

# Materialwissenschaften

Ruhr-Universität Bochum

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## Intro

Materials Science and Engineering (MSE) is one of the research priorities at the RUB where it has strong tradition. It is based on a joint approach from engineering and science departments with the objective to contribute to a better understanding of basic and applied problems related to the use of materials in advanced technologies.

Scientists from different departments work together and share expensive research infrastructure, and they were successful as documented by a number of Collaborative Research Centers (Sonderforschungsbereiche, SFBs) funded by the German Research Foundation (DFG) at the RUB.

SFB 398 („life time oriented design concepts“, speaker: Prof. Dr. F. Stangenberg) concerns the structural reliability of engineering structures within 17 research projects. In SFB 459 (“shape memory technology“, speaker: Prof. Dr. G. Eggeler), scientists force to achieve breakthroughs in shape memory technology within more than 20 collaborative projects. SFB 491 (“magnetic heterostructures: spin structures and spin transport“, speaker: Prof. Dr. Dr. h.c. H. Zabel) investigates the basics of future information- and communication technologies, semiconductor- and metal-physics by common interfaces in spintronic heterostructures. SFB526 (“rheology of the earth“, speaker: Prof. Dr. W. Friederich) is dedicated to the mechanical behaviour of Earth materials. In SFB 558 (“metal-substrate interactions in heterogeneous catalysis“, speaker: Prof. Dr. C. Wöll) investigates the chemical activities of deposited metal clusters as a function of size and the interaction with the oxide substrate.

R. Drautz and O. Kastner

## Interdisciplinary Center for Advanced Materials Simulation – ICAMS



ICAMS Directors from the left: A. Hartmaier, R. Drautz and I. Steinbach

The Interdisciplinary Centre for Advanced Materials Simulation (ICAMS) is a new research centre at the Ruhr-University Bochum (RUB), Germany.

ICAMS is supported by a consortium led by ThyssenKrupp Steel AG, Salzgitter Mannesmann Research GmbH, Robert Bosch GmbH, Bayer Materials Science AG and Bayer Technology Services GmbH together with the Max-Planck-Institute for iron research, the RWTH Aachen and the state of North Rhine Westphalia.

ICAMS was founded to develop the field of advanced materials simulation at the RUB, an interdisciplinary field of materials science and engineering which is increasingly gaining attention. This field has its roots in, and has strong connections to physics, chemistry, to the materials sciences and other branches of engineering as well as to mathematics and computer science.

ICAMS is a truly interdisciplinary institute at the RUB. It covers a highly innovative field of research. The research carried out at ICAMS is highly visible nationally and internationally and will help to bridge the divide between academic and industrial research. This will allow ICAMS to lead the development of highly efficient simulation techniques for materials design that may be transferred directly into industrial applications.

ICAMS focuses on the development and application of a new generation of simulation tools for multi-scale materials modelling with the aim of reducing development cost and time for new materials. Within the approach taken by ICAMS, the different length scales that are relevant for materials - from the atomic structure to macroscopic properties of materials - are bridged by an interdisciplinary team of scientists from engineering, materials science, chemist-

ry, physics and mathematics.

The structure of ICAMS is a matrix formed by the modelling approaches on the different scales and the classes of materials under investigation. In a hierarchical approach the materials are investigated from the atomic structure to the microstructure of the phases to the behaviour under service conditions. Accordingly, three departments form the core of ICAMS. The ICAMS board of directors is formed by the heads of the three ICAMS departments and the speakers of the three so-called advanced study groups that embed ICAMS into research activities at the RUB, the MPIE for iron research and the RWTH Aachen. The ICAMS advisory panel assists the board of directors and supervises its decisions.

The Directors of these the three new departments have been appointed recently. Prof. Dr. Ralf Drautz is leading Department 1

(ICAMS continued)

(atomistic modelling and simulation). He earned his doctoral degree at the Max-Planck-Institute for metals research in Stuttgart and spent his research fellowship at the Department of Materials of the University of Oxford where he worked on the field of the modelling of interatomic interactions. Department 2 (scale bridging thermodynamic and kinetic simulation) is lead by Prof. Dr. Ingo Steinbach, who was formerly a research fellow at the RWTH Aachen.

Prof. Steinbach is working in the field of microstructure evolution, phase field theory and the numerics of free boundary problems. The Director of Department 3 (micromechanical and macroscopic modelling) is Prof. Dr. Alexander Hartmaier, who previously held a professorship in materials science at the Friedrich-Alexander-Universität Erlangen-Nürnberg. Prof. Hartmaier earned his Ph.D. at the Max-Planck-Institute for metals research in Stuttgart. His special research topics are micromechanical simulations as well as dislocation dynamics and large scale atomistic simulation.

The three ICAMS departments are supported by three advanced study groups that represent specific expertise in modelling, characterization and processing: Prof. Dr. Jörg Neugebauer (modelling aspects, MPI for iron research), Prof. Dr. Gunther Eggeler (input data and validation, RUB) and Prof. Dr. Wolfgang Bleck (aspects of processing and characterization, RWTH Aachen). Innovative master and doctoral courses will be built upon the interdisciplinary ICAMS structure. These

will not only embrace mechanical engineering with its materials science focus, but also include in particular the other engineering fields, as well as chemistry, physics, and mathematics. In this way a new generation of materials engineers will be educated with broad interdisciplinary expertise, in particular in the field of materials simulation.

<http://www.icams.rub.de>

G. Eggeler

## High Temperature Materials

There is a continual drive for increased thermal efficiency in energy conversion and aircraft propulsion systems. Therefore operating temperatures have been progressively increasing during the last decades. The critical components for high temperature applications operate in the creep range, where they have to withstand severe service conditions including high temperature plastic deformation, thermal fatigue and high temperature corrosion. Critical high temperature components like steam headers in coal fired power plants or first stage blades in advanced gas turbines are manufactured from high temperature materials which possess a high inherent creep strength in combination with a good high temperature corrosion resistance. Tempered martensite ferritic steels (600°C range) and single crystal super alloys (1000°C range) are examples for classical high temperature materials which receive considerable attention from researchers of the materials science and engineering field. And high temperature intermetallics like TiAl or FeAl represent potential candidates for advanced components in modern high temperature technology which in recent years have seen a slow transi-

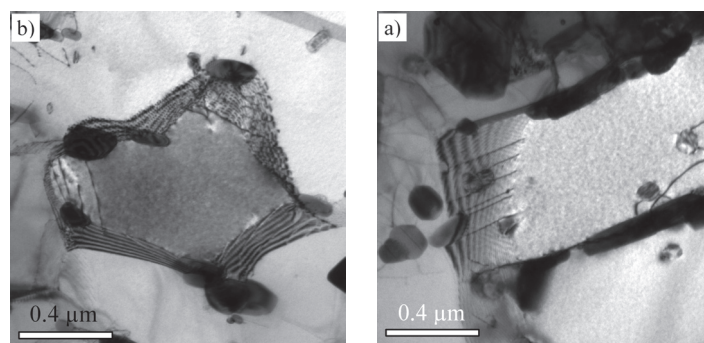
tion from alloy exploration and research to slow industrial development.

But high temperature materials are not only technologically interesting. They are a fascinating subject area for research in different fields of materials science and engineering. They are generally difficult to process and manufacture. Therefore basic research on processing technologies is important. High temperature materials generally have complex microstructures and a good understanding of thermodynamic stability and of microstructural evolution during high temperature service is important. There is a need to use optical microscopy, scanning electron microscopy and transmission electron microscopy (with the new experimental extensions available today like orientation imaging in the SEM or electron loss spectroscopy in the TEM) in combination with quantitative image analysis to investigate microstructures. And today material scientists can chemically analyse 1 µm wide cubic volumes using the 3D atom probe method to study segregation of impurities to interfaces and other solid state reactions occurring in high temperature service. High temperature materials for temperatures

well above 1000°C (beyond superalloy technology) and related mechanical test methods are today being considered. And there is an interest in new specimen geometries for high temperature testing (thermal fatigue, fracture mechanics, miniature and multiaxial specimens). And research on how elementary high temperature deformation processes interact in microstructures of complex engineering materials has just started. Research on high temperature materials at the Ruhr University Bochum takes a broad view focussing on new and interesting mechanical, chemical, microstructural and theoretical work. It considers all aspects of proces-

sing, microstructure, properties and applications of important traditional high temperature materials as well as on new high temperature intermetallics. Research at the Ruhr University Bochum work on recent developments in high temperature materials development, processing, microstructure and constitution, mechanical and micro-mechanical analysis, coupling of elementary deformation and microstructural softening mechanisms, environmental degradation and advanced materials modelling on all length scales.

<http://www.rub.de/ww>



**Figure 1:** Interaction of dislocations with micro grain boundary carbides (a) and (b) the pinning effect of carbides on micro grain boundaries during the high temperature deformation of an important high temperature steel (transmission electron micrograph).

R. Loschen

## International Max Planck Research School „SurMat“

In 1999, the Max Planck Society together with the Association of Universities and other education institutions in Germany launched an initiative to promote junior scientists called the International Max Planck Research Schools (IMPRS). These Schools offer especially gifted students from Germany and abroad the possibility to work towards their doctoral degree in a structured programme providing excellent research conditions.

The doctoral students obtain grants for up to three years.

49 International Max Planck Research Schools have already been established. In April 2004 the IMPRS for Surface and Interface Engineering in Advanced Materials (IMPRS-SurMat)

came to birth. This is a cross-national project between the Max Planck Institutes für Eisenforschung (Düsseldorf) and Kohlenforschung (Mülheim), four faculties of the Ruhr-Universität Bochum and three renowned Chinese institutions: the Department of Materials at the University of Science and Technology in Beijing, the State Key Laboratory of Physical Chemistry in Xiamen and the Department of Chemistry at Fudan University, Shanghai. Since 2004, 44 students from 20 different nations have joined this programme and nine have already received their doctoral degree.

IMPRS-SurMat covers topics ranging from fundamental scientific issues to engineering

applications. This includes topics such as corrosion, adhesion, heterogeneous catalysis, tailoring of surfaces by thin films and nano-structuring techniques or computational material design. As the interdisciplinary collaboration between science and engineering departments is one of the key factors each student is supervised by more than one member of SurMat, typically by members of both the surface science and the materials engineering community. Additionally the interdisciplinary education of students is of particular importance. The curriculum comprises four summer and winter schools which focus on the physical chemistry of surfaces and interfaces, phase transformations induced

by the presence of interfaces, the mechanical properties of interface dominated materials, thin films and nano-scale patterning and processing of thin film covered materials. Besides classes students are also taught in lab courses. The aim is that each student will gain a comprehensive insight into concepts and methods of interface analysis and engineering that can be applied in various fields of materials design. Furthermore regular research symposia give the students the possibility to present their own topics to their fellow students as well as to an international audience.

For further information see:  
[www.imprs-surmat.mpg.de](http://www.imprs-surmat.mpg.de)



**SurMat-Students 2006**, from left to right: Tao Liu, China; Bekir Salgin, Turkey; Paul Sunday Nnamchi, Nigeria; Stephane Y. Kemtchou, Cameroon; Haybat Itani, Lebanon; Edmanuel Torres, Colombia; Cezarina Mardare, Romania; Andrei Mardare, Romania; Hengshan Qiu, China; Maria Benitez Romero, Ecuador; Ali A. Bazazi, Iran; Robert Zarnetta, Germany; Shankhamala Kundu, India; Özlem Özcan, Turkey; Juan Zuo, China; (A. Ludwig, lecturer); Ying Chen, China; Keerthika Balasundaram, India; Genesis N. Ankah, Cameroon.

M. Muhler and C. Wöll

## Adsorption, activation and storage of hydrogen by solids

The interaction of hydrogen with solids is a topic of immense technological importance. In chemistry hydrogenation reactions are among the most important processes in heterogeneous catalysis. One example is methanol synthesis from syngas ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ), where the activation of  $\text{H}_2$  molecules to form

reactive hydrogen species on metal oxide surfaces is the key-step. In physics hydrogen dopants e.g. in ZnO have a pronounced influence on the properties of this large band gap, direct semiconductor. In the engineering sciences the diffusion of hydrogen into metals and the accompanying changes of the

mechanical properties have very important implications.

With regard to the future generation of energy hydrogen is expected to play a key role. Fabrication of hydrogen gas from sources other than oil and coal, storing and transporting this gas in liquid or gaseous form, and finally converting hydrogen to

different forms of energy, are all topics of key interest.

With regard to a clean generation of hydrogen direct splitting of water using just sunlight as an energy source is an important goal, which is attracting considerable research interest presently. Within the collaborative research center SFB 558

(Muhler and Wöll continued)

“Metal-substrate interactions in heterogeneous catalysis”(see [www.sfb558.de](http://www.sfb558.de)) the interaction of hydrogen with oxide surfaces is studied in a systematic fashion. Surprisingly, mostly because of a lack of suitable experimental techniques, only little is known about this most simple adsorbate on a solid substrate. As a result, we have in recent years either modified or newly developed techniques to investigate the nature of hydrogen bonded to surfaces of solids. This effort was rather successful, in the past few years a number of very interesting observations have been made, including the hydrogen induced metallization of ZnO surfaces, the precise role of surface hydrogen species at oxygen vacancies in methanol synthesis, and an un-

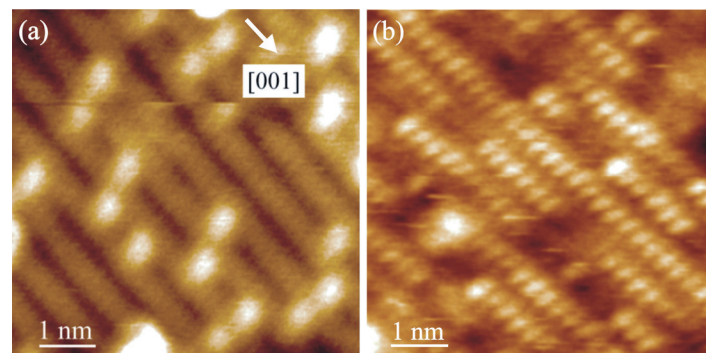
expected large diffusion coefficient of H atoms from the surface into the bulk for  $\text{TiO}_2$ . An example is provided in Fig. 1, where we show high resolution STM micrographs of a clean rutile  $\text{TiO}_2(110)$  surface with a medium-density of hydroxyl (OH) species (a) and a rutile  $\text{TiO}_2(110)$  surface saturated with atomic hydrogen (b). Unexpectedly, even when offering atomic hydrogen, it is not possible to fully saturate the surface. Instead, above the critical coverage shown in Fig. 1(b), hydrogen atoms are found to diffuse into the bulk of the substrate; a perfectly ordered monolayer as commonly observed for solid surfaces, can thus not be obtained.

Recently, we were also able to directly monitor the dissociative heterolytic adsorption of  $\text{H}_2$  on polycrystalline ZnO nano-

particles, presumably at oxygen vacancies, and the subsequent reaction of the adsorbed hydride-type species (Zn-H) with CO to adsorbed formate and methoxy species.

In the next years the research on hydrogen adsorbed on metal and metal oxide surfaces, the

diffusion of hydrogen into the bulk, and also the storage of hydrogen into appropriate materials will be a topic of key importance at the RUB to be studied by colleagues from chemistry, physics, and the engineering sciences.



**Figure 1:** High resolution scanning tunnelling microscopy (STM) images of a clean (a) and a hydrogen saturated rutile  $\text{TiO}_2(110)$  surface (b).

M.R. Hofmann and A.D. Wieck

## Spin-controlled optoelectronic devices

Within the Sonderforschungsbereich 491 (speaker: Prof. Dr. Zabel) the potential for optoelectronic devices that are controlled not only by the charge but also by the electron spin of the injected electrons is investigated.

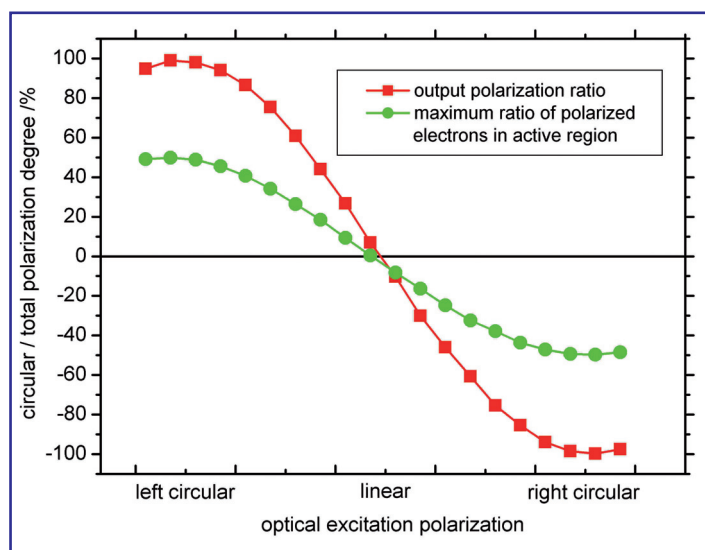
Three different devices for spin controlled photonics working at room temperature are analysed: First, a spin controlled light emitting diode (LED) is demonstrated which exhibits spin injection through ferroma-

gnetic Fe/Tb-multilayer contacts at room temperature. About 4% circular polarization degree of the LED emission is measured at room temperature even in remanence, i.e. without external magnetic fields. Furthermore, the coercive magnetic field intensity is only about 0.35T and thus we do not require a superconducting magnet to switch the magnetisation orientation of the contacts.

Second, the spin-dynamics in a conventional electrically pumped vertical cavity surface emitting laser (VCSEL) device is investigated in order to prove that spin effects overcompensate other polarization determining effects like birefringence due to internal electric fields, and that spin-amplification even occurs up to room temperature. For this purpose a VCSEL is pumped by an unpolarized electrical current simultaneously with a circularly polarized optical excitation that creates spin

polarized carriers. Figure 1 shows the ratio of circular versus total polarization degree of the VCSEL emission as a function of optical excitation polarization degree in comparison to the estimated maximum of the spin polarization degree of the optically injected carriers. The output polarization ratio (filled squares) reaches up to 100% and proves an effective spin-amplification in the VCSEL device at room temperature. A combination of the effective injectors and a common VCSEL could thus be an effective source for long distance spin transfer.

Third, for detection of such spin information a new spin detector was presented. It consists of a pin-diode with Fe/Tb-multilayer contacts and is capable of creating a polarization dependent spin-current also at room temperature and without applied magnetic fields.



**Figure 1:** Output polarization of the VCSEL as a function of the optical input polarization at room temperature. The sample is electrically pumped at 56% of the pure electrical threshold. Simultaneously, an optical excitation of 66% of the optical threshold is applied.

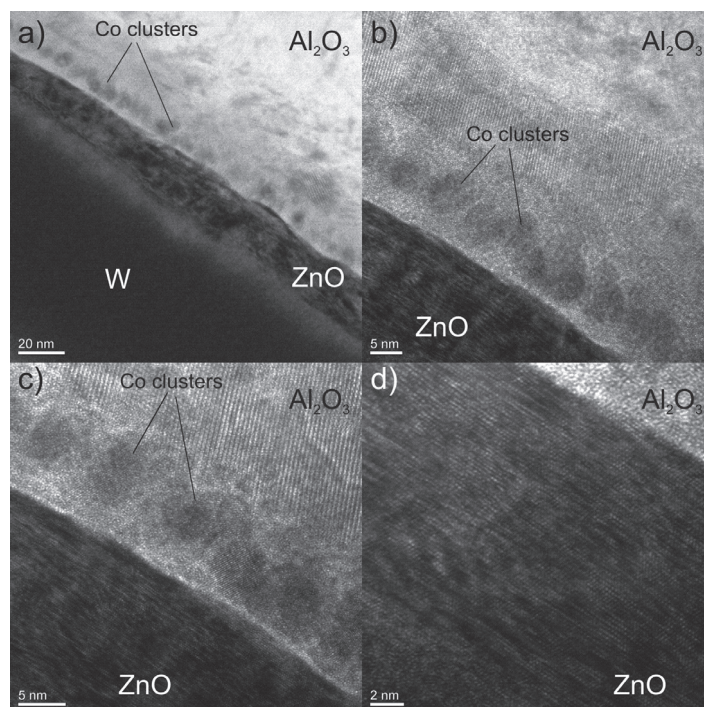
## Materials for Spintronics

In spintronic devices not only the charge of electrons is used for control but also their spin. With spin current the magnetization direction can be switched and domain walls can be moved. Spin valves are used as highly sensitive sensors for magnetic fields, for instance, in hard disk drives. Spin current and spin valves require ferromagnetic metal electrodes, whereas the supporting electronics consists of semiconductors. Full integration could be achieved, if semiconductors were available that are ferromagnetic. GaAs doped with Mn becomes ferromagnetic below 170K, too low for practical applications. Therefore there is presently an intensive search for better solutions. Two very hot candidates are the wide band gap semiconductors ZnO and  $\text{TiO}_2$ , which become ferromagnetic after doping with magnetic transition metal ions. We have prepared and studied thin films of ZnO and  $\text{TiO}_2$ , which have been doped with Co-ions via a 30 keV ion beam implanter. The structural, magnetic, and electronic changes that take place as a function of ion dose were then investigated by a number of experimental methods. For small dose levels the onset of ferromagnetic interaction could be verified at low temperatures, and with increasing ion dose strong ferromagnetism with Curie temperatures up to 800 K was detected. One of the crucial questions concerns the formation of metal clusters in the host matrix, which would disturb the intrinsic ferromagnetism of the doped semiconductor. Usually the limited solubility of magnetic ions in ZnO and  $\text{TiO}_2$  does not allow larger concentrations, which, however, are necessary for ferromagnetism at and above room temperature. Therefore a non-equilibrium method has to be chosen for doping, such as ion implantation by an accelerator. Nevertheless, cluster formation can not be

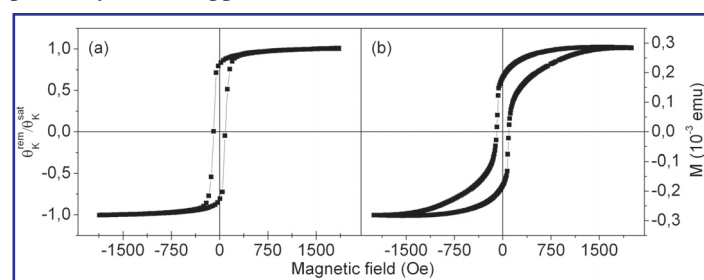
excluded. Ferromagnetic clusters can be discerned by their superparamagnetic behavior. Depending on the size, the ferromagnetic clusters switch frequently the magnetization direction due to thermal excitations. Only below a “blocking”-temperature, the magnetism of these clusters is thermally stabilized. From magnetization curves as a function of increasing temperature after cooling with and without external magnetic field the presence of clusters can be inferred and the blocking temperature can be determined. Clusters can also be imaged by transmission electron microscopy (TEM). Fig. 1 shows a TEM image taken from a thin ZnO film, deposited by rf-sputtering method on a sapphire substrate. The sample has been thinned after ion implantation to enable TEM imaging. With increasing resolution one can recognize the Co ion clusters in the sapphire substrate, whereas the thin ZnO film has retained its structural integrity in spite of the ion bombardment. These images confirm that cluster formation in the substrate is spatially separated from the homogeneously doped ZnO film. Both components can also be identified by their magnetic hysteresis, as shown in Fig. 2. Using the magneto-optical Kerr effect (MOKE) a ferromagnetic square shaped hysteresis is measured from the Co-doped ZnO film at 300K. While MOKE probes only the top film because of the limited penetration depth of the laser light used, with a SQUID-magnetometer both film and substrate are sampled with equal weight. Now the hysteresis consists of a superposition of a square shaped curve with a sharp magnetization reversal at the coercive field, which originates from the film, and a more rounded hysteresis with a high saturation field, which is due to the clusters in the substrate.

We have also shown that the Co-ions in the ZnO host matrix are in the  $\text{Co}^{2+}$ -oxidation state, therefore most likely substituting the  $\text{Zn}^{2+}$ -ions on their lattice sites. While CoO is an antiferromagnet with rock salt structure,  $\text{Co}^{2+}$ -ions in the ZnO host interact ferromagnetically via the polarization of trapped electrons in vacancies. Thus our structural, magnetic, and electronic properties together yield a consistent picture of the fascinating properties of this new class of spintronic materials.

The present work as well as many more results on doped and ferromagnetic semiconductors are documented in the PhD thesis of Dr. Numan Akdogan (Ruhr-Universität Bochum, 2008) and are the result of an intensive collaboration in the frame of the International Max Planck Research School „SURMAT“ (N. Akdogan, A. Nefedov, K. Westerholt, H. Zabel, H.-W. Becker, Ch. Somsen, R. Khaibullin, L. Tagirov, J. Phys. D: Appl. Phys. in print)



**Figure 1:** TEM – images of a thin ZnO – film on a sapphire substrate with increasing resolution from a) to d). The ZnO – film was doped by  $\text{Co}^{+}$ -ion bombardment, resulting in Co- metal clusters primarily in the sapphire substrate.



**Figure 2:** Magnetic hysteresis of Co-doped ZnO. In (a) the magnetic hysteresis is measured with the magneto-optical Kerr effect, which is representative for the ferromagnetism in the thin Zn(Co)O film. In (b) the magnetic hysteresis is shown from the same sample but measured with a SQUID magnetometer. The different shape is due to the fact that with SQUID both contributions, from the ferromagnetic film and from the substrate containing superparamagnetic Co – clusters, are superimposed.

# Micro-Electro-Mechanical-Systems

The development of new materials for microsystems (MEMS: Micro-Electro-Mechanical-Systems) by using combinatorial and high-throughput experimentation methods is the focus of the research group „Werkstoffe der Mikrotechnik“ at the Institute for Materials. The investigated material systems are mainly in the area of multifunctional thin films, i.e. materials which can perform as actuator and sensor simultaneously. Materials of interest include ferromagnetic thin films, shape memory thin films, ferro-magnetic shape memory thin

films, and materials for hydrogen storage. In these areas, ternary and quaternary materials systems are developed. Furthermore the group develops MEMS for innovative material science experiments.

The idea of combinatorial materials science (Fig. 1) is to develop and use advanced materials fabrication methods which produce a large number of different materials on a substrate in one experiment under identical conditions, i.e. a materials library (Fig. 2). The thin film materials libraries are fabricated by special magnetron sput-

ter processes, either by co-deposition or with a multilayer approach. After the combinatorial deposition process, material libraries are screened for desired physical properties by adapted high-throughput characterization tools. Most effectively the screening is performed by parallel (e.g. optical) or fast sequential methods. The group has developed micromachined cantilever arrays and micro-hotplate arrays which serve as platforms for the high-throughput screening experiments.

Figure 2 shows an example of a thin film materials library: the

complete ternary composition space is produced in one experiment and the compositions are mapped by energy dispersive X-Ray analysis. By temperature-dependent resistivity measurements, information about solid state phase transformation are efficiently collected and visualized in composition-function diagrams (Fig. 3).

For further information see: [www.rub.de/wdm/](http://www.rub.de/wdm/)

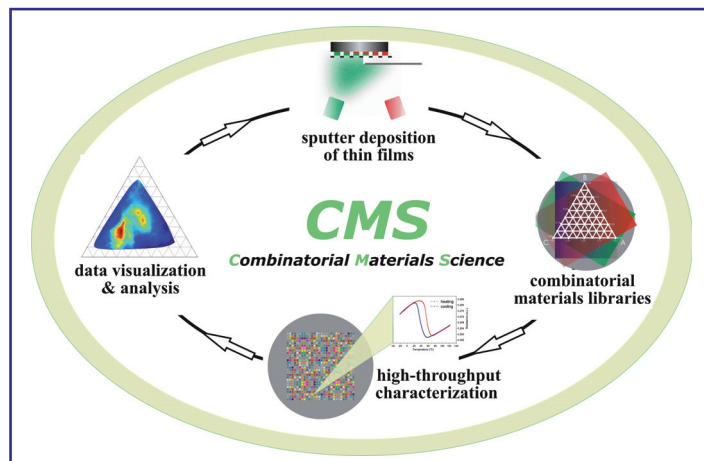


Figure 1: Research concept in combinatorial materials science.

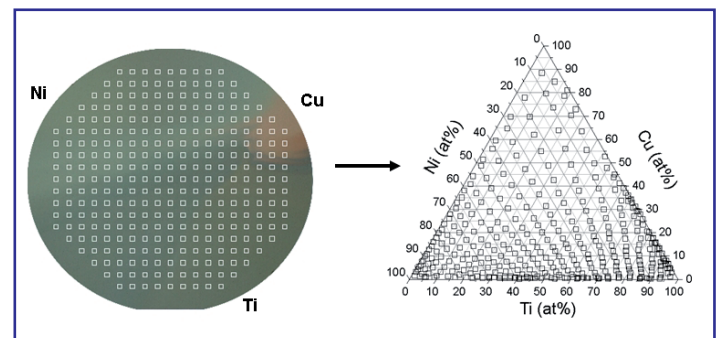


Figure 2: On the left a photo of a continuous composition spread type materials library is shown. The measurement points where the chemical composition was measured are indicated and transferred to a ternary composition diagram.

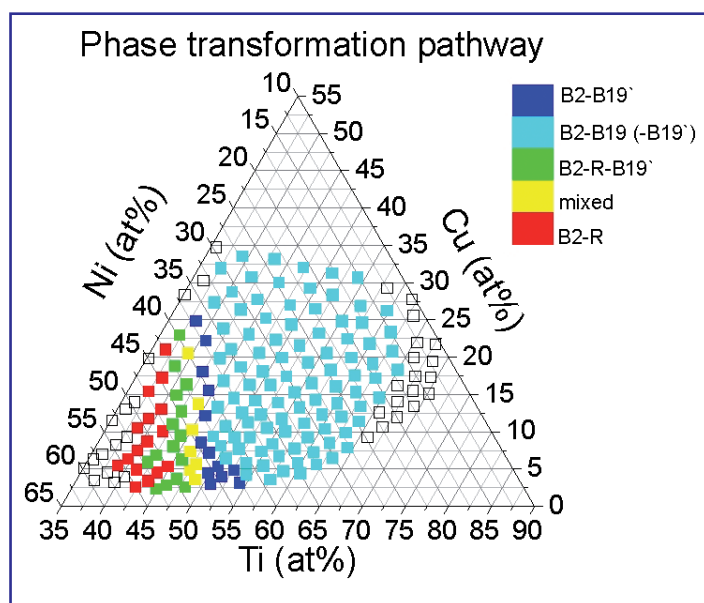


Figure 3: Ternary composition diagram illustrating the range of alloys which show a reversible martensitic transformation and their phase transformation pathway.

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