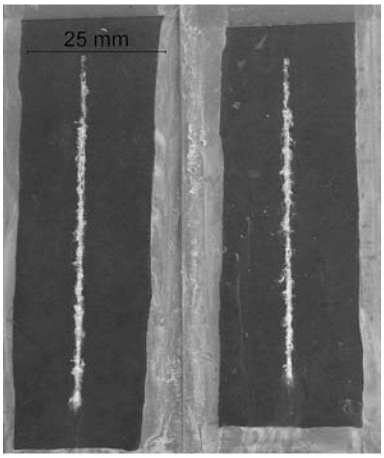

Figure 3: Photo of cerium nitrate containing coatings after 750 hours salt spray test.

Sample name	Coating thickness
Unfilled coating	9 µm
Cerium nitrate	13 µm
Cerium acetylacetonate	9 µm
Cerium sulphate	8 µm
Cerium nitrate plus acac	11 µm

Table 1: Measured coating thicknesses

- Cerium acetylacetonate 9 µm
- Cerium sulphate 8 µm
- Cerium nitrate plus acac 11 µm

The Tafel plots of these coating systems after one hour and 40 minutes immersion in a 3.5 wt% sodium chloride solution are shown in figure 5. The largest corrosion current density of about 5 x 10^{-6} A / cm^2 as well as the lowest OCP of 0.84 V showed the cerium sulphate doped coating system. The second lowest corrosion current density of around 10^{-8} A / cm^2 but the highest OCP of -0.15 V exhibited the cerium nitrate plus acac coating system. The unfilled and the Ce acac doped coating system showed similar corrosion current densities of 2 x 10^{-10} A / cm^2 and 4 x 10^{-10} A / cm^2 as well as similar OCPs of 0.61 V and 0.65 V, respectively. The cerium nitrate coating system showed the same corrosion current density as the Ce acac coating system but a considerably higher OCP of -0.18 V.

The long-term impedance modulus behaviour of the tested coating systems, measured via EIS, is shown in figure 6. Altogether, the unfilled coating system exhibited the highest impedance modulus of up to 180 MOhm cm^2 in comparison with the cerium salt doped coating systems, which only have impedance modulus values under 9 MOhm cm^2. The unfilled coating system, the cerium nitrate and the Ce acac doped coating system showed a relatively fast decreasing impedance modulus in time. In contrast the cerium nitrate plus acac coating system exhibit at the beginning an increasing impedance modulus and then only a slow decrease of the impedance modulus in time. The experiment of the cerium sulphate doped coating system is still running.

The results of the leaching experiments are presented in figure 7. Leaching of cerium was only proven for the cerium nitrate plus acac doped coating system after 96 and 120 h immersion time. The other coating systems are apparently not able to leach out their cerium ions.

Discussion

The cerium compounds examined in this study were selected in order to compare cerium compounds of different solubility with cerium nitrate, which was proposed for corrosion protection on aluminium by Mansfeld [7]. Cerium nitrate and cerium sulphate are soluble in water, while cerium acetylacetonate has only a limited solubility in water due to the chelating properties of acetylacetona-

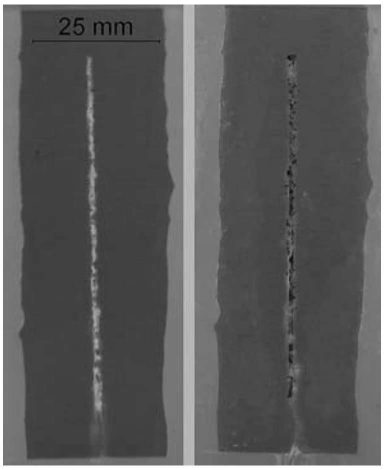

Fig. 4: Image of cerium nitrate plus acetylacetone filled coating after 336 h (left) and 1800 h salt spray testing

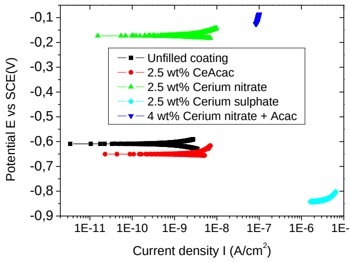

Fig. 5: Tafel plots (± 20 mV vs. OCP) of the four different cerium compound-doped coating systems as well as the unfilled coating.

te. The limited solubility of cerium acetylacetonate may be an advantage, because the dissolution of the corrosion inhibitor may cause porosity which then weakens the barrier properties of the coating, or on the other hand the inhibitors may be leached to the environment without fulfilling their purpose of corrosion inhibition, if the inhibitor is leached out of the coating because of the high solubility.

The different behaviour of the coatings can be explained partially by the differences in solubility. Because of the limited solubility of Cerium acetylacetonate, only a very small amount of cerium will be released from the coating in order to block corrosion sites. In the case of the soluble cerium compounds cerium sulphate and cerium nitrate, the reason for the difference in corrosion protection can be found in the critical inhibitor concentration. As published by Bhattamishra and Banerjee it is necessary that in the case of cerium sulphate a critical concentration of about 500 ppm inhibitor in aqueous 3.5 % NaCl solution is exceeded to facilitate efficient corrosion protection, while even low amounts of cerium nitrate increase the corrosion behaviour of aluminium [3]. In the leaching experiments it turned out that even in the case of cerium nitrate, which showed good performance in the salt spray test, the amount of inhibitor in the diluent was below the limit of detection of the ICP/OES. Only in the case of the cerium nitrate plus acac samples the cerium concentration was higher than the limit of detection.

Concerning the electrochemical examination, the addition of cerium nitrate resulted in ennoblement, i.e. an increase of OCP, of the coated specimens. The absence of the cathodic branch of the cerium nitrate plus Hacac and the cerium sulphate coating system is due to the reduction of metal ions of the passive film or the barrier oxide layer, which resulted in a shift of the OCP toward negative directions [11]

Relating to the results of the SST, leaching, and EIS measurements the best performance of all samples examined exhibited the cerium nitrate plus Hacac coating system in particular in contrast to the cerium nitrate doped coating system without Hacac. It showed the best performance in the salt spray test and was the only system in which a leaching of cerium could be proven. Furthermore, only this coating system shows at the beginning of the long-term impedance modulus measurements an increasing

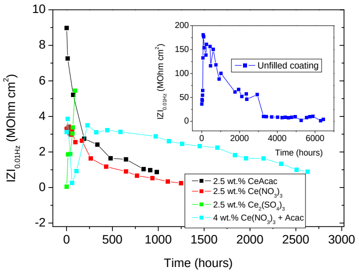

Fig. 6: Impedance modulus Z (at 0.01 Hz) against the immersion time in a 3.5 wt.% sodium chloride solution of four different cerium salts doped coating systems as well as an unfilled coating measured via EIS.

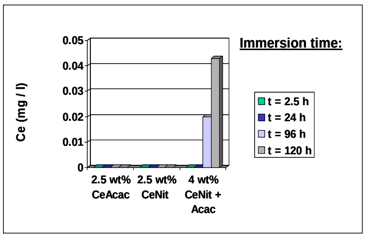

Fig. 7: Contents of cerium in dependence on the immersion time of three different cerium salts doped coating systems as well as the undoped coating system in aqueous media measured by means of Optical Emission Spectrometry.

of the impedance modulus and at the same time only a slightly decrease of that value in time. Altogether, the presented results can be taken as clear evidence of self-healing properties of the hybrid coating doped with cerium nitrate in combination with acetylacetone on AA2024.

The findings presented in this paper may be interpreted as evidence, that in the case of the cerium nitrate plus acac doped coating system the amount of released corrosion inhibitors is sufficient for efficient corrosion protection in contrast to the cerium nitrate, cerium sulphate, and cerium acetylacetonate doped coating systems. However, up to now it is not clear if this behaviour is caused by the higher cerium concentration, the beneficial combination of cerium nitrate with acac, or a mixture of both. The effect of the addition of acetylacetone to coating systems with varying cerium nitrate concentrations is subject of currently running experiments.

Conclusions

Cerium nitrate in combination with acetylacetone is an efficient corrosion inhibitor, when used as additive to hybrid organic-inorganic coatings. The results of the salt spray test, leaching experiments, and EIS measurements show clear evidence of self-healing behaviour in that coating system during the first 300 h. Cerium nitrate is according to the salt spray test perfomance the second best additive to the hybrid coating system used in this study.

The other cerium compounds examined show only limited corrosion protection abilities due to the results of the electrochemical- and salt spray tests.

Outlook

Further experiments will be conducted in order to analyse the leaching behaviour of the coatings. New pathways of storing corrosion inhibitors in the coating will be tested soon.

Acknowledgements

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Annotation

The results presented here have also been published during the EUROCORR 2007.

Microstructure investigation of reflective coatings interference multilayers produced by sol-gel method

Mohammad Hossein Jilavi, Ebru Devrim Sam, Ulf Werner, Peter William Oliveira, Michael Veith

1. Introduction

Reflective and antireflective coatings play an important role in different branches of industry like optical devices, solar panels, medical devices (endoscopes), architecture, etc. The reason for this is the increase or reduction of transmittance or reflectance of the surfaces to the desired values. Transmittance and reflectance have to be optimized at different wavelengths depending on the application of the products.

There are different methods to change the reflectance of the surfaces: a) reflectance of the surface can be increased by coating the surface with metal (Al, Ag); b) reflectance of the surface can be decreased by coating the surface with moth eye pattern (coating with micro roughness on the surface or etching of the surface); c) reflectance of the surface can be decreased or increased by coating the surface with interference multilayers (the layers contain low and high refractive index materials). This paper is focused on the interference multilayers for increasing the reflectance of glass substrate from 8% up to 80%.

Producing of interference multilayers for performance of high or low reflectance can be achieved by different technological coating methods, like PVD-, CVD- and sol gel methods.

In this paper, sol-gel method is chosen as a coating method. The reason for this selection is the economical point of view. In general, the sol-gel method does not require expensive vacuum equipments. This makes sol-gel systems popular for coating large substrates. Generally, for low to high optical performance, the sol-gel method is cost effective in comparison to the other methods, especially if stack firing is used. Nowadays, it is possible to coat the interference layers not only on the glass substrate but also on the plastic foils. In this paper, the interference layers are coated on glass substrates. The main motivation for this paper is to investigate the microstructure of five layers reflective coatings by high resolution transmission and scanning electron microscopes (HRTEM, HRSEM) regarding pores, micro cracks and crystallinity of nano particles inside the layers.

2. Experimental details:

2.1. Optical performance simulations

The design for a 5 layer reflective interference filter with a maximum of reflectance at 550 nm was elaborated by computer simulation (simulation software: TF calc, version 3.5). The appropriate refractive indices were measured experimentally (ellipsometry) at a single layer coating of SiO_2 and TiO_2 sols on the glass substrates.

2.2. Optical performance dip coating

At INM, coating solutions based on surface modified high (TiO_2) and low (SiO_2) refractive index nanoparticles have been developed [1]. These sols are well suitable for the preparation of interference multilayer systems on glass [2].

In order to clean the glass substrate, it was polished at first with CeO_2 and washed in a dishwasher with a detergent at a particular program for glass substrate.

The multi layer design was realized on glass substrate in size 21 x 29,7 cm^2 using a dip coating machine in a clean room. This technique allows the deposition of layers with the same thickness on both sides of a glass pane in one coating step.

After each coating step, the coated sheet was dried for 3 minutes at 120 °C. Finally, the whole stack (up to 5 single layers) can be fired in one step at 450 °C, so called stack firing [3]. (Stainless steel muffle, 0.5 m x 0.5 m x 0.5 m). This is a cost saving heating process compared to the single layer firing process [4]. The furnace was heated from 25 °C to 450 °C with a heating rate of 2.5 K/min, the temperature was held for 45 minutes at 450 °C and cooled down to 25 °C with an estimated rate of 0.7 K/min by switching off the heating and keeping the door closed over night.

The surface modified nanoparticles arrange themselves to very dense and smooth layers (average roughness < 10 nm [5]) during the film formation.

Coating thickness, refractive indices and reflectance loss were measured by UV-VIS-spectroscopy (Cary 5E spectrometer, VARIAN Australia, Pty-Ltd) and spectral ellipsometry (SOPRA, ES4G).

2.3. TEM investigation

For TEM specimen preparation, a cross- sectional specimen preparation method was used. The samples were cleaved with a diamond pen and were glued face to face on the coating sides with epoxy (Gatan), which hardened after 30 minutes at 100 °C. After cutting the glued sample by an ultrasonic driller in a cylinder form, it was fitted into the rigid brass tube. The glued sample in the tube was glued again with epoxy. Disks of approximately 500 µm thick were cut from the tube with diamond plate, polished, and dimpled to approximately 20 µm thickness in the center of the TEM specimens. They were then ion milled with an argon ion beam (Baltec RES 010), operating at 5 kV accelerating voltage on rotating specimens inclined to the argon beam (2°). Finally the specimens were carbon coated for electron conduction during TEM-investigation.

The microstructure and the microanalysis of the coated glass samples were examined by a field emission gun TEM (Philips CM200 FEG) operated at 200 kV, equipped with x-ray energy dispersive spectrometer (EDS).

2.4. SEM investigation

The microstructure and the microanalysis of the coated glass samples we examined and conducted by

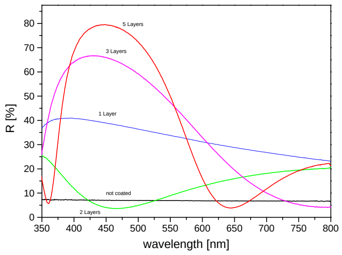

Fig. 1: The spectra of the glass substrate before coating, the single layer (H), two layer system (HL), three layer system (HLH) and five layer system (HLHLH) show the reflectance (R) versus the wavelength between 350 and 800 nm
H: high refractive index,
L: low refractive index.

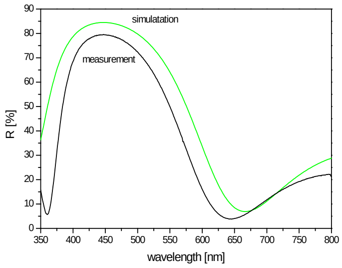

Fig. 2: Measured and simulated spectra of the five layer system (HLHLH) show in the reflectance (R) versus the wavelength between 380 and 800 nm.

HRSEM operated at 10 kV (JEOL 6400F), equipped with x-ray energy dispersive spectrometer (EDS), in planar and cross-sectional views. The cross-sectional views of multilayers were recordered at the broken samples. The planar views were recordered at the surfaces of the layers. All SEM samples were decorated with a very thin layer of gold coating (10 nm) for electron conduction.

2.5. Spectroscopic measurements

Refractive indices and reflectance were measured by UV-VIS-spectroscopy (Cary 5E spectrometer, VARIAN Australia, Pty-Ltd) and spectral ellipsometry (SOPRA, ES4G). Reflectance was measured at middle part of coated sample. For the determination of the refractive index of a single layer, a very thin layer was coated using dip coating method on the same type of glass substrate. The layer was thermally cured as described in part 2.2.

3. Results and discussion

3.1 Spectra

A five interference layer system was realized on a glass substrate by the deposition of TiO_2 (H) and SiO_2 (L) layers using a dip coating method in order to develop a high reflective coating in the visible range (H and L stand for high and low reflective material). The refractive indices of H-Sol (TiO_2) and L-sol (SiO_2) are 1.90 and 1.49 (at 550 nm) respectively. All glass substrates were coated on both sides. Figure 1 shows the spectra of the different coating systems. The single layer (H) increases the reflection in the whole visible range from 8% to about 30%, whereas the coating system of two layers (HL) produces an antireflective coating with 3% reflection at around 470 nm. A three layer system (HLH) increases the reflectance in visible region up to 67%. Four layer system produces an antireflective coating (HLHL). Finally, the system consisting of five layers (HLHLH) increases the reflection in the visible region to approx. 80% (at 450 nm).

Figure 2 shows the measured and simulated spectra of the five layer system (HLHLH). The real five layer system indicates a main maximum reflection value of 80% at 448 nm but the simulated five layer design has its main maximum of 84% at 448 nm. It can be supposed that this difference comes from a diffusion process at the phase boundary between the layers. In this case a refractive index

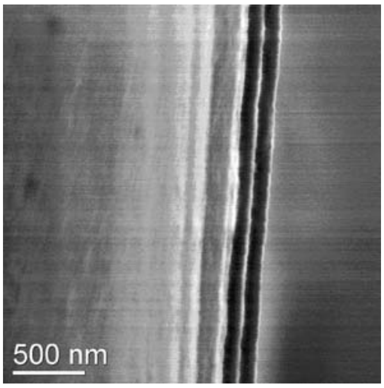

Fig. 3: Cross-sectional overview of the layers. Only two layers can be seen clearly. Coating thickness are around 100 nm, which can be exactly determind by HR-TEM.

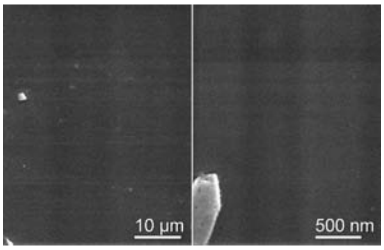

Fig. 4: An overview (a) and high magnified (b) SEM- micrographs of the surface last layer. There are no cracks or micro-pores on the sur face. The artefact particles on the surface are just a help to make sure that the images are in focus.

gradient should occur between the layers. One can verify this assumption through investigating the phase boundary by using transmission electron microscopy. Unfortunately, this multilayer coating is not proper for such an investigation of phase boundary interdiffusion because both sols (H and L) contain TiO_2 and SiO_2 nanoparticles. But in the near future, pure TiO_2 and pure SiO_2 nanoparticles are going to be used for sols H and L respectively. These pure layers should allow to investigate exactly the interdiffusion between layers using microchemical analysis by HRTEM.

SEM-investigations show that the coatings are very smooth and homogeneous. The SEM-micrographs of the surfaces prom first to forth layer look all alike as shown in figure 4. Both SEM- micrographs show that the surface is free of cracks and pores. The cross sectional SEM micrograph of the fracture surface did not show the five layers together (it could be that some layers are broken during sample preparation or they could not be brought to focus simultaneously). Nevertheless this micrograph reveals the approximate value of layer thickness. In order to know the exact thickness of the layers, it is necessary to make a very fine polished SEM sample or a thinned TEM sample.

The cross-sectional TEM micrographs (figures 5 and 6) show that the layers are very homogeneous and there are no pores or cracks in the layers. The coating thickness can be measured exactly. For the TiO_2 layers they were found to be 45, 49, and 55 nm respectively. The thickness of the two SiO_2 layers are very similiar around 65 nm. The diffraction patterns of the TiO_2 and SiO_2 layers (figure 6) indicate that they are made of crystalline and amorphous phases respectively.

Microanalysis of the layers are shown in figure 7. TiO_2 layers contain, as expected, small amounts of SiO_2 particles and also SiO_2 layers contain small amount of TiO_2 particles. Different variation of sols has shown that this chemical compositions results in very homogeneous layers when processed by the coating process.

4. Conclusion

It was shown that a system of five reflective layers can be produced by sol gel method with a stack firing as final heat treatment. The microstructure studies of the layers by HRTEM and HRSEM showed that there are no cracks or pores in submicrometer

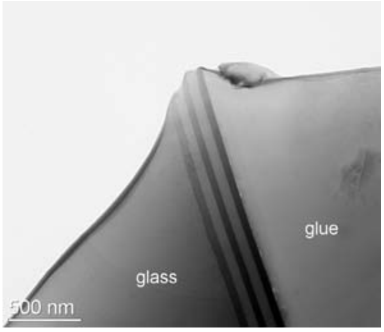

Fig. 5: TEM micrograph of cross sectional overview of the interference multilayers

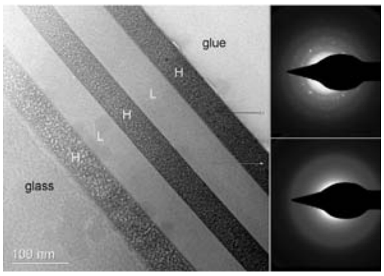

Fig. 6: High magnification of cross sectional view of multilayers by HR TEM. Dark layers are TiO_2 layers and bright layers are SiO_2 layers

size in and at the surface of layers and especially on the top layer. The thicknesses of TiO_2 and SiO_2 layers are in the range between 45-55 nm and 65 nm respectively. The crystalline phase of TiO_2 and amorphous phase of SiO_2 nanoparticles were observed by HRTEM. A small reflectance differences between simulated and real interfrence multilayers could be originate from interdiffusion of TiO_2 and SiO_2 nanoparticles at the phase boundaries. This is an issue for the next investigation in which pure TiO_2 and pure SiO_2 layers have to be produced for such an investigation. The purity of layers may allow to investigate the phase boundaries with respect to interdiffusion in detail via michrochemical analysis by HRTEM.

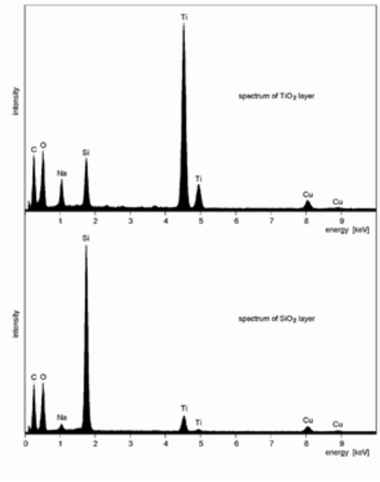

Fig. 7: Energy dispersive x-ray spectra of the TiO_2 and SiO_2 layers

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Investigation on thermal and chemical stability of polymer based easy-to-clean nanocomposite systems

Ralf.Gerdes, Pamela Kalmes,
Carsten Becker-Willinger

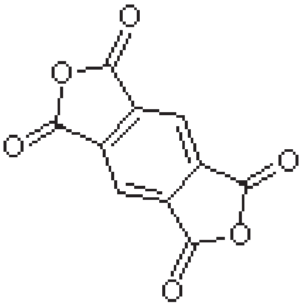
Abstract

Anti-adhesive coatings are of significant importance for many industrial processes such as pigment and paint production as well as also food processing industry, because they can help to significantly reduce the cleaning effort. For this reason, the amount of cleaning chemicals and waste water can be reduced, which should have a remarkable effect on the process costs. In this investigation abrasion resistant low surface free energy coatings based on fluoroalkyl group and SiC particles containing polyimides have been synthesised which show surface properties comparable to PTFE and can be coated like a paint on surfaces. Especially in food production processes a high chemical stability is required for coating materials to withstand the cleaning procedures which are used in order to maintain the hygienic situation in the production facilities. The investigations revealed a high abrasion resistance (weight loss approx. 12 mg after 1000 cycles taber abrader test) and a moderate chemical stability of the coating systems. A chemical attack by sodium hydroxide solution as

well as by oxidising substances such as nitric acid (HNO_3) at elevated temperatures (90°C) led to a fast destruction of the coating performance caused by damage of the organic matrix. Also the exposure with carrot juice and milk at 90°C showed some influence. The contact angles against water decreased by about 20-30% whereas the oleophobic properties remained almost unchanged. On the other hand the polyimide nanocomposites showed a low surface roughness ($R_a \leq 0.2$ µm) and adjustable antistatic properties, what enables to use them in dry food processing (e.g. in flour mills). By using a nanocomposite system filled with 10 wt.-% carbon black FW 200 a resistivity of 1.5x103 Ω and a charge decay time of 0 s were obtained.

Introduction

Since many decades coatings based on polytetrafluoroethylene (PTFE) and its derivatives have been and still are in use to create anti-adhesive coatings for surfaces, which are in contact with food such as e.g. kitchenware and pans [1, 2]. In order to obtain long lasting coatings on this basis, an intensive pre-treatment and the use of primers is necessary to obtain sufficient adhesion to the substrate. The application is followed by a thermal treatment of the surface at temperatures in the range of 400°C, which limits the types of substrate materials and requires an industrial process for the application on parts. For the use of anti-adhesive coatings in food production industry it is important to provide materials, which can be applied on site on already existing equipment and show adhesion to different kinds of substrate materials such as stainless steel, plastics and even sometimes on glass. Starting from the early nineties also thin anti-adhesive coatings based on the sol-gel process and fluorosilanes have been investigated intensively, which combined an excellent adhesion to almost all types of substrate materials with transparency and excellent hydrophobic and oleophobic properties [3, 4]. Besides their interesting base properties these types of materials finally could not be used in food production processes, because they showed a low resistance against mechanical abrasion and high pH cleaning substances such as sodium hydroxide solution at elevated temperature. Some years ago now a new class of organic-inorganic nanocomposite materials has been developed that combines high abrasion stability with alkaline resistance and paint ability [5]. Especially the polyimide



Pyromellitic dianhydride - PMDA [89-32-7]

Fig. 1: Chemical structure of used anhydride compounds

types [6] and polyurethane types [7] based on this approach have been investigated more in detail regarding to abrasion resistance in combination with heat resistance and chemical resistance respectively. The polyimides in particular allow many variations with regard to the monomer composition which enables to vary flexibility, polarity as well as their chemical stability [8-27]. In order to reduce the water uptake of polyimides, many investigations have been carried out to incorporate hydrophobic components, such as fluorine containing hydrocarbons [28-40]. As the above approach [5, 6] described mainly the influence of the type of (nano)particulate filler on the mechanical, thermal and chemical properties, it was of high interest for the present work to investigate the influence of monomer composition and fluorocarbon content of such type of polyimide nanocomposite systems on the anti-adhesive behaviour under technical conditions.

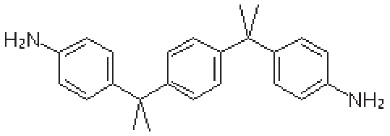
2 Experimental

Materials and preparation procedures

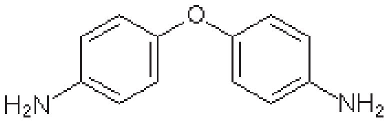
For all coating compositions pyromellitic dianhydride - PMDA (ABCR) was used as anhydride component, SiC (H.C. Starck SiC Grade UF 10, average particle size/ d50: 0.70 µm) as ceramic powder filler and Fluorolink D (Solvay Solexis, average equivalent weight: 1000) as reactive fluoro compound. In order to investigate the influence of the matrix structure on the properties of the polyimide based coatings with respect to the mechanical and chemical stability the different amine compounds Bis(4-aminophenyl)-1,4-disopropyl-benzene – Bisaniline P (Aldrich), 4,4'-Oxydianiline - ODPAm (Aldrich), 3-Aminophenyl sulfone – 3-APS (Aldrich), 4,4'-Bis(3-aminophenoxy) diphenyl sulfone – BAPPS (ABCR) have been used. The chemical formulars of the monomers used are shown in Figure 1 and Figure 2 respectively.

Table 1 gives an overview about the variations in the matrix system. The amount of SiC filler has been kept constant at 40 wt.-% in the solid content. All starting materials were used without further purification.

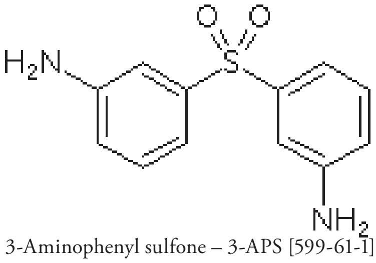
For the preparation of coating materials monomers (PMDA, amine compound, SiC and Fluorolink D) were mixed using a bead mill (Dispermat) in NMP as solvent. For this purpose the starting chemicals were filled together with NMP and glass beads (diameter: 1.7-2.0 mm) in the mil-



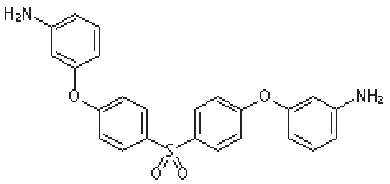
Bis(4-aminophenyl)1,4-disopropyl-benzene – Bisaniline P [2716-10-1]



4,4'-Oxydianiline -ODPAm [1013-80-4]



3-Aminophenyl sulfone – 3-APS [599-61-1]



4,4'-Bis(3-aminophenoxy)diphenyl sulfone - BAPPS [30203-11-3]

Fig. 2: Chemical structures of used amine compounds

ling container and were stirred with the corresponding milling tool for 2 hours at 60°C and 2000 rpm. Then the coating material was separated from glass beads by filtration using a sieve to obtain a mixture ready for application. All coating compositions have been applied on stainless steel substrates (1.4301 – dimension: 100x100 mm) using the spray-coating method followed by thermal curing for 2 hours at 200°C.

Measurements

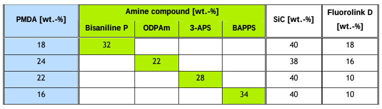
The determination of static contact angles was performed according to the horizontal drop method using a goniometer. For this purpose drops of corresponding solvent (water and hexadecane) with a defined size (about 3 µl) were applied and the angle between the baseline of the drop and the tangent at the drop boundary was measured. The measurement was performed at room temperature (approx. 20°C) and three drops per sample and test liquid respectively were measured.

The determination of surface roughness was carried out by a perthometer, whereas the surface which should be characterized was scanned with a diamond stylus (scan length: 5.0 mm, scan speed: 0.1 mm/ s, stylus force: 15 mg). Afterwards, the different roughness values like Ra, Rz and Rmax were automatically calculated from measured surface data.

The verification of mechanical stability, was performed by Taber Abraser Test according to DIN 53 754. For a further quantification of mechanical stability of the different coating compositions the static contact angles against water and hexadecane were measured by goniometer.

In order to determine the thermal stability the coated substrates were exposed in a convection oven at 150°C for at last 120 hours. After cooling down at ambient temperature (approx. 20°C) the static contact angles against water and hexadecane were measured by goniometer to quantify the thermal stability.

In order to verify the chemical resistance the corresponding test liquids (NaOH 2%, HNO_3 2%, milk (UHT-milk) and carrot juice) were filled in small pots, which were fixed on the coated substrates (cp. figure 3). Afterwards the so prepared samples were put in a convection oven and were exposed for 24 hours at 90°C. After cooling down at ambient temperature (approx. 20°C) the static contact angles against water and hexadecane were measured by goniometer to quantify the chemical stability.



PMDA [wt.-%]	Amine compound [wt.-%]				SiC [wt.-%]	Fluorolink D [wt.-%]
	Bisaniline P	ODPAm	3-APS	BAPPS		
18	32				40	18
24		22			38	16
22			28		40	10
16				34	40	10

Table 1: Investigated compositions of imide based coating materials depending on used amine compound

Fig. 3: Experimental setup for determination of chemical resistance of coatings. Blue pot is filled with corresponding test liquid and fixed on the coated substrate.

3 Results and discussion

3.1 Anti-adhesive polyimide nanocomposite base systems

In order to investigate the influence of the matrix structure in polyimide based anti-adhesive nanocomposite coating systems on the anti-adhesive properties under different loading conditions, different types of aromatic diamine monomers have been chosen to form the intended polyimide structures in combination with pyromellitic dianhydride and carboxylic acid terminated perfluoropolyether (Fluorolink D). As can also be derived from the chemical formulas in Figure 2 the polarity of the diamine monomers increases in the sequence Bisaniline P, ODPAm, 3-APS and BAPPS. It was of interest to investigate the influence of the type of monomer on the initial hydrophobic and oleophobic properties and the stability of the anti-adhesive effect in dependence on the type of external load. Because these monomers have different molecular weight, the variation of the type of diamine should also have an influence on the network density which determines the mechanical surface properties. SiC has been used as nanoparticulate filler at a constant concentration of 40 wt.-%. All monomers and the filler particles have been mixed in a bead mill at 60°C for two hours using NMP as solvent. During this procedure a polyamic acid structure has been formed. This reactive mixture has been coated by spraying technique on stainless steel plates and has been cured at 200°C for again two hours. Figure 4 shows the dependence of the initial static contact angles on the monomer composition in the polyimide nanocomposites on stainless steel.

From Figure 4 it can be derived that all the systems show a behaviour in the contact angle quite comparable to PTFE (contact angle against water/ hexadecane: 118°/ 55°). The observed small differences can be attributed to differences in surface roughness between all the nanocomposite systems and also the PTFE. No distinction can be made also with respect to the monomer composition, which means that the monomer polarity has no influence on the initial static contact angle. This behaviour can be explained by the fact that the Fluorolink D component has enough mobility during the curing process in order to orient its hydrophobic and oleophobic chain to the coating air interface. This enrichment leads to a saturation of the coating surface with perfluorinated carbon chains, which

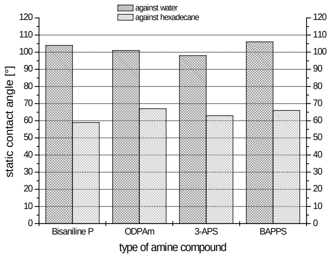
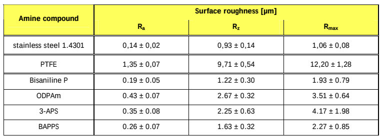


Fig. 4: Initial anti-adhesive properties: Static contact angles (by goniometer) against water and hexadecane depending on used amine compound – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C.



Amine compound	Surface roughness [µm]		
	R_a	R_z	R_{max}
stainless steel 1.4301	0,14 ± 0,02	0,93 ± 0,14	1,06 ± 0,08
PTFE	1,35 ± 0,07	9,71 ± 0,54	12,20 ± 1,28
Bisaniline P	0.19 ± 0.05	1.22 ± 0.30	1.93 ± 0.79
ODPAm	0.43 ± 0.07	2.67 ± 0.32	3.51 ± 0.64
3-APS	0.35 ± 0.08	2.25 ± 0.63	4.17 ± 1.98
BAPPS	0.26 ± 0.07	1.63 ± 0.32	2.27 ± 0.85

Table 2: Surface roughness from perthometer depending on used amine compound – substrate material: stainless steel (1.4301) – coating technique: spray coating – curing conditions: 2 h at 200°C.

then dominates the surface properties. To facilitate the interpretation of the contact angle behaviour, table 2 shows the surface roughness of the polyimide nanocomposites from perthometer measurements.

Table 2 shows that smooth surfaces could be obtained with the nanocomposite coatings. The roughness is only slightly higher than that of the stainless steel, whereas the PTFE roughness is about three times higher compared to the nanocomposites. This micro-roughness explains the higher initial contact angle against water of the PTFE. Taking this into account the initial contact angles of the nanocomposites are on a quite reasonable level. In order to use the coatings in practical applications such as food production industry the mechanical resistance of the resulting coated surfaces is of high importance. The durability of the anti-adhesive effect has been investigated using the taber abrader test. Figure 5 shows the percental decrease of the static contact angle after 1000 cycles taber abrader test in dependence on the type of diamine monomer used in the polyimide matrix.

It can be derived from Figure 5 that the monomer composition with the diamine having the lowest polarity also shows the lowest degradation of the anti-adhesive properties after mechanical abrasion. Nevertheless the highest decrease of about 20 % for the system with BAPPS is still tolerable and a sufficient anti-adhesive effect is expected also for this system.

Figure 6 gives additional information about the temperature stability of the nanocomposite systems. This property is especially important if dry processes during the food production are in the focus of the application but also in wet processes such as ultra high temperature treatment of e.g. milk a high temperature stability is required.

From the behaviour of the contact angle in dependence on the duration of temperature load at 150°C in Fig. 6 it can be derived that all the nanocomposites should have enough long term thermal stability with respect to the anti-adhesive effect. The PTFE sample on the other hand does also not degrade in this test.

After these basic investigations it was of interest to obtain information about the behaviour under chemical load conditions. During food production process several cleaning steps are required to be performed by the producer to maintain an uncritical hygienic situation in the components of the production system,

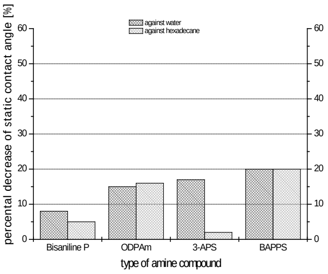


Fig. 5: Percental decrease of static contact angle against water and hex adecane after 1000 cycles taber abraser test – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

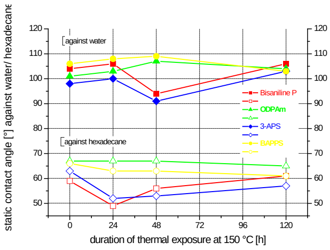


Fig. 6: Static contact angles against water and hexadecane depending on type of amine compound as well as on duration of thermal exposure at 150°C – substrate material: stainless steel (1.4301) – coating technique: spray coating – curing conditions: 2 h at 200°C

which are in direct contact with the food in order to avoid germ formation and growth of bacteria to occur. Of course also the coating materials have to withstand these cleaning conditions even though they have been applied originally to reduce the cleaning effort in order to ensure maximum product safety at any time during the production process. Two typical cleaning agents, sodium hydroxide solution (NaOH, 2 %) and nitric acid (HNO_3, 2 %), have been chosen. The temperature during exposure was chosen to be 90°C to simulate the cleaning step in the facilities. Table 3 shows the results of the cleaning simulation in comparison to two products (milk and carrot juice), which are critical for deposition phenomena in thermal treatment processes.

It is obvious from the results in Table 3 that after 24 h chemical attack by NaOH and HNO_3 at 90°C leads for almost all polyimide systems to destruction of the coating layer. This behaviour was somewhat expected before, because the hydrolytic stability of the imide groupings is limited. In addition to that the HNO_3 has oxidising capability and can attack the organic matrix also by this mechanism. Also the PTFE is not completely unaffected. The real substances milk and carrot juice also show some influence on the remaining anti-adhesive behaviour. The decrease in contact angle against water and hexadecane is more pronounced than in case of e.g. mechanical impact from the taber abrader test, as can also be derived from figure 7 and figure 8, which show the percental decrease of the contact angle after exposure to milk and carrot juice at 90°C respectively.

In the case of milk the oleophobic properties seem to be almost unaffected whereas the hydrophobic properties show a decrease of about 20-30 % during the exposure.

The polyimide nanocomposite comprising BAPPS as diamine monomer shows a significant decrease especially in the oleophobic properties after thermal treatment with carrot juice. It should be mentioned that this coating surface has been visually affected by the carrot juice resulting in discolouration. For this reason, it could not completely be excluded that some deposits of components of the carrot juice have been built, which are responsible for the minimisation of the oleophobic effect. The deposits may have been built especially in the case of the most polar co-monomer BAPPS. This assumption will be further proved by

Amine compound	Contact angle [°] against water/ hexadecane				
	initial	after 24 h NaOH (2%) pH 13	after 24 h HNO_3 (2%) pH 1	after 24 h milk	after 24 h carrot juice
PTFE	118/ 55	86/ 52	77/ 51	118/ 55	115/ 54
Bisaniline P	104/ 59	destroyed	destroyed	84/ 57	84/ 56
ODPAm	101/ 67	80/ 57	destroyed	76/ 65	77/ 64
3-APS	98/ 63	destroyed	71/ 63	71/ 61	68/ 60
BAPPS	106/ 66	destroyed	destroyed	81/ 61	73/ 31

Table 3: Measured static contact angles against water and hexadecane depending on type of amine compound as well as on chemical exposure (NaOH, HNO3, milk and carrot juice) at 90°C for 24 h – substrate material: stainless steel (1.4301) – coating technique: spray coating – curing conditions: 2 h at 200°C

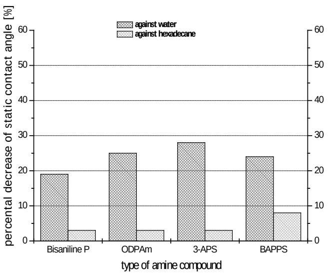


Fig. 7: Percental decrease of static contact angle against water and hexadecane after 24 h of exposure with milk at 90°C – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

additional investigations on the local mechanisms occurring directly at the coating surface.

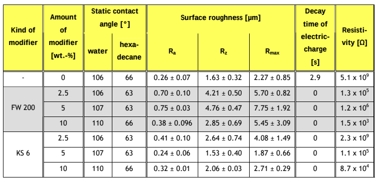
Overall it can be stated that the anti-adhesive polyimide based nanocomposites obviously have some limitations for the use in wet and hydrolytic environment. For this reason further investigations have been performed to find possible compositions useful for dry processes.

3.2 Influence of modification with carbon black (FW 200) and graphite (KS 6) on the antistatic behaviour of the anti-adhesive polyimide nanocomposites

In dry processes concerning food production such as e.g. flour milling it is important to provide coating systems with antistatic behaviour in order to prevent explosions caused by electrostatic discharge phenomena. From the viewpoint of costs carbon fillers such as carbon black (FW 200, Degussa) and graphite (KS 6, TIMCAL AG) have been dispersed in different amounts in a selected polyimide nanocomposite system from above, in order to elucidate the optimum concentration of these additives for an electrostatic effect while maintaining the abrasion stability of the coatings at the same time. Table 4 shows the results of the charge decay time and the resistivity in combination with the surface roughness for the two different additives in dependence on the concentration. The polyimide system with BAPPS co-monomer has been chosen though the other systems showed slightly better behaviour in the previous testing program, because smooth layers could be created in the unfilled case without carbon filler and the matrix was somewhat more polar, a fact which should be important to provide a good basis for antistatic properties.

From Table 4 it can be derived that beginning with a concentration of 5 wt.-% the resistivity indicates antistatic behaviour of the coating systems. The charge decay time already goes down to 0 s starting from a concentration of 2.5 wt.-% carbon additive. Especially the KS 6 graphite filler seems to have almost no negative effect on the roughness of the coatings. The maintenance of a smooth surface is an important advantage useful for transfer the coating materials towards the practical application. Finally Figure 9 and Figure 10 show the behaviour of the coatings containing carbon black and graphite respectively in the taber abrader test.

It can be concluded from the taber abrader test, that the carbon additives have no negative effect on the



Kind of modifier	Amount of modifier [wt.-%]	Static contact angle [°]		Surface roughness [µm]			Decay time of electric-charge [s]	Resistivity [Ω]
		water	hexadecane	R_a	R_z	R_{max}		
-	0	106	66	0.26 ± 0.07	1.63 ± 0.32	2.27 ± 0.85	2.9	5.1×10^9
FW 200	2.5	106	63	0.70 ± 0.10	4.21 ± 0.50	5.70 ± 0.82	0	1.3×10^5
	5	107	63	0.75 ± 0.03	4.76 ± 0.47	7.75 ± 1.92	0	1.2×10^6
	10	110	66	0.38 ± 0.096	2.85 ± 0.69	5.45 ± 3.09	0	1.5×10^3
KS 6	2.5	106	63	0.41 ± 0.10	2.64 ± 0.74	4.08 ± 1.49	0	2.3×10^9
	5	107	63	0.24 ± 0.06	1.53 ± 0.40	1.87 ± 0.66	0	1.1×10^5
	10	110	66	0.32 ± 0.01	2.06 ± 0.03	2.71 ± 0.29	0	8.7×10^4

Table 4: Influence of modifier (carbon black – FW 200/ graphite (KS 6) and modifier amount on static contact angles against water/ hexadecane, surface roughness as well as conductivity determined by decay time and resistivity – coating material: PMDA/ BAPPS with 10 wt.-% Fluorolink D and 40 wt.-% SiC – substrate material: stainless steel (1.4301/ 1.4571) – coating technique: spray-coating – curing conditions: 2 h at 200°C

wear resistance of the coatings, even though the additives are soft compared to the SiC filler used. Especially the carbon black FW 200 seems to exert some tribological properties which result in a slight decrease of the percentage decrease in contact angle with increasing FW 200 concentration.

4 Conclusion

The investigations revealed that interesting polyimide based anti-adhesive nanocomposites could be created, which show similar anti-adhesive behaviour like PTFE surfaces. Their big advantage compared to PTFE is their ability to be applied by spray coating on almost every type of substrates and to be cured under comparably mild conditions. Although the chemical stability in wet, hydrolytic environment is quite limited for these types of systems, they show an excellent behaviour which makes them suitable for applications in dry processes. It is important to note, that an antistatic behaviour can be installed without loosing the mechanical stability. Overall a material basis has been worked out which after appropriate optimisation and technology development has a big potential to be used as anti-adhesive surface in industrial processes.

5 Acknowledgements

The "Bundesministerium für Wirtschaft und Technologie (BMWi)" and the "Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V. (AiF)" is greatfully acknowledged for financial support of the work (FV-Nr. 14228 N/2).

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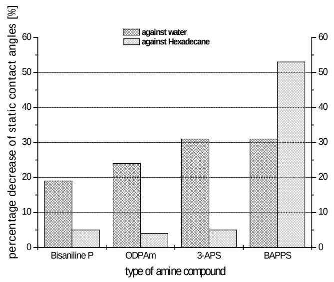

Fig. 8: Percental decrease of static contact angle against water and hexadecane after 24 h of exposure with carrot juice at 90°C – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

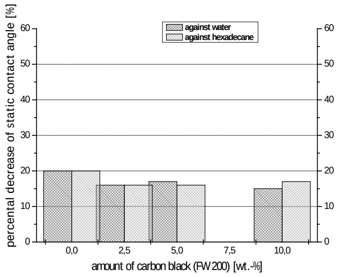

Fig. 9: Influence of the amount of carbon black (FW 200) on wear resistance determined by decrease of static contact angles against water and hexadecane after 1000 cycles taber abrader test respectively – coating material: PMDA/ BAPPS with 10 wt.-% Fluorolink D and 40 wt.-% SiC – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

Quantitative spectrochemical Analysis of Na_3AlF_6, $ZrSiO_4$ and InSb with the Analytical Electron Microscope (TEM & SEM)

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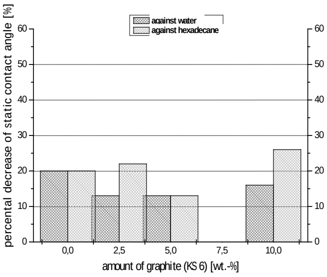

Fig. 10: Influence of the amount of graphite (KS 6) on wear resistance determined by decrease of static contact angles against water and hexadecane after 1000 cycles taber abrader test respectively – coating material: PMDA/ BAPPS with 10 wt.-% Fluorolink D and 40 wt.-% SiC – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

Quantitative spectrochemical Analysis of Na_3AlF_6, $ZrSiO_4$ and InSb with the Analytical Electron Microscope (TEM & SEM)

Eine Reihe zertifizierter natürlicher Mineralien und synthetisierter Zwei- und Mehrelementverbindungen, Kryolith (Na_3AlF_6), Zirkon ($ZrSiO_4$) und Indiumantimonid (InSb) [1] - teilweise in oxidischer Form vorliegend - wurde nach standardfreier Methodik mittels energiedispersiver Rönt-

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[1] Reference Standards for TEM, registered Stand. No. 5998, Science Services München

genspektrometrie (EdXS) sowohl im TEM als auch ergänzend bzw. vergleichend im SEM chemisch analysiert. Zur quantitativen Auswertung der Röntgenspektren wurden für die Analytik im TEM ein Dünnschichtmodell und für die Analytik im SEM die für dicke Proben übliche ZAF-Korrektur genutzt. Die analytischen Befunde werden bewertet, und es wird unter dem Aspekt der praxisbezogenen Anwendung auf die mit der TEM-Dünnschichtanalytik verbundenen Probleme hingewiesen.

Introduction and methodical background

X-ray spectrometric investigations of certified powder materials using TEM and SEM attached with EDXS are concerned with questions about the reliability of microanalytical results in connection with the morphologic structural information of electron microscopical imaging. The results are of importance with respect to the knowledge of structure property relations and take influence on conceptions and design of relevant problems and objetives in materials science.

Compared with the ZAF correction (Z – atomic number, A – absorption, F – fluorescence) in the SEM the analytical thin film model applied in the TEM generally yields wider distributed, i.e. less reliable results; thus, - if suitable for the problem and materials - SEM/EDXS should be prefered or additionally applied. This fact is associated with the morphological structures of the powder-like materials. They are prepared as TEM specimens and therefore deposited onto holey carbon films at Cu grids. A typical example demonstrating the morphological properties of the materials is given in Figure. 1: It was taken in the SEM by the secondary electron signal and the image shows widespread powder particles of irregular habitus having diameters up to 20 µm, average sizes are some µm. From this reason the applicability of the thin film approximation in the analytical TEM is affected, and the estimation of an absorption correction may be necessary.

In terms of analytical investigations in the TEM the properties of specimens (habit, size and shape of particle aggregations) and the micro-geometry (roughness, porosity, shadowing effects by adjacent phase constituents) of the X-ray excited specimen ranges can modify the generated X-radiation in such a way that lower energetic photons may suffer a relatively stronger absorpti-

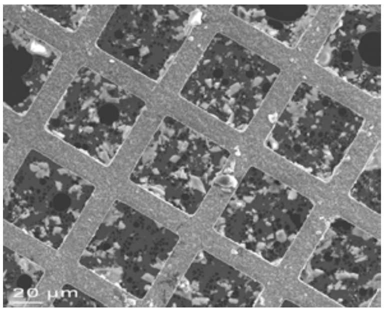

Fig. 1: Cryolyte (Na_3AlF_6), prepared at holey C film on Cu grid, SEM, 20 keV, SE

on on their way to the detector than higher energetic ones. Besides the influences of the geometrical parameters the chemical composition – on the one hand the presence of light elements together with heavier ones (esp. oxides) or otherwise only small Z differences of the material – plays an important role for the certainty of the quantitative analytical results. Finally, the available software package determines the quality of handling and evaluation of the original spectral data. From the co-operation of the discussed influences one can conclude: A general valid specification of the accuracy of the quantification preferably should be replaced by introduction of an error budget which is associated with the special analytic problem, i.e. the parameter of influence as discussed before.

Experimental and Discussion of Results

The software packages of standardless procedures for quantitative electron probe microanalysis apply the so-called *first principles calculations*. These account for all physical aspects of X-ray excitation and propagation in the material as well as the detection of X-ray photons by means of characteristic parameters of the spectrometer system.

The analytical measurements were carried-out with equipments and under working conditions as follows:

- TEM: CM200 FEG (Philips), ED X-ray spectrometer using thin materials quantification software (EDAX Genesis); time of analysis = 300 s (life time), primary energy = 200 keV.
- SEM: JSM-700F (JEOL), spectrometer with ZAF software package (EDAX Genesis); time of analysis = 300 s, primary energy = 20 keV.

The spectra accumulated in the SEM only show slight fluctuations. Thus, the acquisition of 3 to 5 spectra was sufficient to estimate reliable averages. Significant stronger local variations appear in the TEM. Therefore, up to 20 spectra were taken to recognizing and exclude partially strong deviations of the spectral structures caused by imponderable micro-geometrical influences on the X-ray excitation and propagation.

Into the thin film approach[2] to quantitative electron probe microanalysis a theoretical model for the calculation of ionization cross sections[3] was included. Generally, the model is very suitable; however, in presence

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of low-energetic spectral lines (esp. oxides) the thin film approximation often reveals very imperfect data. The results could be improved in a lot of cases by means of an empirical determined absorption correction (i.e. estimation of the thickness of analyzed ranges). Furthermore, a suitable method for analyses of oxides is given with the option *Oxygen by difference* which is offered in the set-up for quantification; this option excludes Oxygen from direct evaluation, and it is determined by normalization to 100%.

Selected results of quantification of identical specimens analyzed as well in the TEM as in the SEM are summarized in Tables 1 to 3.

Table 1 shows the data of a low Z material: Na Al Fluoride, which is a specimen prepared from natural mineralic powder (Cryolite). Using TEM/EDXS the application of an absorption correction results in good agreement with the data of SEM investigation; here, the minority constituents are not taken into account.

Results of the quantification of Zircon (nat. mineral, stoichiometric ZrO_2 + SiO_2) are shown in Table 2. The elemental concentrations from analysis in the SEM fit the mineral data as certified very well. This also is the case for the results of thin film analysis in the TEM if the *Oxygen by difference* option was applied. If the elements are quantified independently and additionally, an empirical absorption correction was introduced the light elements, Oxygen and Silicon, exhibit systematic differences with opposite signs. But, the results remain within acceptable limits of confidence. Finally, if stoichiometric oxides are suggested the resulting concentrations are in very good agreement with the certified data.

Due to the high primary voltage in the TEM the K-radiation of Zr ($EK_\alpha \approx 15.7$ keV) – not overlapped by neighboured spectral lines - can be used in the quantification procedure. This is not possible by working with the SEM; here, the lower energetic L series must be evaluated. Consequently, peak extraction (within the series) is required which may appear as a source of uncertainties of the quantification procedures. Such a case is demonstrated with the data in Table 3: The binary compound InSb ($Z_{In} = 49$, $Z_{Sb} = 51$) was analyzed in the SEM by means of L radiation and in the TEM using both, L and K radiations. In the SEM the results are in good agreement with the certification. This is also the case for TEM/EDXS if the high energetic K lines

	Major Constit.			Minor Constit.		
Spectr. Line	F K	Na K	Al K	Si K	Cl K	Ca K
Certif. Comp.	54,3	32,85	12,85	---	---	---
Weight % by Element, SEM						
Mean Value	55,8±1,9	31,6±1,6	12,6±0,5	---	---	---
Weight % by Element, Absorption t = 250 nm, TEM						
Mean Value	55,0±5,7	28,6±3,4	15,8±4,6	0,4±0,4	0,1±0,1	0,1±0,1

Table 1: Cryolite, Na-Al-Fluoride, Na_3AlF_6

A contribution to climate protection - Electrochromic windows fabricated with the sol-gel technology

Sabine Heusing

were analyzed. In difference to this, the evaluation of the L spectra results in a significant systematic error (> 10% relative). It may be explained with uncertainties in the computation of the ionization cross section at the high excitation energy.

Summary

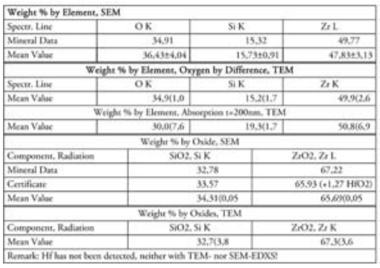
Comparative chemical analyses carried-out by standardless TEM/EDXS and SEM/EDXS analytical procedures have shown the resulting compositions of Na_3AlF_6, $ZrSiO_4$ and InSb agree within acceptable confidence ranges with certified data. The evaluations of selected materials consisting of lower and higher Z components reveal the analytical strategy using the TEM is – related to the SEM - much more sensitive against imponderable parameters of excitation and propagation of X-radiation in the specimen chamber. The micro-morphological structures of the materials can be verified in the SEM more precisely. Therefore, as far as it is possible from properties of the materials and methodical circumstances the analytical SEM should be accompany spectrometric analyses in the TEM. In comparison with SEM/EDXS an advantage of the TEM consists in the possibility to evaluate higher energetic X-radiation (> 20 keV). In this way the determination of the spectral intensities – as an important step of the quantification – becomes more certain because of the presence of energetic separated, non-overlapping spectral lines.

A contribution to climate protection - Electrochromic windows fabricated with the sol-gel technology

Electrochromic systems - Introduction

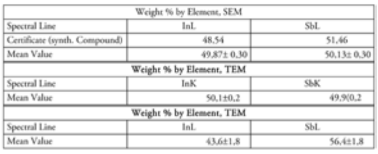
Electrochromic (EC) windows, also called "smart windows", change their optical properties (transmittance or reflection) in a reversible manner when a voltage is applied and a current flows through them [1, 2]. Large EC glazing are of considerable interest for architectural, automotive and aeroplane applications in order to control the solar radiation entrance to save energy costs for air conditioning in summer and for heating in winter (especially for buildings and automotives) and also to add comfort factors like privacy and to avoid glare and fading.

Further applications for EC systems are EC displays and self-dimming rear-view mirrors for



Weight % by Element, SEM			
Spectr. Line	O K	Si K	Zr L
Mineral Data	34,91	15,32	49,77
Mean Value	36,43±4,04	15,73±0,91	47,83±3,13
Weight % by Element, Oxygen by Difference, TEM			
Spectr. Line	O K	Si K	Zr K
Mean Value	34,9(1,0	15,2(1,7	49,9(2,6
Weight % by Element, Absorption t=200nm, TEM			
Mean Value	30,0(7,6	19,3(1,7	50,8(6,9
Weight % by Oxide, SEM			
Component, Radiation	SiO2, Si K	ZrO2, Zr L	
Mineral Data	32,78	67,22	
Certificate	33,57	65,93 (+1,27 HfO2)	
Mean Value	34,31(0,05	65,69(0,05	
Weight % by Oxides, TEM			
Component, Radiation	SiO2, Si K	ZrO2, Zr K	
Mean Value	32,7(3,8	67,3(3,6	
Remark: Hf has not been detected, neither with TEM- nor SEM-EDXS!			

Table 2: Zircon, $ZrSiO_4$



Weight % by Element, SEM		
Spectral Line	InL	SbL
Certificate (synth. Compound)	48,54	51,46
Mean Value	49,87± 0,30	50,13± 0,30
Weight % by Element, TEM		
Spectral Line	InK	SbK
Mean Value	50,1±0,2	49,9(0,2
Weight % by Element, TEM		
Spectral Line	InL	SbL
Mean Value	43,6±1,8	56,4±1,8

Table 3: Indium Antimonide, InSb

cars, which were already on the market for several years (Gentex, Magna Donnelly). Examples for electrochromic materials are inorganic complexes (e.g. Prussian blue), organic molecules (e.g. viologens => application in EC rear-view mirrors), organic polymers (e.g. polyaniline, PEDOT) and a large amount of transition metal oxides (e.g. tungsten oxide (WO_3), niobium oxide (Nb_2O_5) and nickel oxide (NiO).

The most studied EC material is the tungsten oxide (WO_3) due to its high coloration efficiency. The cathodic electrochromic WO_3 colours reversibly from transparent to dark blue by reduction and simultaneously insertion (intercalation) of small ions (e.g. H^+, Li^+) from the electrolyte and bleaches by oxidation and extraction of the ions.

There are three major configurations of EC windows: battery-like, solution phase and hybrid structures. A typical configuration of a battery-like electrochromic (EC) device is shown in figure 1. It consists of a five layer system: between two glass substrates, coated with a transparent electrically conducting layer (e.g. ITO or FTO), are an electrochromic coating (EC1, e.g. WO_3), an ion-storage (IS) coating or a second EC-layer (EC2) and in between an ion conducting electrolyte (e.g. Li^+, H^+).

After applying a voltage with negative polarization at the side of the WO_3-layer, WO_3 is reduced and Li^+-ions diffuse into the WO_3-layer leading to a deep colored Li_xWO_3. After change of the polarization Li_xWO_3 is oxidized and the Li_+-ions diffuse through the electrolyte into the ion-storage layer. The ion-storage layer should either not change its transmittance during the intercalation of ions or should have anodic electrochromic properties (EC2, as e.g. nickel oxide or Prussian blue, which colours after oxidation and bleaches after reduction), which intensify the coloration of the EC-device.

This configuration is often used for prototypes of large area EC-windows for architectural or automotive use and also the EC-windows developed in the INM have this configuration [3]). There also exist monolithic systems, in which all layers were deposited on one glass substrate e.g. by vacuum deposition method (Saint-Gobain glass [4], SAGE Electrochromics [5]).

As EC-layer commonly blue coloring WO_3 is used. In the INM-Leibniz-

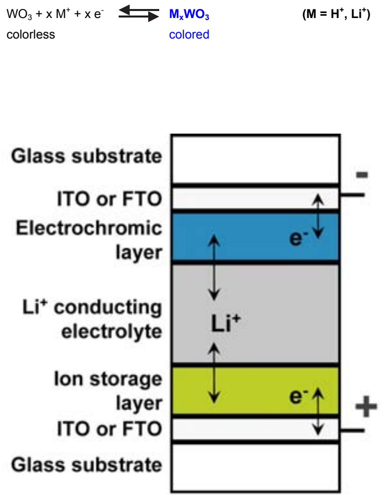


Fig. 1: Scheme of a battery-like EC-device (ITO, FTO: transparent conducting coatings of In_2O_3:Sn and SnO_2:F)

Institut für Neue Materialien blue, grey and brown coloring EC-layers were developed based on tungsten oxide (WO_3) and niobium oxide [6] (figure 3). As counter electrode either a non-coloring ion-storage layer (E-Control [7], INM [3] or an anodic electrochromic layer is used (Prussian blue, Ges*imat* [8]).

The layers of the EC-device can be deposited using different techniques:

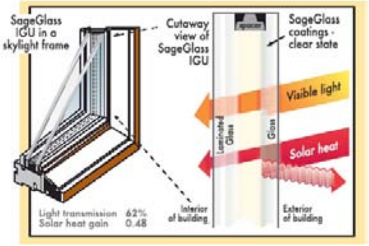
- vacuum deposition method (e.g. E-Control; Saint Gobain glass, Sage-Glass®)
- electrodeposition method (e.g. Gesimat GmbH)
- sol-gel deposition method (INM - Leibniz-Institut für Neue Materialien)

For these methods the investment for production machines is very different.

As electrolytes different materials were used: The company E-Control uses a polymer electrolyte, the INM uses an inorganic-organic composite electrolyte [3] which is thermally solidified after filling into the EC-device. The Gesimat GmbH uses an ionic conductive PVB (p*olyvinylbutyral)* foil, which gives the EC-windows similar properties as laminated sheet glass (LSG) [8], which is advantageous. The advantage of the sol-gel technology used in the INM is, that this technology can be used for the deposition of coatings on bent glass [9], which is important for the fabrication of EC-windows for automotive application, and that the investment costs are relatively low.

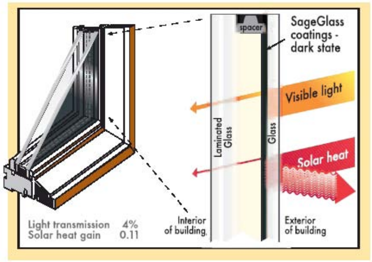
Properties and energy saving

By applying a small voltage (< 3 V) the transmission of an EC window can be changed in the visible (VIS) and near infrared (NIR) range, whereby it remains transparent. Thus colored EC-windows do not only keep out a part of the visible light but also a part of the solar heat (figure 2). The bleached and colored state and the states between are stable for a long time without a voltage supplied. Therefore only for the change of the transmission a voltage is applied and a current flows through. Due to this the energy consumption of EC windows is very small (0.04 – 0.1 Wh/m²). The switching of the EC windows can be done manually or automatically. The switching times were dependent on the size of the EC-windows and the temperature and lie in the range from 2 to 10 min, which is acceptable for architectural glazing.



Light transmission (TL): 62 %

Solar heat gain: 48 %



Light transmission (TL): 4 %

Solar heat gain: 11 %

Fig. 2: Functionality of EC windows ([10]]

Due to the switchable transmission of the VIS- and NIR light EC windows can reduce the peak electricity demand for cooling during summer and heating during winter, thus contributing towards the reduction of greenhouse gases. A study of Lawrence Berkeley National Lab on SageGlass® EC windows for their energy saving potential as well as their effect on human factors has shown that the use of SageGlass windows results in up to 20% cooling energy savings, up to 60% reduction in lighting, and up to 30% reduction in peak electricity demand [10]. On the human factors side, the people evaluated said they overwhelmingly preferred to be in the room with SageGlass windows vs. the room with static glass windows. Better thermal insulation provided, it will also reduce the amount of space heating required during winter. Furthermore, such a glazing will facilitate better day lighting of buildings and offices which can also lead to significant cost savings due to the improvement of workers productivity [11]. Figure 3 shows the SageGlass® EC windows of this study with sensors inside the room monitoring the temperature and light transmission of the windows.

An energy life cycle inventory analysis was implemented to a 400 mm x 400 mm prototype electrochromic window [12]. The raw material production and EC device fabrication processes were analyzed and the total embodied energy was calculated and compared with the energy savings during operation. It was found, that 0.7 years of operation are required to anticipate the embodied energy for the plain EC part.

Large area electrochromic glazing – State of the art in the architectural range

Various prototypes up to a size of 2000 mm x 1200 mm (Flabeg [13], E-Control-Glas [14]), 1200 mm x 800 mm (Firma Gesimat GmbH [8]) and 800 mm x 500 mm (INM gGmbH [15]) were fabricated and tested. The worldwide first electrochromic window for sun protection was sold by the company Flabeg in 2000. The EC-windows were installed e.g. in a glass facade of the "Stadtsparkasse Dresden" but due to switching problems of the EC-windows they were taken from the market in 2001 and taken into a "redesign phase". The new founded company E-Control improved the EC windows and will bring their product on the market by August 2007 [16]. Recently only the EC-windows from the company Sage glass were on the market. The were

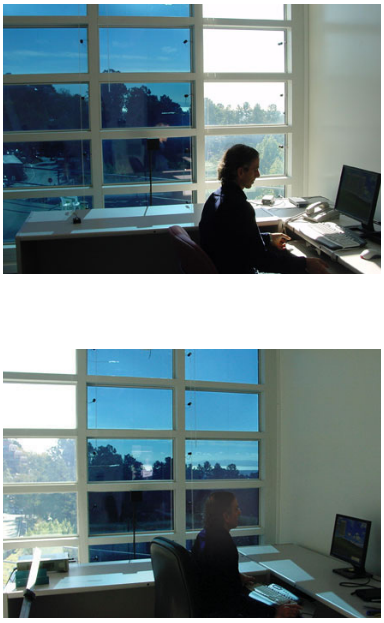


Fig. 3: SageGlass® EC windows in coloured and bleached state (with sensors inside the room monitoring the temperature and light transmission of the windows).

sold as roof windows from VELUX America up to a size of 1175 mm x 776 mm. Due to SAGE glass the high requirements for UV stability and thermal stability and cycle stability were fulfilled for the use of the windows in the architectural range.

For automotive applications Saint Gobain fabricated an electrochromic sunroof for a limited edition of Ferrari 575 which made its worldwide debut at the Detroit Motor Show in January 2005.

The price for an EC window from VELUX America is with 2000 €/m^2 comparably high and thus we are far away from a broad application of EC-windows in the architectural and automotive range. In order to reduce the energy consumption and the emission of greenhouse gases appreciably a broad application is preferable. Yet for a broad application the price should be drastically reduced. One way to reduce it could be the fabrication of EC-windows using the sol-gel technology of the INM.

Sol-Gel EC-windows of the INM

The EC-windows on the market and the prototypes of the industries mentioned above always color blue and use WO_3 as EC layer. The INM developed a wet coating technology for the realization of blue, grey and brown coloring EC-windows [3, 17, 6] with the configuration shown in figure 1, in which the various colours were obtained by varying the EC-layer: The EC-layer consists of WO_3 for blue coloring windows, Nb_2O_5:Mo for grey coloring and Nb_2O_5:Li for brown coloring windows. As IS layer a non coloring CeO_2-TiO_2 layer and as electrolyte an inorganic organic composite is used.

The sol-gel layers were deposited on FTO-glass (K-glass) by dip-coating process and than heat treated at 240°C, 500°C, 400°C and 450^{0}C to 500^{0}C for WO_3, Nb_2O_5:Mo, Nb_2O_5:Li and $(CeO_2)_x(TiO_2)$ layers respectively. After mounting of the EC devices, the electrolyte is filled into the device and solidified by thermal treatment (105°C). After cooling down the EC-windows were sealed using butyl rubber.

By applying a small voltage (up to 3 V) the transmission in the visible range can be changed continuously from 70 % down to about 25 % (T_L values) for blue coloring EC-devices and from 60 % to 20 % for grey coloring EC-devices (see figure 4, 5). Due to the change in the visible and the near infra red (NIR) range a high change of the total solar heat transmission (g-value, DIN EN 410) is

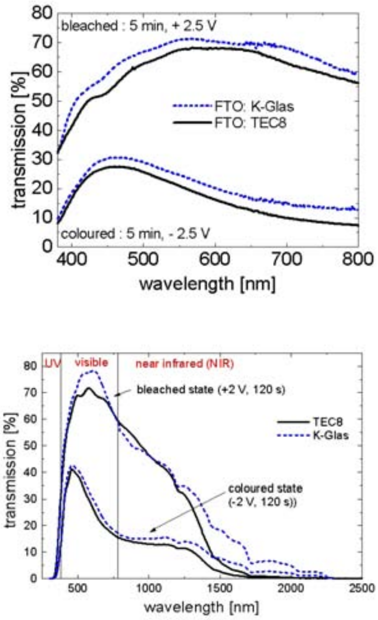


Fig. 4: UV-VIS- and UV-VIS-NIR spectra of blue coloring EC-windows with the configuration FTO / WO_3 / composite electrolyte / CeO_2-TiO_2/ FTO.

obtained varying from 42 % to 17 % so that the energy entrance into the buildings can be varied in a wide range. The switching time depends on the size of the window and lies between 2 and 5 min. The coloration is homogeneous over the whole area as shown in figure 6 where the transmission at 650 nm is shown as a function of the time during the coloration and bleaching process at different points of the EC-window (size: 500 x 800 cm). The voltage is only necessary to change the transmission of the EC window so that the energy consumption is small (0.1 Wh/m^2). The windows shows an UV stability for 1000 hours (Heraeus suntest 800 W/m^2), without change of the switching behaviour. The long-term switching stability could be improved from 15000 to > 60000 switching cycles for blue and grey coloring EC-devices by adding a small amount of water to the composite electrolyte[6, 18]. Prototypes up to a size of 500 cm x 800 cm and 300 cm x 400 cm were fabricated for blue and grey coloring EC windows respectively (figure 7).

Using the blue coloring EC system of the INM (tungsten oxide as EC layer) a curved EC window of the size 300 cm x 400 cm with a bending radius of 2000 mm was fabricated by bending the K-glass in an oven at 600°C before the dip-coating process (figure 8). The dip-coating of the curved glass was successful and a homogeneous blue coloring bent EC-device was obtained.

Furthermore a patterned EC-window of 5 x 5 pixels with a size of 300 mm x 300 mm has been fabricated (figure 9). The WO_3 coating and the $(CeO_2)_x(TiO_2)_{1-x}$ coating were patterned with the FTO coating below by laser ablation in 5 stripes. Each stripe was contacted at the FTO layer. Then the EC-device was mounted in that way that the stripes of the functional layers were perpendicular to each other in order to get a matrix display of 5 x 5 pixels (pixel size: 50 mm x 50 mm). Afterwards the electrolyte was filled in and solidified by heat treatment and the EC-window was sealed as described above.

The coloration and bleaching of the pixels were controlled by a PC program and a display interface developed at the INM (figure 9). Each pixel could be colored and bleached individually, but also different patterns as 4 different pixels together, horizontal or vertical stripes or the whole area could be colored and bleached together (figure 9). A structured EC-window could be used to show information as e.g. prizes in a shop window or a company logo in an

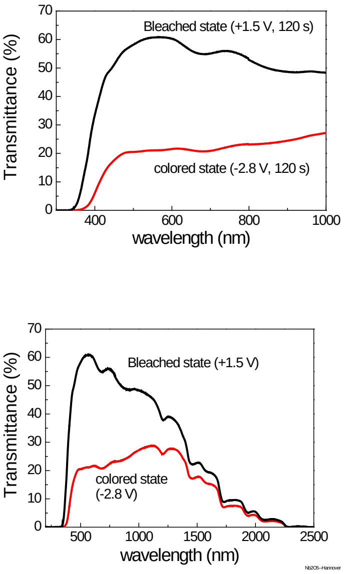


Fig. 5: UV-VIS- and UV-VIS-NIR spectra of a grey coloring EC-window with the configuration K-glass / Nb_2O_5:Mo / composite electrolyte / CeO_2-TiO_2/ K-glass.

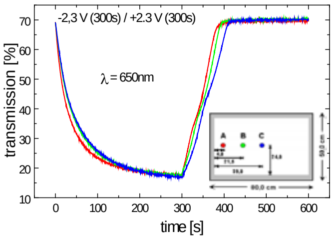


Fig. 6: Transmittance of a blue coloring EC-device (size 500 mm x 800 mm) at wavelength 650 nm as a function of the time during the coloration and bleaching process, measured at different places of the window (see inset).

office building. Because only for the change of the transmission energy is necessary, the information could be shown for a long time with low energy consumption.

The brown coloring EC windows with Nb_2O_5:Li as EC-layer showed only a small transmission change from 72 % to 50 % and are therefore of small interest for the application [6]. Another form of brown coloring EC devices was studied with nickel oxide titanium oxide layers as EC-layers, $(CeO_2)_x(TiO_2)_{1-x}$ as ion-storage layer and 1 mol/l KOH in water. These windows showed a transmittance change from 65 % to 35 % (-1 V, 1 min/ +1.2 V, 1 min), but the long-term stability was relatively small with 7000 cycles [19].

Furthermore an ion-storage layer was developed which can be hardened at low temperature by UV treatment. This is advantageous, because the normally used CeO_2-TiO_2 IS-layer has to be heat treated at high temperatures (450 to 550 °C), which leads to a high energy consumption during the fabrication process and makes the layer not useful for the deposition on plastic substrates. The low temperature deposition was realized by development of CeO_2-TiO_2 nanoparticles, which can be redispersed in a solvent and after mixture with a binder and a UV initiator the dispersion could be deposited by dip-coating and hardened by UV-treatment. Windows using this IS-layer showed a transmission change from 70 % to 30 % after 13 min [20], which shows that the kinetics is not as fast as for the standard heat treated CeO_2-TiO_2 layer, but a first step to fabricate EC-windows on plastic substrates has been done. The fabrication of EC-foil by the roll-to-roll process is an aim, which could be reached by development of UV-curable EC- and IS-layers and an UV-curable electrolyte

In cooperation with the university of Sao Carlos, Brasil (PROBRAL) the development of new cost-efficient electrolytes for EC-windows based on renewable primary products were done, whereby gelatine, starch and agar-agar were used for gelification and $LiClO_4$, $LiClO_3$ or acetic acid were used for ion conduction. First results of EC-windows using the new electrolytes in EC windows of the configuration shown in figure 1 using WO_3 as EC-layer and CeO_2-TiO_2 as IS layer showed that a small transmission change (from about 60 % to 40 %) could be obtained. Further work has to be done to improve these results.

Fig. 7: Bleached and grey colored EC window of the INM (size 400 mm x 300 mm). The transmission in the visible range (TL value, DIN EN 410) can be varied from 60 % (bleached) to 20 % (grey colored, voltage < 3 V, switching time 2-3 min).

Outlook and comparison with other switchable glazings

The results show that the sol-gel technology is an alternative for the fabrication of EC windows on glass. It is suggested, that the fabrication of EC-windows with the sol-gel technology could reduce the price of EC-windows. However before the production process could start, some stability tests and climate change tests have to be done.

Another possibility for the fabrication of low cost EC-devices is the development of EC-foil which can be laminated on the architectural glazing of the buildings. A first step for fabrication of EC-windows on plastic foil has been done, but further work is necessary as the development of an UV-treatable EC-layer, a better UV-curable IS layer and a UV-curable electrolyte. An EC-foil could then be fabricated fast and cheap by roll-to-roll process and laminated on glass of different sizes and probably also on curved glass. This would reduce the price of EC-devices for architectural and automotive glazing drastically. Problems to be solved are the contact of the foil after the fabrication and the sealing.

Beside electrochromic systems described above, there are other switchable glazings as e.g. gasochromic [21], photochromic and thermochromic coatings and suspended particle devices (SPD) and polymer dispersed liquid crystal (PDLC)-systems. The photochromic and thermochromic coatings color after irradiation or after increase of temperature respectively and cannot be influenced actively. The gasochromic systems consist of a WO_3 layer which colours after reduction with hydrogen gas. Problems are here the tightness of the system. The PDLC and SPD systems are already on the market (PDLC: SGG PRIVA-LITE, Saint-Gobain Glass [22], SPD: Research Frontiers [23]). The functionality of the devices depends on the orientation of liquid crystals or optical anisotropic particles in an electrical field after applying a voltage. Without a voltage applied they are opaque (PDLC) or dark blue colored (SPD) and only with an applied voltage the systems are transparent and clear, whereby the voltage is about 100 V for SPD devices. This leads to a higher energy consumption than EC-devices need and in addition no change of the solar heat transmission (g-value) is obtained, because only the visible part of the spectrum is change. Thus no energy saving effect can be obtained using SPD or PDLC systems.

Fig. 8: Curved blue colored EC window of the INM (size 400 mm x 300 mm, curve radius 2000 mm). The transmission in the visible range (TL value, DIN EN 410) can be varied from 70 % (bleached) to 25 % (blue colored, voltage < 3 V, switching time 2-3 min).

Acknowledgements

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Fig. 9: Patterned electrochromic window with 5 x 5 pixels, whereby each pixel can be colored and bleached individually and different structures can be colored and bleached.

Shown: EC-Display with control unit (laptop and display interface) and three colored stripes, four colored pixels and whole area colored.

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Plasma-assisted Modulation of Morphology and Composition in Tin Oxide Nanostructures for Sensing Applications

Sanjay Mathur*, Rajesh Ganesan, Thomas Ruegamer, Hao Shen, Sven Barth

Detecting small quantities of gases and chemicals is becoming increasingly important for consumer, health and security applications such as monitoring the ecological constituents and to control the concentration of toxic and hazardous gases.[1] Nanostructures are especially attractive for detector and quantifier applications, particularly due to their high surface-to-volume ratio and higher sensitivity towards surface reactions, which results in charge penetration layers being comparable to nanostructure dimensions.[2] Tin oxide (SnO_2) represents the class of IV-VI compound semiconductors with a wide band gap (3.6-4.0 eV) at room temperature and intrinsic n-type electrical conductivity.[3] Given their low electrical resistivity (10^{-2}-10^{-4} Ωcm), high chemical resistance, thermal stability and mechanical strength,[4] SnO_2 nanostructures offer promising potential for improved chemical sensing behaviour due to its redox switching between different states, which facilitates a reversible transformation of the surface composition from Sn^{4+} cations on the surface into a reduced surface with Sn^{2+} cations depending on the oxygen chemical potential of the system.[5]

Tin oxide nanostructures have been synthesized by a number of methods such as chemical vapor transport at high temperatures,[6] thermal evaporation of tin oxide powders[7] and plasma enhanced chemical vapor deposition.[8] Although a large body of data is available on the synthesis of tin oxide nanostructures (particles, films, nanowires and nanobelts) in pure and doped compositions, synthetic pathways for their controlled growth and modification remains an overarching task. We have recently reported a molecule-based chemical vapor deposition (CVD) process for the synthesis of tin oxide and other semiconductor nanowires.[9-11]

The pre-formed Sn-O units in the precursor molecule $[\mathrm{Sn(O^tBu)_4}]$ and the facile and clear stripping of organic ligands resulted in single crystalline SnO_2 nanowires at relatively low temperatures. [9] Herein we describe the controlled growth of single crystal tin oxide platelets followed by modulation of their morphology and composition induced by argon and oxygen plasma.

Semiconductor oxide nanostructures with ideal stoichiometric balance (electro-neutrality) are poor transducers for chemical sensing due to low signal-to-noise ratio, making excessive signal amplifications and/or high operating temperatures mandatory for optimal sensing performance. Since electrical properties of tin oxide depend on oxygen vacancies, mobility and concentration of charge carriers and surface states, an effective lowering of operation temperature and enhanced gas sensing ability can be obtained by modifying surface and chemical composition of stoichiometric nanostructures, for instance, through incorporation of metallic impurities in the oxide semiconductor. For example, an effective band bending effect can be achieved by increasing the concentration of donor atoms or defects in the material. We have exposed CVD grown tin oxide nanoplates to a sputter-redeposition process in low power Ar/O_2 plasma, in order to modulate the defect concentration and the Sn:O stoichiometry followed by investigations on the chemical sensing properties of as-deposited and plasma treated samples.

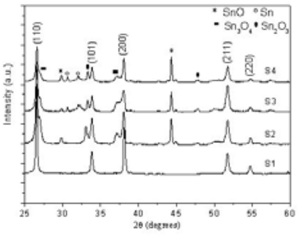

Fig. 1: XRD patterns of as-deposited (S1) and SnO_2 nanoplates treated with plasma powers 25 W (S2), 40 W (S3) and 55 W (S4), for 3 minutes.

Growth of tin oxide nanoplates: Crystal structure, composition and morphology

Tin oxide nanoplatelets were deposited by CVD of $[\mathrm{Sn(O^tBu)_4}]$ in the temperature range 700-725 °C. Post-deposition modification of tin oxide nanostructures have been carried out by treating the samples (3 min) in r.f. plasma, as a versatile nano-modification and fabrication tool, containing reactive oxygen gas and argon carrier gas in 3:1 ratio. To study the influence of plasma treatment over the physical and chemical properties of the CVD grown tin oxide nanostructures (S1), samples were treated with the plasma powers of 25 (S2), 40 (S3), 55 (S4) and 125 (S5) W.

XRD patterns (figure 1) of as-deposited and plasma treated SnO_2 nanoplates showed a Casseterite tetragonal rutile structure. No other crystalline impurities were detected in the samples. The intensity of the peaks corresponding to the SnO_2 phase was found to gradually diminish upon plasma-treatment with increasing plasma power, which was accompanied by incipient crystallization of tin sub-oxides. Samples treated at 25 W plasma power (S2) revealed X-ray diffraction peaks corresponding to mix- and sub-valent tin oxide species (Sn_2O_3, Sn_3O_4 and SnO) possibly formed by the etching of lattice oxygen atoms from the SnO_2 deposits. With further increase in plasma power (40 W), intensity of the peaks attributed to Sn_3O_4 and Sn_2O_3 were decreased apparently due to progressive reduction reactions, which was supported by the observation of metallic tin phase. Apparently, the enhanced etching of oxygen by high momentum particles impinging on the surface is responsible for the observed reduction of tin oxide.[8] It was also noted that the content of metallic Sn was proportional to the increase in applied plasma power. Treatment of tin oxide with pure Ar plasma produced samples with high tin content and conductance, which were not suitable for sensing applications.

The SEM analysis of S1 (figure 2) showed uniform SnO_2 nanoplates with the thickness of 30-40 nm, which were transformed to elongated granular structures by the ion bombardment at 25 W. The inhomogeneous morphological change suggested a selective and preferential etching of certain facets in the nanoplates. Samples treated at higher plasma energy showed the formation of nanoglobular particles (samples S3 and S4), indicating advanced etching phenomenon and/or sputter-redeposition process. Given the reduced pressure in the plasma chamber (~4 Pa), the mean free path of the etched species was rather short which can lead to redeposition and rearrangement of etched tin and oxygen species on the surface of tin oxide platelets. At much higher plasma power (125 W), a large number of pores were found in the surface of the sample S5, exhibiting a predominant etching effect with suppressed redeposition.

XPS characterization of the samples S1, S3 and S5 (figure 3) confirmed the inherent changes observed in XRD, in the tin oxide CVD samples after exposure to r.f. plasma. As-deposited SnO_2 sample exhibited the characteristic double peak for the Sn 3d orbital with the main peak (Sn $3d_{5/2}$) at binding energy 486.6 eV (FWHM 1.4). Upon plasma treatment at 40 W, the appearance of an additional peak at lower binding energy (484.7 eV) was observed, which corresponds to the metallic tin phase.[12] The peak surface area analysis of the metallic phase revealed

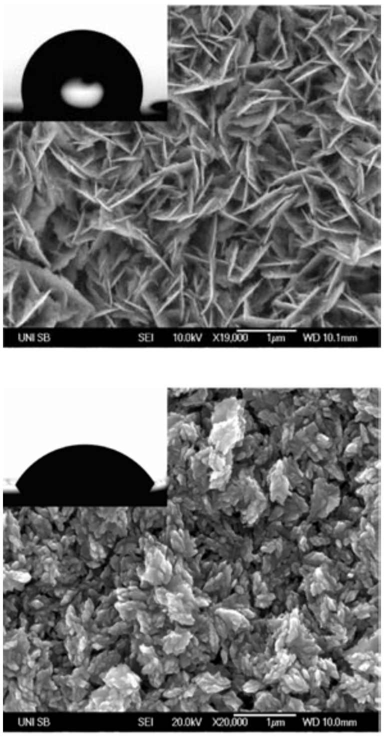

Fig. 2: SEM micrographs of (a) as deposited and (b) plasma-treated SnO_2 nanoplates along with their corresponding surface wetting behaviors.

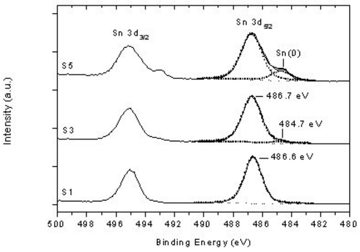

Fig. 3: XPS analysis of as-deposited and plasma-treated SnO_2 nanoplates.

approximately 3.0 at.% Sn(0) in the sample. XPS investigation of the sample S5, evidently showed that increased plasma energy (125 W) produced higher amount of metallic tin (up to 15.6 at.%), in accordance to the higher degree of chemical transformation.

Wetting behaviour and contact angle measurements

Interfering effects of water vapor in the detection of gaseous species on metal oxide surfaces is a well-known limitation (cross-sensitivity). Enhancement of gas sensing response in the presence of water vapor is commonly accepted although the corresponding mechanisms are complex and difficult to model. Since plasma treatment of SnO_2 surface can influence the degree of chemisorbed and rooted –OH groups (groups including lattice oxygen), the wetting properties of samples S1-S5 were investigated. Contact angle of water droplets on as-deposited and plasma treated nanoplates (Inset, figure 2) revealed a hydrophobic nature for as-deposited samples, with a contact angle of 108°. No notable changes were observed in the water repellent nature of sample S2 (contact angle 104°) treated at low plasma power (25 W). Samples treated at higher plasma powers (S3 and S4) showed an increase in wetting behaviour with a decrease in the contact angles of 86° and 56°, respectively. The determination of contact angle on samples treated with 125 W was not possible and extreme hydrophilicity of the surface, evident in immediate film formation was observed.

Sensing characteristics

For chemical sensing experiments, 100 ppm ethanol in synthetic air was fed into the chamber with 15 sccm flow rate. The sensitivity of the SnO_2 samples was calculated as the ratio of its base resistance (R_{air}) to the shift due to ethanol exposure (R_{eth}).

Temperature dependent sensitivity of the samples treated at different plasma power conditions were measured by exposing the samples to air/ethanol/air cycles, in the temperature range 220 – 250 °C (figure 4). At 250 °C, the sensitivity towards ethanol molecules in samples S1, S2 and S3 was found to be 1.6, 2.1 and 5.9, respectively indicating a substantial augmentation of the gas sensing ability of SnO_2 deposits upon plasma treatment. Further increase in plasma power resulted in enhanced reduction of tin oxide as confirmed by higher metallic content (cf.

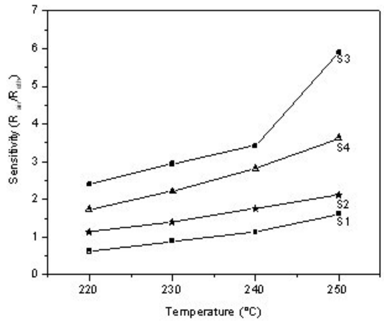

Fig. 4: Dependence of electrical response of tin oxide samples against operation temperature.

XRD), which reduced the sensitivity of the sample S4 to 3.6. In general, plasma treatment showed a positive effect on the gas sensing behaviour of as-deposited tin oxide deposits, which allowed to achieve substantial sensitivity of the samples even at lower operating temperature. However an increasing metallic character alters the conduction behaviour suppressing the semiconductor properties, detrimental for the transduction mechanism.

At room temperature, S3 (24.2 kΩ) showed lower resistance in comparison to S1 (44.1 kΩ), which can possibly be attributed to increased surface charge carriers in the oxygen deficient layers created through interaction of energetic species with surfacial –Sn–O– units. The sensing response cycles (figur 5) of S3, at 250 °C showed the base resistance of S3 was found to be higher than that of S1 apparently due to oxygen chemisorption at the newly generated active sites, which trap the electrons on the surface. Effective oxygen chemisorption, was favoured in non-stoichiometric S3 (cf. XRD and XPS), because neutral oxygen molecules adsorb in a more facile manner on plasma induced lattice oxygen vacancies and consequently, show better adsorption behaviour over stoichiometric surfaces (S1). On exposure to ethanol gas at 250 °C, the sheath resistance of S3 (~29 kΩ) was lower than that found in S1 (~67 kΩ) possibly due to redox reaction induced shift in the Fermi energy on the surface.[5] This also indicated the presence of partially reduced tin oxide species in S3, supporting higher chemisorption and therefore increased the molecular interactions between the reducing analyte and the surface, when compared to S1. As the chemisorbed oxygen atom does not attract the electrons so strongly as lattice atoms do, the resulted filled energy level is bent above the valence band. Since the segregated Sn atoms are expected to be less electropositive when compared to lattice bound Sn atoms, their energy levels are lower than the conduction band levels in stoichiometric tin oxide, as schematically described in figure 6.

As a result, new donor levels, created by plasma induced reduction, act as a source of additional charge carriers, which can be promoted to the surface with lower threshold energies, thus facilitating an effective redox reaction at lower temperature.

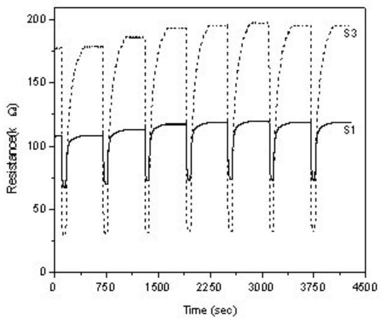

Fig. 5: Sensing response of S1 and S3 for ethanol at 250 °C.

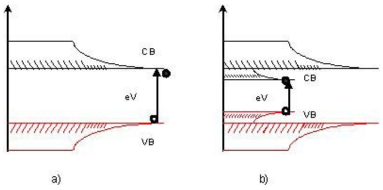

Fig. 6: Surface energy level model for SnO_2 suggesting the work function: (a) before and (b) after plasma treatment.

Plasma treatment at elevated power (55 W) apparently etched larger number of bridging oxygen atoms leading to pronounced SnO_2 reduction with formation of in-plane oxygen vacancies, which reduced the semiconductor properties and thus the sensitivity of the samples. The gradual chemical transformation model (figure 7), in as-deposited sample is evidented by the emergence of Sn(0) peak as shown in the XRD and XPS data.

The response and recovery times were defined as the time needed for the resistance of the sensors to reach its final equilibrium value (± 10%) for given reaction conditions (figur 8). Response time was nearly identical for all samples within the range of 10 seconds. Recovery time for S2 and S3 increased proportionally with higher plasma power used for surface modification whereas abrupt increase in recovery time for S4 suggested that removal (desorption) of chemisorbed oxygen in oxygen-deficient samples is energetically less favoured thereby demanding a longer time period to reach the equilibrium condition.

In summary, the plasma-chemical transformation of metal oxide nanostructures is a versatile strategy to modify the morphology, composition and functional behaviour of advanced ceramics with wide-reaching technological implication in the field of sensors and transparent conducting oxides.

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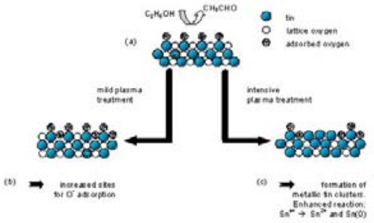

Fig. 7: Schematic representation of Sn:O stoichiometry in as-deposited and plasma-treated samples.

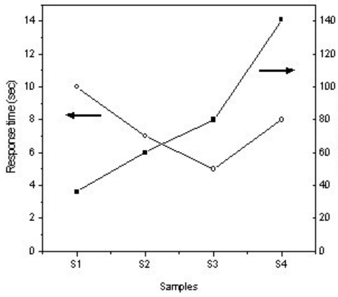

Fig. 8: Response and recovery times of SnO_2 nanoplates for ethanol sensing.

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Innovationen durch Nanotechnologie: Mehrwert für Zulieferer der Automobilindustrie,
21.03.2006, Saarbrücken

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INM, 24.11.2006, Saarbrücken

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Thematischer Mitglieder-Workshop, Schering AG,
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R. Gerdes, G. Heppe, P. Kalmes, F. Hollmann, S. Albayrak, C. Becker-Willinger

Nanomer – Beschichtungen und kompakte Werkstoffe
CC – Nanochem Seminar „Innovationen durch Nanotechnologie: Mehrwert für Zulieferer der Automobilindustrie“, 21.03.2006, Saarbrücken

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7. International Meeting on Electrochromism (IME-7),
3 – 7. 09.2006, Istanbul, Turkey

S. Heusing

Elektrochromie
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Innovationen durch Nanotechnologie: Mehrwert für Zulieferer der Automobilindustrie, 21.03.2006, Saarbrücken

M. Kölbel

Was ist Nanotechnologie? - Grundlagen der Nanotechnologie und ihre Anwendungsbereiche
Innovationen durch Nanotechnologie: Neue Materialien für den Maschinen- und Anlagenbau, 13.06.2006, Saarbrücken

M. Kölbel

Kompetenzzentrum CC-NanoChem - Chemische Technologien und Prozesstechniken für Nanomaterialien und deren Anwendungen
kompetenznetze.de – Innovationscluster in Deutschland, 25.04.2006, Hannover

M. Kölbel

Towards a Saar-Lor-Lux Network for Nanotechnology and New Materials
Nanotechnology and Nanosciences, 08.-09.06.2006, Nancy, France

M. Kölbel

Sicherheits- und Umweltsaspekte
Summer School Chemische Nanotechnologie, 24. - 28.07. 2006, Saarbrücken

M. Kölbel

Sicherheits- und Umweltsaspekte
Summer School Chemische Nanotechnologie, 09. – 13.10.2006, Saarbrücken

M. Kölbel

Gesundheit – Sicherheit – Umwelt / Risiken und die Akzeptanz durch den Verbraucher
Innovationen durch Nanotechnologie: Neue Oberflächen für Architektur, Möbel und Design, 25.10.2006, Köln

M. Kölbel

Neuartige Oberflächen für Möbel und Design durch Nanotechnologie
Seminar „Kunststoffe für Möbel und weiße Ware“, 14.11.2006, Mannheim

M. Kölbel

Chemical Nanotechnology from the INM
Gemeinsamer Workshop von Luxinnovation, NanoBioNet und cc-NanoChem, 15.12.2006, Luxemburg

A. Kraegeloh

Mikroorganismen in der Nanotechnologie
Summer School Chemische Nanotechnologie, 24.-28.07.2006, Saarbrücken

P. Kuhn

CVD of Titanium oxide and -carbonitride Coatings: Thermal and plasma assisted processes
10. International conference of plasma surface engineering, PSE 2006,
10.-15. 09.2006, Garmisch-Patenkirchen

P. Kuhn

Nanostrukturierte Oberflächen mittels Gasphasenabscheidung
Summer School Chemische Nanotechnologie, 09. – 13.10.2006, Saarbrücken

P. Kuhn

Plasma and thermally activated CVD of nanostructured Titanium oxide and nitride coatings
5. International conference of solid state surfaces and interfaces, SSSI 2006, 19.-24.11.2006, Smolenice (Slovakia)

A. Kurz, M.A. Aegerter

Novel transparent conducting sol-gel oxide coatings
6th International Conference on Coatings on Glass and Plastics– ICCG6, 18.-22.06.2006, Dresden

S. Mathur

Invited talk
Molecular derived Nanomaterials
Asian Institute of Technology,
09. 01.2006, Pathumthani, Thailand

S. Mathur

Invited talk

Nanomaterials through Chemistry: Processing and Applications
NanoSingapore, IEEE Conference on Emerging Technologies – Nanoelectronics
10. – 13. 01.2006, Singapur

S. Mathur

Invited talk
Nanomaterials through Chemistry: Synthesis and Applications
Christian-Albrechts-Universität, Technische Fakultät, 19.01.2006, Kiel

S. Mathur

Invited talk
Chemical Synthesis of Nanostructured Materials
American Ceramic Society Meeting, 22. – 27.01.2006, Cocoa Beach, Florida, USA

S. Mathur

Invited talk
Chemische Nanotechnologie: Vom Molekül zur Anwendung
Anorganisch-Chemisches Kolloquium, Technische Universität München,
30.01.2006, München

S. Mathur

Invited talk
Nanomaterials through Chemistry: Synthesis and Applications
Martin-Luther-Universität,
12.02.2006, Halle-Wittenberg

S. Mathur

Nanostructured Surfaces for Bio-medial Applications
NanoMed 2006 – 5th International Workshop on Biomedical Applications of Nanotechnology,
16. – 17.02.2006, Berlin

S. Mathur

Neue Materialien durch kontrollierte Mineralisation in ionischen Flüssigkristallen und peptidkontrollierte Fällungsreaktionen
Chemiedozententagung ADUC, Universität Hamburg,
19.– 22.03.2006, Hamburg

S. Mathur

Invited talk
Molecular derived Nanomaterials
Tata Institute of Fundamental Research (TIFR), , 27.03.2006, Bombay, Indien

S. Mathur

Invited talk
Materials Innovations Through Chemistry
The World Nano-Economic Congress (WNEC),
28.- 29.03.2006, Bombay, Indien

S. Mathur

Invited talk
Nanomaterials through Chemistry: Processing and Applications
National Chemical Laboratory (NCL),
30.03.2006, Pune, Indien

S. Mathur

Invited talk
Nanomaterials and Thin Film Systems
Devi Ahilya University,
31.03.2006, Indore, Indien

S. Mathur

Protective and Bio-Compatible Nanostructured Surfaces by CVD Techniques: Controlled Modulation of Surface
MRS Spring Meeting,
17. – 21.04. 2006, San Francisco, USA

S. Mathur

Invited talk
Chemically controlled synthesis of nanostructures: properties and device applications
Symposium "Nanostructured metal oxides: synthesis and applications",
28.04.2006, Hasselt, Belgium

S. Mathur

Invited talk
Nanomaterials and Thin Film Systems
Conference on Nanocoatings and Ultra Thin Films,
16. – 18. Mai 2006, Miami, USA

S. Mathur

Tuning Functionality in Materials Through Chemical Design
Fourth International Workshop On Polymer Routes to Multifunctional Ceramics for Advanced Energy and Propulsion Applications,
30.07. – 05.08.2006, Boulder, Colorado, USA

S. Mathur

One-dimensional oxide nanostructures: growth, applications and devices
SPIE Symposium on Solar Hydrogen & Nanotechnology, 13. – 17.08.2006,
San Diego, California, USA

S. Mathur

Invited talk

Chemical Nanotechnology: From Molecules to Product Applications
ARCI, International Advanced Research Center for Powder Metallurgy & New Materials,
30.08.2006, Hyderabad, India

S. Mathur

Invited talk
Nanostructures through Chemistry: Processing and Biomedical Applications
Nanobio-Workshop, KIST EUROPE,
29.09. 2006, Saarbrücken

S. Mathur

Nanodrähte: Von den Grundlagen bis zur Bauteilentwicklung
SFB Klausurtagung,
13.10.2006, Homburg

S. Mathur

Nanostructured Surfaces through Chemical Nanotechnology: Opportunities and Applications
Thin Films 2006,
11.-15.12.2006, Singapore

S. Mathur

Invited talk
Chemical Nanotechnology: From Molecules to Product Applications
Fraunhofer-Institut für Silicatforschung ISC, 18.12.2006, Würzburg

K. Moh

Übersicht zur Synthese von FePt-Nanopartikeln
Universität des Saarlandes,
04.05.06, Saarbrücken

K. Moh

Synthese und Eigenschaften von FePt-Nanopartikeln
INM, 08.12.06, Saarbrücken

Th. S. Müller

Photokatalytisch aktive Oberflächen - Schadstoffabbau und vereinfachte Reinigung durch UV-Licht und superhydrophile Schichten
CC-Nanochem Workshop: Innovationen durch Nanotechnologie: Mehrwert für Zulieferer der Automobilindustrie, 21.03.2006, Saarbrücken

Th. S. Müller

Transparent Photocatalytic Coatings on Glass and Plastics
International Conference on Coatings on Glass and Plastics (ICCG 6),
18.06. -22.06. 2006, Dresden

J. Pütz

Printing of ITO inks
ROLLED/OLLA Workshop 'Organic LED Technologies for Future Lighting Applications', 09. 03.2006, Oulu, Finland

J. Pütz

Gravurdruck von Nanopartikeln für transparente Elektroden
CC-NanoChem Workshop, BASF AG, 10.04.2006, Ludwigshafen

J. Pütz

Sol-Gel-Beschichtung von Displaygläsern
6. Symposium 'Zukunft Glas – Von der Tradition zum High-Tech-Produkt', 31.05.-01.06.2006, Zwiesel

J. Pütz, S. Heusing, M.A. Aegerter

Gravure printing of ITO anodes, Rolled/Contact Symposium,
13.06.2006, Brussels, Belgium

J. Pütz, M.A. Aegerter

Gravure printing of nanoparticle coatings on thin glass and plastic foils
6th International Conference on Coatings on Glass and Plastics– ICCG6,
18.-22.06.2006, Dresden

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Summer School 'Chemische Nanotechnologie',
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Summer School 'Chemische Nanotechnologie', 09.-13.10. 2006, Saarbrücken

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3. Fachkonferenz 'Nanotechnologie in der Lackpraxis', 12.10.2006, Stuttgart

J. Pütz

Application of Nanotechnology in Flexible Packaging, Flexible Packaging Europe - TC Meeting,
19.10.2006, Freising

J. Pütz, M.A. Aegerter

Gravure printing of nanoparticle patterns for smart packaging applications
2nd Plastic Electronics Conference,
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B. Reinhard, A. Altherr, K. Endres, D. Strauss, C. Trenado, M. Veith

Chemical Nanotechnology and Applications in Fire Protection
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14. - 15.09.2006, Berlin

B. Reinhard, A. Altherr, C. Trenado, D. Strauss, M. Veith

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M. Schem, T. Schmidt, J. Gerwann, W. Kochanek, G. E. Thompson, P. Skeldon, I. S. Molchan

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8. – 22.06.2006, Kliczkow, Poland

T. Schmidt, M. Schem, J. Gerwann, W. Kochanek, G. E. Thompson, P. Skeldon, I. S. Molchan

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M. Schubert

Wo geht die Reise hin?
Forum Mensch Architektur Design,
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Informationen aus erster Hand: CC-NanoChem und INM

Innovationen durch Nanotechnologie: Mehrwert für Zulieferer der Automobilindustrie, 21.03.2006, Saarbrücken

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Innovationen durch Nanotechnologie: Neue Materialien für den Maschinen- und Anlagenbau,
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M. Schubert

Vom Molekül zum Material
Summer School Chemische Nanotechnologie, 24. - 28.07.2006, Saarbrücken

M. Schubert

Nanotechnologie
Workshop „Nanotechnologie im Unterricht“, 25. - 26.09.2006, Heidelberg

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Innovationen durch Nanotechnologie: Neue Oberflächen für Architektur, Möbel und Design, 25.10.2006, Köln

D. J. Strauss

Universal Newborn Hearing Screening – Experiences in Germany
Ministry of Health and Ministry of Science and Technology, 2006, Malaysia

D. J. Strauss

Computational Approaches to Clinical Problems in Audiology
Universiti Teknologi Malaysia, 2006, Malaysia

D. J. Strauss

Current Trends in Biomedical Engineering
Universiti Teknikal Malaysia Melaka, 2006, Malaysia

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Biomedical Engineering in the State of Saarland, Germany
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M. Veith

Surfaces for Cells
LCC, 19.01.2006, Toulouse, France

M. Veith

Nanotechnologies à l’Institut INM a Sarrebruck
Université de Franche-Compte, 27.02.2006, Besançon, France

M. Veith

From Sophisticated Molecules to Nano-Materials

Laboratoire de Chimie de Coordination, UMR 7513 CNRS,
19. - 20.02.2006, Toulouse, France

M. Veith

Physical Methods for the Structural Investigation of New Materials
International Research Training Group 532, Medienzentrum der Universität des Saarlandes, 20.03.2006, Saarbrücken

M. Veith

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M. Veith

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Workshop „Architektur und Nanotechnologie“
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M. Veith

From Molecules to nano-Materials
Northwestern's International Institute for Nanotechnology, Northwestern University
04.04.2006, Chicago, USA

M. Veith

Vom Molekül zum Material: Metastabile Phasen und strukturierte Metall / Metalloxid-Mischphasen
GDCh Ortsverband München, TU München,
09.05.2006, München

M. Veith

„Synthese und Eigenschaften neuer anorganischer Nanostrukturen“
Physikalisches Kolloquium an der TU Braunschweig am 16.05.2006

M. Veith

What's New in Organosilane Chemistry and Applications?
Surface & Interface Solutions Center Open Day Event
08.-09.06.2006, Feluy, Belgien

M. Veith

“Nano-Technologie pour tout le monde“
Einladung des Bürgermeisters von Forbach am 04.05.2006

M. Veith

Intermolecular Recognition of Molecular Alumosiloxanes with Diamino-Alkanes Forming One-, Two- and Three-Dimensional Aggregates with Rings and Cages
11. International Symposium on Inorganic Ring Systems (IRIS)
30.07.-04.08.2006, Oulu, Finnland

M. Veith

Aluminium basierte nanostrukturierte Schichten - eine Bestandsaufnahme
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M. Veith

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Wissenschaftliche Weiterbildung an der Universität des Saarlandes
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Nanopartikel und Nanowerkstoffe für Life Sciences und Umwelttechniken
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NanoDe: Branchendialog im Bauwesen
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Molekulare Aspekte zur Schichtherstellung
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Metal Oxides, also with rare earth elements from molecular precursors
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Neue Aspekte im Bauwesen durch added value im Nanobereich
VDI, Fachgespräch Nanotechnologie im Bauwesen (Nanotecture)
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U. Werner

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M. Wittmar

Projektidee Nanoförderband
SAW-Vorbereitungstreffen der Sektion D der WGL, Ferdinand-Braun-Institut für Höchstfrequenztechnik,
15.09.2006, Berlin

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M. A. Aegerter, V. Kirchoff (Eds)

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N. Al-Dahoudi, M. A. Aegerter

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A. Al-Kalhout, A. Pawlicka, M. A. Aegerter

Brown coloring electrochromic devices based on NiO-TiO_2-layers

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A. Al-Kalhout, S. Heusing, M. A. Aegerter

Electrochromism of NiO-TiO_2 sol gel layers

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M. Akarsu, M. Asiltürk, F. Sayilkan, N. Kiraz, E. Arpac, H. Sayilkan

A novel approach to the hydrothermal synthesis of anatase titania nanoparticles and the photocatalytic degradation of Rhodamine B
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M. Asilturk, F. Sayilkan, S. Erdemoglu, M. Akarsu, H. Sayilkan, M. Erdemoglu, E. Arpac

Characterization of the hydrothermally synthesized nano-TiO2 crystallite and the photocatalytic degradation of Rhodamine B

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H. P. S. Chauhan, U. P. Singh, N. M. Shaik, S. Mathur, V. Huch

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R. G. F. Costa, C. O. Avelllaneda, A. Pawlicka, S. Heusing, M. A. Aegerter

Optoelectrochemical Characterization of Electrochromic Devices with Starch based Solid Electrolytes

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G. Guzman, B. Dahmani, J. Pütz, M. A. Aegerter

Transparent conducting sol-gel ATO coatings for display applications by an improved dip coating technique

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F. Hernández-Ramírez, A. Tarancón, O. Casals, J. Rodríguez, A. Romano-Rodríguez, J. R. Morante, S. Barth, S. Mathur, T. Y. Choi, D. Poulikakos, V. Callegari, P. M. Nellen

Four-probe Measurements and Impedance Spectroscopy of Individual SnO_2 Nanowires

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S. Heusing, D.-L. Sun, J. Otero-Anaya, M. A. Aegerter

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J. Hopf, M. Aslan, H. Schmidt

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H. Ivankovic, E. Tkalcec, R. Rein, H. Schmidt

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H. Kaddami, C. Becker-Willinger, H. Schmidt

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M. Kölbel

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M. Kölbel, M. Veith

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M. Veith, T. Voigt, V. Huch

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Contributions to Conference Proceedings / Konferenzbeiträge

A. Al-Kalhout, M.A. Aegerter

Coloration Mechanisms of Sol-Gel NiO-TiO_2 Layers studied by EQCM

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Electrochromism of NiO-TiO_2 Sol-Gel Layers and Devices made of them

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Protective and bio-compatible nanostructured surfaces by CVD techniques: controlled modulation of surface and phase structures

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Microporous ZrO_2 Film Preparation by Chemical Vapor Deposition

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S. Mathur, T. Ruegamer

Vanadium Oxide Nanostructures: Growth, Characterization and Applications

in Nanoparticles and Nanostructures in Sensors and Catalysis, edited by Chuan-Jian Zhong, Nicholas A. Kotov, Wayne Daniell, Francis P. Zamborini (Mater. Res. Soc. Symp. Proc. 900E, Warrendale, PA, 2006) 0900-O13-09

S. Mathur, H. Shen, S. Barth, N. Donia

One-Dimensional Semiconductor Nanostructures: Growth, Characterization and Device Applications

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Posters / Poster

S. Mathur, H. Shen, N. Donia

Chemical Nanotechnology: From Molecules to Applications

In: Nanostructured Metal Oxides: Processing and Applications, ECS Cancun Meeting 2006, Eds. E. Traversa et. al., ECS Transactions – Cancun, 3 (2006)

Th. S. Müller, K. Moh, M. Mennig, H. Schmidt

Transparent Photocatalytic Coatings on Glass and Plastics

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J. Pütz, M.A. Aegerter

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in: Tagungsband 6. Symposium 'Zukunft Glas – Von der Tradition zum High-Tech-Produkt', 31.05. – 01.06.2006, Zwiesel, Germany (2006) 28

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J. Pütz

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3. Fachkonferenz 'Nanotechnologie in der Lackpraxis', 12.10.2006, Stuttgart, Germany, Vincentz, Hannover (2006)

C. Trenado, D. J. Strauss, T. Smuc, A. Maksimovic, B. Reinhard, A. Altherr, K. Endres, H. K. Schmidt

Modeling of Fire Protective Materials

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M. Tuomikoski, R. Suhonen, M. Välimäki, T. Maaninen, A. Maaninen, M. Sauer, P. Rogin, M. Mennig, S. Heusing, J. Puetz, M. A. Aegerter

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M. R. S. Castro, N. Al-Dahoudi, P. W. Oliveira, H. K. Schmidt

Transparent conductive carbon nanotube films onto PC substrate deposited by sol-gel method

Plastic Electronics 2006 – 2nd International Conference & Showcase, Sheraton Hotel & Towers Conference Centre, 24.10. – 25.10.2006, Frankfurt, Germany

M.R.S. Castro, H.K. Schmidt

Development of a carbon nanotube-modified transparent conductive coating

Summer School on Nanotubes 2006, 03.07. -15.07.2006, Cargèse, France

S. Gerbes, S. Kiefer, B. Schäfer, Y. Wolf, W. Metzger, S. E. Motsch, M. Oberringer, R. Gerdes, P. Olivera, M. Veith

Structured Surfaces for Cell Differentiation

BioStar 2006, ICBN 2006, 09 – 11.10.2006, Stuttgart

S. Mathur, H. Shen, T. Ruegamer, V. Sivakov, S. Barth

Ge and Core-Shell Ge/Si-C-N Nanowires: Mechanistic Investigations on Auto-Catalytic Growth

MRS Spring Meeting San Francisco, 17.-21. April 2006, San Francisco, USA

S. Mathur, H. Shen, S. Barth, T. Ruegamer

Metall Oxide Nanowires: Growth, Applications and Devices

MRS Spring Meeting San Francisco, 17.-21. April 2006, San Francisco, USA

S. Mathur, S. Barth, E. Hemmer, J. Altmayer, H. Shen

Protective and Biocompatible Nanostructured Surfaces by Chemical Vapor Deposition

E-MRS-Spring-Meeting, 29.05. – 02.06.2006, Nizza, Frankreich

S. Mathur, T. Rügamer

Phase controlled Deposition of Vanadium Oxide Gas Sensing Devices

E-MRS Spring Meeting, 29.05. – 02.06.2006, Nizza, Frankreich

S. Mathur, R. Ganesan, S. Barth, H. Shen

Tin Oxide Nanostructures: Growth, Applications and Devices

The American Ceramic Society’s 108th Annual Meeting combined with MS&T ‘06 – Materials Science and Technology 2006 Conference and Exhibition, 15. -19.10.2006, Cincinnati, USA

S. Mathur, E. Hemmer, S. Barth, J. Altmayer, N. Donia, N. Lecerf, I. Kumakiri, R. Bredesen

Microporous ZrO_2 Membrane Preparation by Liquid-Injection MOCVD*

ICIM9 – 9th International Conference on Inorganic Membranes, 25. – 29.06.2006, Lillehammer, Norway

*ausgezeichnet mit dem Poster Award

S. Mathur, J. Altmayer, S. Barth, C. Cavelius, E. Hemmer, P. Kuhn, T. Ruegamer, H. Shen

Chemical Nanotechnology: From Molecules to Applications

NDVAK,19. – 20.06.2006, Dresden

T. Ruegamer, P. Kuhn, N. Donia, J. Kondratiuk, S. Mathur

Deposition of Functional PECVD-Coatings for Industrial ApplicationsNDVAK, 19. – 20.06.2006, Dresden

Lectures / Vorlesungen

Lectures / Vorlesungen

M. A. Aegerter

Optik und dünne Schichten

Universität des Saarlandes, (WS 05/06)

M. A. Aegerter

Werkstoffwissenschaftliches Seminar Nichtmetalle

Universität des Saarlandes, (WS 05/06)

S. Mathur

Spezielle Kapitel der Chemie für Lehramtsstudenten

Universität des Saarlandes, (WS 05/06)

S. Mathur

Allgemeine Chemie und Grundlagen der Hauptgruppenchemie

Universität des Saarlandes, (WS 05/06)

S. Mathur

Technische Chemie, Beschichtungstechnologie

Universität des Saarlandes, (WS 05/06)

S. Mathur

Ringvorlesung "Mikro- und Nanostrukturen"

Universität des Saarlandes, (WS 05/06)

S. Mathur

Anorganische und Analytische Chemie

Julius-Maximilians-Universität Würzburg, (WS 06/07)

D. J. Strauss

Modelling und Simulation (WS 05/06) (Vorlesungen D. J. Strauss im Masterstudiengang „Biomedizinische Technik" an der Hochschule für Technik und Wirtschaft des Saarlandes in Kooperation mit den Universitätskliniken des Saarlandes und dem Fraunhofer Institut für Biomedizinische Technik)

D. J. Strauss

Biomaterialien (WS 05/06)

D. J. Strauss

Einführung in die medizinische Messtechnik (WS 06/07)

D. J. Strauss

Biomedizinische Signal- und Bildverarbeitung I und II (SS 06),

D. J. Strauss

Audiologie (SS 06)

D. J. Strauss

Informatik (WS 05/06, WS 06/07)

M. Veith

Allgemeine Chemie und Grundlagen der Hauptgruppenchemie (SS 06, WS 06/07)

M. Veith

Metallorganische Chemie (SS 06)

M. Veith

Molekülchemie der Hauptgruppenelemente (SS 06)

M. Veith

Materialien aus molekularen Vorstufen (SS 06)

M. Veith

Spezielle Kapitel der Anorganischen Chemie (WS 06/07)

M. Veith

Molekülchemie der Hauptgruppemelemente II (SS 06)

M. Veith

Allgemeine Chemie für Pharmazeuten (WS 06/07)

Practical courses / Praktika

M. A. Aegerter

Fortgeschrittenenpraktikum “Nichtmetalle I” (WS 2005/06)

M. Veith et al

Anorganisch-Chemisches Praktikum für Fortgeschrittene (SS 06)

M. Veith et al

Vertiefungspraktikum Anorganische Chemie (SS 06)

M. Veith et al

Fortgeschrittenenpraktikum für Lehramtsstudierende (SS 06, WS 06/07)

M. Veith et al

Chemisches Praktikum für Studierende der Physik, Werkstoffwissenschaften, der Biologie und der Metalltechnik (SS 06, WS 06/07)

M. Veith et al

Chemisches Grundpraktikum Einführungspraktikum Allgemeine und Anorganische Chemie (SS 06)

M. Veith et al

Schwerpunktpraktikum Anorganische Chemie (WS 06/07)

U. Werner

Kontraste in der Elektronenmikroskopie

Praktikum für Studenten der Werkstoffwissenschaften der Universität des Saarlandes

Other courses / Weitere Lehrveranstaltungen

M. Schubert

Innovationen durch Nanotechnologie: Mehrwert für Zulieferer der Automobilindustrie

21.03.2006, Saarbrücken

M. Schubert

Innovationen durch Nanotechnologie: Neue Materialien für den Maschinen- und Anlagenbau

13.06.2006, Saarbrücken

Patents / Patente

M. Schubert

Workshop Nanotechnologie im Unterricht

25. - 26.09.2006, Heidelberg

M. Schubert

Innovationen durch Nanotechnologie: Neue Oberflächen für Architektur, Möbel und Design

25.10.2006, Köln

M. Schubert

Summer School Chemische Nanotechnologie

24. - 28.07.2006, Saarbrücken

M. Schubert

Summer School Chemische Nanotechnologie

09. – 13.10.2006, Saarbrücken

D. J. Strauss

Models of Auditory Processing and Perception, One day professional course,

Advanced Technology Centre, Jalan Semarak, UTM City Campus, 24.02.2006, Kuala Lumpur, Malaysia

M. Veith et al.

Fachdidaktik (WS 06/07)

M. Veith

Fachdidaktisches Seminar für Lehramtsstudierende (SS 06)

M. Veith et al

Seminar zum Schwerpunktpraktikum Anorganische Chemie (WS 06/07)

Patents / Patente

Im Jahr 2006 wurden sieben neue Patentanmeldungen hinterlegt, die noch nicht offengelegt sind. Es wurden 16 Patente erteilt, davon fünf innerhalb von Europa und zehn auf internationaler Ebene. Eine Anmeldung wurde sowohl in Europa als auch international erteilt. Somit wurden insgesamt ca. 135 Patentanmeldungen durch das Leibniz-Institut für Neue Materialien vorgenommen. Rund die Hälfte dieser Schutzrechte ist erteilt.

In 2006, INM has filed seven new patent applications which are not yet published and 16 patents have been granted. Five of these patents are granted in Europe and ten in foreign countries. One patent application is granted both in Europe and international. INM applied around 130 patent families in total and around 50 percent of them are granted until today.

Erteilte europäische Patente:

EP 1487908 B1

Titel: „Kunststoffolie mit Mehrschicht-Interferenzbeschichtung“

Erfinder: A. Berni, M. Mennig, P.W. Oliveira, H. Schmidt

EP 1242522 B1

Titel: „Spritzgussversätze aus nanoskaligen Pulvern“

Erfinder: J. Kraus, R. Nonninger, H. Schmidt

EP 1113992 B1

Titel: „Verfahren zur Herstellung von Suspensionen und Pulvern auf Basis von Indium-Zinn-Oxid und deren Verwendung“

Erfinder: R. Nonninger, C. Goebbert, H. Schmidt, R. Drumm, S. Sepeur

EP 1287061 B1

Titel: „IR-absorbierende Zusammensetzungen“

Erfinder: M. Döbler, W. Hoheisel, H. Schmidt, R. Nonninger, M. Schichtel, M. Jost

EP 1230040 B1

Titel: „Substrat mit einem abriebfesten Diffusionssperrschichtsystem“

Erfinder: M. Mennig, P.W. Oliveira, H. Schmidt

EP 1284307 B1

Titel: „Verfahren zum Versehen einer metallischen Oberfläche mit einer glasartigen Schicht“

Erfinder: M. Mennig, G. Jonschker, H. Schmidt

Erteilte internationale Patente:

Japanisches Patent Nr. 3777386

Stammanmeldungstitel: „Verfahren zur Herstellung eines für optische Zwecke geeigneten Formkörpers“

Erfinder: B. Braune, E. Geiter, H. Krug, P. Müller, H. Schmidt

US-Patent Nr. 7,022,305 B2

Stammanmeldungstitel: „Nanoskalige Korundpulver, daraus gefertigte Sinterkörper und Verfahren zu deren Herstellung“

Erfinder: R. Drumm, C. Goebbert, K. Gossmann, R. Nonninger, H. Schmidt

US-Patent Nr. 7,026,269 B2

Stammanmeldungstitel: „Metallische Hydrierkatalysatoren“

Erfinder: D. Vanoppen, M. Veith, K. Valtchev

Malaysisches Patent Nr. MY-122234-A

Stammanmeldungstitel: „Nanostrukturierte Formkörper und Schichten sowie Verfahren zu deren Herstellung”

Erfinder: E. Arpac, P. Müller, H. Schmidt, B. Werner, H. Krug, P.W. Oliveira, S. Sepeur

US-Patent Nr. 7,037,596 B1

Stammanmeldungstitel: „Beschichtungsmasse auf Silanbasis mit katalytischer oxidativer und desodorisierender Wirkung“

Erfinder: T. Benthien, S. Faber, G. Jonschker, S. Sepeur, H. Schmidt, P. Stößel

Japanisches Patent Nr. 3802048

Stammanmeldungstitel: „Optische Elemente und Verfahren zu deren Herstellung“

Erfinder: H. Krug, R. Naß, H. Schmidt, L. Spanhel

Kanadisches Patent Nr. 2,249,609

Stammanmeldungstitel: „Verfahren zur Herstellung agglomeratfreier nanoskaliger Eisenoxidteilchen mit hydrolysebeständigem Überzug“

Erfinder: C. Lesniak, T. Schiestel, R. Naß, H. Schmidt

Koreanisches Patent Nr. 10-0602076

Stammanmeldungstitel: „Verfahren zur Herstellung optischer Mehrschichtsysteme“

Erfinder: M. Mennig, P.W. Oliveira, H. Schmidt

US-Patent Nr. 7,135,206 B2

Stammanmeldungstitel: „Beschichtete Titanoxid-Teilchen“

Erfinder: M. Schichtel

Taiwanesisches Patent Nr. I 268364

Stammanmeldungstitel: „Verfahren zur Herstellung optischer Elemente mit Gradientenstruktur“

Erfinder: U. Dellwo, M. Mennig, P.W. Oliveira, H. Schmidt, H. Schneider

Koreanisches Patent Nr. 10-0587243

Stammanmeldungstitel: „Verfahren zum Versehen einer metallischen Oberfläche mit einer glasartigen Schicht“

Erfinder: M. Mennig, G. Jonschker, H. Schmidt

Events / Veranstaltungen

Nano tech 2006, International Nanotechnology Exhibition & Conference, Tokyo, 21.-23.02.2006

Hannover Messe, Hannover, 24.-28.06.2006

Nano Korea 2006, International Nanotech Symposium & Exhibition in Korea, Seoul, 30.08.-01.09.2006

Materialica 2006, World of Product Engineering, München, 10.-12.10.2006

Veranstaltungen des Kompetenzzentrums cc-NanoChem e.V.

NanoMed 2006 – 5th International Workshop on Biomedical Applications of Nanotechnology, 16.-17.02.2006, Berlin

Innovationen durch Nanotechnologie: Mehrwert für Zulieferer der Automobilindustrie, 21.03.2006, Saarbrücken

Mitglieder-Workshop BASF AG, 10.04.2006, Ludwigshafen

Mitglieder-Workshop Netzsch Feinmahltechnik GmbH, 23.05.2006, Selb / Tirschenreuth

Innovationen durch Nanotechnologie: Neue Materialien für den Maschinen- und Anlagenbau, 13.06.2006, Saarbrücken

Summer School Chemische Nanotechnologie, 24.-28.07.2006, Saarbrücken

Lehrer-Workshop: Naturwissenschaft entdecken! Nanotechnologie im Unterricht, 25.-26.09.2006, Heidelberg

Mitglieder-Workshop Life-Science-Anwendungen, BAYER Schering Pharma, 29.09.2006, Berlin

Summer School Chemische Nanotechnologie, 09.-13.10.2006, Saarbrücken

Innovationen durch Nanotechnologie: Neue Oberflächen für Architektur, Möbel und Design, 25.10.2006, Köln

Nanotechnologies for Competitive Advantage Cross-Border Partnership Opportunities, 15.12.2006, Luxembourg

Cooperations / Kooperationen

Kooperationen des INM mit saarländischen Forschungseinrichtungen

Prof. Matthias Hannig, Universität des Saarlandes, Paradontosevermeidung

Prof. Jürgen Breme, Universität des Saarlandes, Kooperationen im Rahmen der Fortsetzung des Kompetenzzentrums CC-Nanochem

Prof. Günter Fuhr, IBMT, St. Ingbert, Kooperationen im Rahmen des EU-Projekts CellPROM und der Fortsetzung des Kompetenzzentrums CC-Nanochem

Dr. J.-C. Pyun, KIST EUROPE Forschungsgesellschaft mbH, Saarbrücken, Sensorentwicklungen

Prof. Frank Mücklich, Universität des Saarlandes, Charakterisierung und Strukturierung der Dünnschichtsysteme.

Sowie diverse Kooperationen mit der Universität des Saarlandes im Rahmen des DFG Sonderforschungsbereich 277 und in diversen Projekten wie z. B. im EU-Projekt CellPROM

Kooperationen des INM mit weiteren Forschungseinrichtungen

Prof. Samuel S. Mao, Lawrence Berkeley National Laboratory EETD Advanced Energy Technologies, USA New Generation Oxide Semiconductors

Dr. Lionel Vaysseires, National Institute for Materials Science (NIMS), Ibaraki, Japan, Purpose-built Functional Metal Oxide Nanostructures

Prof. J. R. Morante, Universitat de Barcelona, Spanien, Device Application of One Dimensional Nanostrcutures

Dr. Kurt Benkstein, National Institute of Standards and Technology (NIST), Gaithersburg, USA, Metal Oxide Gas Sensors

Prof. Ulrich Gösele, Max-Planck-Institute of Microstructure Physics, Halle, Atomic Layer Deposition

Dr. Monica Lira Cantu, Institut de Ciència de Materials de Barcelona, Universität Bellaterra, Barcelona, Spanien, Functional Properties of Oxide Nanowire

Dr. Hagen Thielecke, Fraunhofer Institute for Biomedical Engineering (IBMT), Biohybrid System Department, Cell-based Sensors & Biomonitoring, St. Ingbert, Zusammenarbeit im Rahmen DFG Schwerpunktprogramm “Bio-Nano-Responses”

Dr. Heidi Van den Rul, IMEC vzw, Division IMOMEC & Hasselt University, Diepenbeek, Belgien, Precursor Development

Dr. Rune Bredesen, SINTEF Materials Technology, Oslo, Norwegen, Funktionalisierung von Keramikmembranen

Prof. Gunnar Westin, Ångström Laboratory, Universität Uppsala, Schweden, Precursor Development

Prof. Witold Gulbinski, Vilnius University, Vilnius, Polen, Kooperation im Rahmen DAAD geförderter Projekte

Prof. Gerardo F. Goya, Universidade de São Paulo, Brasilien, Kooperation im Rahmen der Förderung durch die Volkswagenstiftung „Molecule-based Synthesis of Nanophase Materials“und Instituto Universitario de Investigación en Nanociencia de Aragón (INA), Universität Zaragoza, Spanien

Prof. Joydeep Dutta, Asian Institute of Technology (AIT), Pathumthani, Thailand, Self-assembly of Nanowires

Prof. Arzum Erdem, Ege University, Izmir, Türkei, Kooperation im Rahmen des Sokrates/Erasmus, „Biosensors“

Prof. Pyun, Yonsei University, Materials Science and Engineering, Seoul, Korea, Functional Nanostructures for Biosensors

Dr. Wilfried Goldacker, Institut für Technische Physik, Forschungszentrum Karlsruhe, Karlsruhe, MgB_2 Superconductors