4th Dresden Nanoanalysis Symposium

"Materials modeling and characterization"

Abstract booklet

June, 15th 2016
Dresden, Germany

Sponsors:
”From data to knowledge”

Functional nano imaging workflows for industrial applications

Ivan Lazić, Eric G.T. Bosch, Joerg R. Jinschek and Jens Greiser

FEI Company, Eindhoven, The Netherlands

Abstract: Ongoing strong research focus on more efficient energy use and conversion, on more efficient transportation, and on environmental protecting technologies relies heavily on the advancement of (new) functional nano materials and nano systems. At any stage in research and development, studies of these nanomaterials’ structure, properties, and function are critical, including detailed atomic-scale insights.

To our advantage, atomic scale electron microscopy (EM), markedly advanced by utilizing recent hard- and software improvements, has become a powerful and indispensable tool for characterizing those nanostructures. Ongoing activities concentrate on methodological aspects of state-of-the-art EM and thereby open routes towards atom sensitive imaging of nanostructures that play a crucial role in numerous applications.

Imaging the phase of the transmission function has always been the ultimate goal of any (S)TEM imaging technique as it is, for thin samples, directly proportional to the projected potential in the sample. Customarily this information is obtained using Holography [1] or by performing focus series reconstruction in TEM (FSR-TEM) [2], recently also in combination with Phase Plates (PP) [3] and/or image Cs correction.

The recently introduced Integrated Differential Phase Contrast (iDPC) STEM imaging technique [4, 5] is enabling live imaging of the phase of the transmission function of thin samples. One of the first striking advantages of this new technique is that it is able to image light (C, O, N …) and heavier elements (Sr, Ti, Ga …) together in one image whereas a standard (HA)ADF-STEM image shows only the heavier atoms. Another one is full frequency transfer which enables direct detection of low frequency information such are strain or contact/inner potentials.

However, the actual state and function of nanomaterials ‘in operation’ cannot always be inferred from examination under standard EM high vacuum and room temperature conditions or from postmortem EM studies. In situ techniques enable visualization of structural evolution under operational (or environmental) conditions, thereby providing new insights in important materials science questions [6, 7].

Moreover, the integration of a heater into a gas-flow MEMS nano reactor enables operando EM combining structural characterization of e.g. catalytic materials with simultaneous measurement of its activity for gaseous reactions [8]. These advancements open up for unprecedented control over experimental conditions in advanced EM experiments of dynamic phenomena in materials sciences.

3D Nano-characterization using electron tomography, from acquisition to quantitative analysis

T. Printemps\textsuperscript{1,2}, Z. Saghi\textsuperscript{1,2}, P. Bleuet\textsuperscript{1,2}, L. Hervé\textsuperscript{1,2}

\textsuperscript{1} Univ. Grenoble Alpes, F-38000 Grenoble, France
\textsuperscript{2}CEA, LETI, MINATEC Campus, F-38054 Grenoble, France.

Electron tomography (ET) is a 3D imaging technique with a resolution of around 1 nm. ET is performed by acquiring many 2D projection images all around a sample in a transmission electron microscope (TEM). After careful alignment of the acquired tilt series, inversion algorithms are used to reconstruct the volume of the sample. Main ET limiting factors are (i) projection misalignment, (ii) imprecisely determined tilt axis, (iii) limited data set, (iv) noisy projections, (v) and sample deformation during the acquisition. All those limiting factors are responsible for the resolution loss between 2D TEM images and reconstructed volume. Many recent works in ET try to correct those limiting factor by improving the alignment process \cite{1}, performing denoising \cite{2}, correcting sample deformation \cite{3}, or developing new reconstruction algorithms incorporating prior knowledge on the object \cite{4}, \cite{5}…

During this talk, ET-compatible TEM imaging modes, projections alignment and mathematical inversion theory will be briefly introduced. Some state-of-the-art results will be given and an erbium doped porous silicon sample will be used all along the presentation to better explain the different steps of the reconstruction process. 3D quantitative analysis results for this porous silicon sample will also be given showing the necessity for ET as a 3D nano-characterization technique with a nanometer resolution. To finish, advantages and remaining difficulties of ET will be discussed.

References:


Quantitative atomic scale inelastic STEM imaging
Gerald Kothleitner\textsuperscript{1,2}

\textsuperscript{1}Institute f. Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz, Austria
\textsuperscript{2}Centre f. Electron Microscopy (ZFE), Graz, Austria

Abstract: Z-contrast imaging in the scanning transmission electron microscope (STEM) has now become a routine technique for atomic scale imaging. Accompanied by developments like high-brightness guns and monochromators, improved electron energy-loss spectrometers or new Xray detector concepts, elemental-specific imaging at that scale has become feasible too. To date many examples of atomic resolution elemental maps have been published - mostly as color maps - often missing a profound explanation of the inelastic intensities and colors contained therein. As it turns out, the complex physics of scattering of the electron probe along aligned atomic columns produces a nonlinear relation between signal and composition and invalidates a simple relationship between the observed analytical intensities from the projected atomic positions.

Quantification of atomic resolution maps on an absolute scale (i.e. in units of atoms/nm\textsuperscript{3}), is an even bigger challenge. First of all, the conversion of analytical intensities into concentration values for a particular quantification scheme often requires extra parameters that are not readily at hand. Secondly, to recover the true concentrations, approaches to compensate for channeling need to be taken into account. With the use of the so-called quantum excitation of phonons (QEP) model, for example, a calculation of the underlying elastic and thermal diffuse scattering is possible and quantitative comparisons between experiment and quantum mechanical calculations for both EDXS (energy-dispersive X-ray spectroscopy) and EELS (electron energy-loss spectroscopy) can be made (figure 1). By implementing an inversion process, the correct numbers can be recovered approximately. Another possibility to reduce the effects of channeling is tilting or precessing the beam, with the drawback of losing resolution in the direction tilted. The signal obtained that way may serve, however, for normalizations of the channeled data set. Possibilities for a quantitative analysis on the atomic scale will be presented in this paper.

Figure 1. X-ray absolute volumetric concentrations for oxygen in strontium titanate [001] (upper row) together with QEP simulations (lower row), showing the elastic and thermal (scaled by x10) scattering components. cf. G Kothleitner et al, Phys. Rev. Lett. 112 (2014) 085501
Multilayer Laue lenses – Novel optics for nano X-ray tomography in a wide range of photon energies
J. Gluch¹, A. Kubec², S. Niese³

¹Fraunhofer Institute for Ceramics Technologies and Systems (IKTS), Dresden, Germany
²Fraunhofer Institute for Material and Beam Technology (IWS), Dresden, Germany
³AXO DRESDEN GmbH, Applied X-ray Optics, Dresden, Germany

Abstract: High-resolution nondestructive characterization of materials and structures, including kinetic processes in materials, is a highly ranked request in basic research, e. g. in materials science and nanotechnology, as well as in industrial research for process and quality control in several branches of industry including microelectronics, energy storage and lightweight construction. There is a particular need for 3D high resolution structural and chemical characterization of materials and devices with spatial resolution of 100 nm and below. Here multilayer Laue lenses (MLL) are promising optics addressing both aspects by focusing hard X-rays into small focal spots with high efficiency [1]. Such MLLs are linear zone plates made by thin film technologies such as magnetron sputter deposition. To achieve a two-dimensional imaging two MLL have to be combined to a so-called crossed-MLL. Highest resolution can be achieved with high numerical apertures and small zone widths while high efficiency is the result of large aspect ratios and perfect alignment of the zones according to their Bragg condition. We have added a stress layer on the side of the MLL structure bending it into the wedged geometry (wedged-MLL) [2]. Based on those MLL designs we show a concept and proof-of-principle experiments to perform full-field X-ray microscopy at photon energies significantly above 8.0 keV. This energy range is interesting to investigate 3D IC devices, since the increased transmission of the silicon substrate reduces the demands of sample preparation.


Modelling of thermal residual stresses and fracture in metal-ceramic composites

M. Basista, W. Węglewski, K. Bochenek and Z. Poniżnik

Institute of Fundamental Technological Research, Warsaw, Poland

Abstract: In processing of metal-ceramic composites thermal residual stresses may result from different CTEs of the constituent materials, variable cooling rates inside the bulk material, or irregular pore shapes causing thermal stress concentrations. This paper investigates the interplay between material microstructure and processing-induced thermal residual stresses (TRS) in particulate bulk metal-matrix composites (MMC) and infiltrated phase composites (IPC) with the main objective to explore the combined effect of TRS and microstructure on the macroscopic mechanical properties (E modulus, bending strength, fracture toughness) of the composite. The main focus is on numerical modelling of TRS, fracture toughness and effective elastic properties, while taking into account the real material microstructure from micro–computed tomography (micro-CT) experiments.

The modelling methodology will be developed on examples of a hot pressed chromium-alumina bulk MMC doped with rhenium and on an IPC obtained by squeeze casting infiltration of an alumina porous preform with molten Al alloy or Cu. Our interest in these particular composites is motivated by their potential applications in transport and energy sectors. The paper will include highlights on the processing technologies used (HP, SPS, ceramic tape casting/squeeze casting infiltration), microscopic analysis of material microstructure with special focus on micro-CT scanning, measurements of TRS by neutron diffraction (ND) method, and numerical modelling of TRS by FEM using micro-CT images of real material microstructure.

A numerical micro-CT based model developed to predict the TRS, Young’s modulus with account of TRS-induced damage of the ceramic phase will be shown (cf. Fig. 1). The grain size effect on TRS and Young’s modulus will be addressed. A good predictive capability of these TRS models was achieved which may become important considering the cost of beam time for ND experiments at neutron sources.

Another model to be presented is concerned with micro-CT FEM modeling of fracture in infiltrated metal-ceramic composites. The model accounts for crack bridging toughening mechanism, large plastic deformations of metal ligaments, and matrix-ligament decohesion. Here the results on $J$ integral in the case of compact-tension test specimen made of real interpenetrating phase composite will be discussed.

Finally, the large pool of obtained experimental data and modelling results will be wrapped up and conclusions will be drawn.

Fig. 1. Thermal residual stresses in Cr(Re)/Al$_2$O$_3$: experimental data vs. numerical results
Characterization and modelling of thermo-mechanical degradation in power electronic modules

O. Wittler¹, A. Grams¹, M. van Dijk¹, H. Walter¹, C. Ehrhardt¹, M. Schneider-Ramelow¹, K.-D. Lang¹,²

¹Fraunhofer IZM Berlin, Germany
²Technische Universität Berlin, Germany

Abstract: Typical power modules consist of power semiconductors soldered to the top side metallization layer of a DBC substrate. The top side of the semiconductor is connected to the substrate with Al wire bond and the set-up is covered with a silicone potting. The lifetime of these modules is limited by degradation of solder and Al-wire bonds due to thermo-mechanical loads in active power cycling. In order to overcome this limit and to achieve higher power densities together with a high lifetime, a range of research is undertaken, which is supported by material analysis and finite element modelling (FEM). The presentation will give an overview of recent activities at Fraunhofer IZM.

Recent reliability improvements of the die-attach by using silver sintering or transient liquid phase bonding instead of conventional soldering have led to longer lifetimes of power modules, because these materials show much less plastic deformation during thermal cycling [1]. Nevertheless, also these highly robust interconnects can show thermo-mechanical fatigue due to plastic creep deformation and thermo-mechanical modelling can identify main influence factors for reliability [2, 3, 4].

With the increase of lifetime of the die-attach, the reliability bottleneck is shifted to the heavy wire bonds on top of the chips. Due to the difference in coefficient of thermal expansion (CTE) between wire and chip material, the bonding interface is degrading rapidly during temperature cycling. This commonly results in interface cracking. An FEM-based lifetime model has been developed, which is capable of describing this failure mechanism independently from the geometry [5]. Based on this, a process modification was suggested that incorporates the introduction of trenches in the Al-wedge [6]. This results in a gain in lifetime of about 30% for a realistic laser modification processed wire (see Fig. 1), while theoretically more than 100% seem to be possible. Another promising option for lifetime improvement is the modification of the Al-wire material and its structure with respect to its structure and corresponding plastic deformation behavior [7].

References:
Collisional Computer Simulation of Ion Processing and Ion-Based Analysis of Nanostructures

W. Möller¹, K.-H. Heinig¹, T. Prüfer¹, A. Johannes², C. Ronning², J. Huang³, E. Zschech³,⁴

¹ Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
² Friedrich-Schiller-Universität, Jena, Germany
³ Technische Universität Dresden, Dresden Center for Nanoanalysis (DCN), Dresden, Germany
⁴ Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Germany

Collisional computer simulation based on the binary-collision approximation (BCA) has been widely applied to describe effects of ion irradiation on flat solid surfaces, such as ion implantation, surface sputtering, ion-induced damage and atomic mixing. Recent extensions allow fully three-dimensional simulations of irradiated nanostructures both in static [1,2] and dynamic [3] mode, the latter addressing the shaping of nanostructures under high-fluence ion irradiation as well as compositional modifications and the development of point defect damage. Three application examples will be addressed to demonstrate the potential of the simulations in nanophysics and processing of electronic nanomaterials as well as for ion-based nanoanalysis.

(i) The irradiation of free-standing ZnO nanowires of 150…200 nm diameter with 175 keV Mn ions incident at 45° in a rotating sample geometry has been investigated both experimentally and theoretically. Where available, the experimental results are in excellent agreement with the predictions from the simulation [4].

(ii) Feasibility studies have been started towards the fabrication of a room-temperature single-electron transistor using conventional CMOS technology. For this purpose, a single Si nanodot of 2…3 nm diameter is to be positioned in a thin SiO₂ layer, which will be accomplished by ion-mixing of a Si/SiO₂/Si layer stack and subsequent thermal phase separation. First predictions by combined dynamic BCA and kinetic Monte-Carlo (KMC) simulation demonstrate the feasibility for Ne nanobeam irradiation of a flat sample and broad beam Si irradiation of a nanopillar [5].

(iii) One- and three-dimensional dynamic BCA simulations of Ga focused ion beam erosion of Si for, e.g., TEM lamella preparation describe the shaping and the evolution of near-surface Ga implantation and sample amorphization, the latter being based on a critical-point-defect density model. For glancing-angle irradiation at energies between 1 and 30 keV, the predicted amorphization depths are in good agreement with experimental results. In particular, potential effects of surface roughness will be addressed [6].

[5] This part of the work is being funded by the European Union’s Horizon 2020 research and innovation program under Grant Agreement No 688072 (Project IONS4SET).
[6] This part of the work is being funded partially by BMBF (German Federal Ministry of Education and Research) within the “MaKiZu” project (16ES0066).
Properties and applications of novel visible light photocatalysts

George Kiriakidis

Physics Dpt. Univ. of Crete and IESL/FORTH, Crete, Greece

Abstract: Buildings are intended to provide protection to the occupants from atmospheric conditions and support their activities. Since buildings are major capital investments the prospect of the occupants experiencing the adverse health effects of air quality and/or poor thermal comfort conditions strongly contradict the aforementioned basic building’s function. Especially in the case of large scale structures which host large number of occupants like office buildings or schools, several studies link indoor environmental quality (IEQ) not only to human health problems, but also to decreasing productivity. This highlights indoor climate (air quality and comfort temperature) as essential qualities these buildings must feature.

In the past decades a large number of studies have identified the presence of many polluting chemical substances in indoor environments (buildings, homes). The solution to this problem is expected by a systematic and effective way to improved indoor environment quality utilizing the Photo-Catalytic (PC) oxidation technique generally accepted as an effective way to tackle the pollutant emission problem and contribute to comfort levels indoors.

An overview and recent advances on the synthesis and characterization of TiO2 materials doped with transition metals in different concentrations capable to absorb and activate under visible light irradiation will be presented including a report on novel PC materials as effective pollutant reducing agent, suitable for indoor besides outdoor applications. The structure and elemental analysis of the materials will be analyzed along with the corresponding photocatalytic efficiencies both for material in powder form as well as additives in a number of building envelope material matrices. Consequently an account of doped TiO2 as an effective photocatalytic material will be presented as a promising energy saving material for coatings in buildings and coatings for road tunnel applications.
Extraction of mechanical and thermal properties of thin films using nanoindentation combined with FEM
I. De Wolf\textsuperscript{1,2}, K. Vanstreels\textsuperscript{1}, O. Orkut Okudur\textsuperscript{1,2}, H. Zahedmanesh\textsuperscript{1} and U. Hangen\textsuperscript{3}

\textsuperscript{1}imec, Leuven, Belgium
\textsuperscript{2}Department Materials Science, Fac. Engineering, KU Leuven, Leuven, Belgium
\textsuperscript{3}Hysitron, Inc., Dennewartstrasse 25, 52068 Aachen, Germany

Nanoindentation increasingly finds applications in microelectronics. One of the reasons is that mechanical stress in films, structures and active devices, becomes of increasing importance for robustness and reliability. We discuss two applications of nanoindentation on ultra-low-k films: The determination of the mechanical properties of very thin films, and the determination of their thermal expansion coefficient. Both applications require support by finite element modelling. Ultra-low-k films are used for isolation of Cu interconnect lines in the back-end-of-line (BEOL) process. These films, which are made by introducing porosity in the matrix structure, offer a better electrical performance (less RC delay), but at the cost of a reduced mechanical strength. Nanoindentation can be used to study these films, but due to their porosity and low film thickness, the analysis and correct extraction of the intrinsic E-modulus of the films is complicated. Substrate effects and the indenter tip shape highly affect the results. In [1], we proposed a method where FEM was used to fit the data assuming elastic solutions, taking into account the shape of the indenter tip (Fig. 1, left). This model was found to work very well for various thin films (Fig. 1, center), allowing to subtract the E-modulus, but takes a lot of time (~60 min/sample). Comparing this model to the intrinsic thin film model (iTF) based on the work of Li-Vlassak [2], showed a very good match. The latter offers a software controlled solution, using iteration to fit the model to the data, taking on average ~3 min/sample. We showed that this model also fits our data obtained with different tips on various ultra-low-k films very well, but needs extension to lower indentation depths.

As a second example, nanoindentation experiments were performed at different temperatures on porous ultralow-k films. These films have a relatively high CTE compared with other components of integrated circuits and exhibit intrinsic tensile stresses, so, thin film cracking and adhesion are serious thermal-mechanical reliability issues. Tests were done using cube-corner indentations at different temperatures in a controlled atmosphere on a Hysitron TI950 triboindenter. The force at which cohesive crack initiation started was shown to depend on temperature. The Young’s modulus was found to be independent of temperature. Combining these results and verifying them with FEM-analysis, showed that this technique allows to deduce the CTE of the low-k films [3].

High-resolution mechanical studies of glass fiber composites

J. Lukes¹,¹, V. Cech²

¹Hysitron, Inc., Prague, Czech Republic
²Brno University of Technology, Brno, Czech Republic

Abstract: Improving a bond between a fiber and surrounding matrix by controlling the physical properties of fiber-matrix interface can enhance the bulk mechanical properties of a fiber reinforced composite. The interphase comprises the functional interlayer and the part of the matrix affected by the presence of the coated fiber [1]. In this study, we focus on mapping the mechanical properties of fiber-matrix interphase by means of high resolution Modulus Mapping™ technique and in-situ Scanning Probe Microscopy available on commercial TriboIndenter™ instrument. Monitoring a contact stiffness and a phase shift between modulating force signal and resulted signal of harmonic deformation over a cross-section of fiber-matrix interface clearly reveals sharp changes in mechanical properties of an interlayer of plasma polymer coated fibers and polyester matrix at a length scale <1μm [1]. The influence of surface topography on acquired stiffness maps is also discussed [2, 3].

Fig 1. In-situ Scanning Probe Microscopy image of a cross-section of plasma coated glass fiber and polyester matrix

References:

Mechanical characterization of ultra-thin coatings

T. Chudoba

ASMEC GmbH, Radeberg, Germany

Abstract: Nowadays coatings can be found in many applications. The coating thickness is determined by the original purpose and therefore more and more ultra-thin coatings with a thickness below 200nm are applied. This can be for instance optical coatings for anti-reflective or heat-shield purposes, barrier coatings to protect organic materials from humidity or oxygen or electrical coatings in microelectronics. Beside their original purpose coatings often have a mechanical protection function and should be scratch resistant. They further should show a good adhesion to the substrate or to an intermediate layer. Therefore a mechanical characterization is also necessary for ultra-thin coatings. However the commonly applied mechanical characterization methods like nanoindentation or scratch test come to their limit when the coating is thinner than 200 – 300nm and special demands exist for the calibration of the instruments.

In the talk the reasons of the limits for a comparable and quantifiable characterization will be explained. They are mostly depending on the tip which is in contact with the surface during characterization. Further several non-standard methods will be presented which allow a quantifiable measurement of coatings below 200nm. Some of the methods can only be applied in combination with the calculation of stress fields or deformations during mechanical contact of coated surfaces. Such calculations are meanwhile an indispensable tool for the analysis of the experiment as well as for its planning. An example is shown in fig. 1. It shows the von Mises stress field during indentation of a 50nm coating with a spherical indenter of 1µm radius. In this case it is impossible to generate plastic deformation in the coating because the glass substrate fails first and the coating cracks when the plastic deformation in the substrate is big enough.

Fig. 1: von Mises stress field in a 50nm hard coating on glass, indented by a spherical tip of 1µm radius and a load of 1mN
The challenge of measuring strain in FDSOI device structures - HRXRD as a potential method of resolution

H. Geisler¹, P. Hofmann¹, H.-J. Engelmann¹

¹GLOBALFOUNDRIES Dresden Module One LLC & Co. KG, Dresden, Germany

Abstract: Strain engineering is commonly used to boost the CMOS transistor performance on microelectronic circuits of sub-40nm technology nodes. PMOS devices show better electrical functionality if the transistor channel is subject to compressive stress, NMOS if the channel is under tensile stress. On bulk Si products, high compressive stresses can be obtained by means of an epitaxial Si₁₋ₓGeₓ filling of source-drain cavities. On Silicon-on-Insulator (SOI) and more recently on fully depleted SOI (FDSOI) chips, strain engineering plays an important role, too. However, the device integration scheme on FDSOI follows a different path. At the beginning of the FEoL processing route, a very thin (typically <10nm) single crystalline Si film (sc-Si) exists on top of a thin buried oxide on bulk Si. On PMOS areas, this thin sc-Si film is transformed into a sc-Si₁₋ₓGeₓ film by a certain condensation process which is more or less a diffusion reaction driving a pre-defined amount of Ge atoms into the existing sc-Si layer. Si atoms are removed from the original sc-Si film by preferential oxidation, and they are replaced by Ge atoms. The crystalline perfection and the strain state of the final sc-Si₁₋ₓGeₓ film are critical for the transistor performance. Both properties should survive all subsequent processing steps (STI, patterning, annealing, etc.) until the fabrication of the device structures will be completed. The physical characterization of such ultra thin sc-Si₁₋ₓGeₓ films is challenging due to their small volume and the miscut of their lattice planes relative to the bulk-Si lattice. It will be shown here that High-Resolution X-Ray Diffraction (HRXRD) is a powerful technique to fulfill this task. HRXRD is applied to small FDSOI pad structures with sc-Si₁₋ₓGeₓ films. Periodic trench structures with various widths of the active areas containing sc-Si₁₋ₓGeₓ films are measured after different processing steps. A high brilliance X-ray beam with a small diameter (down to ≈50µm on the specimen) is needed for this purpose, facilitated by an advanced X-ray diffractometer with a combination of a high brilliance rotating anode, Montel optics, monochromator, and an efficient 1D X-ray detector. High resolution Reciprocal Space Maps (RSMs) were measured with this experimental setup to obtain in-plane and out-of-plane lattice spacings of the sc-Si₁₋ₓGeₓ structures on FDSOI. It will be shown that the sc-Si₁₋ₓGeₓ films do not maintain a biaxial strain state after the patterning of the STI line structures. A considerable elastic strain relaxation is observed in one direction, whereas the original magnitude of strain is maintained along the other in-plane direction. It was recently suggested that the best PMOS transistor performance is obtained if such a uniaxial rather than a biaxial strain state exists in the channel region. Consequently, a simple one-dimensional strain or stress characterization is not sufficient to support the development and optimization of FDSOI devices. It will be shown that sc-Si₁₋ₓGeₓ films start to degrade if the annealing conditions pass a limit. HRXRD can be used to monitor the strain and/or strain relaxation with high precision and good accuracy on product wafers, and in such a way, it becomes a powerful metrology for reliable FDSOI device fabrication.
Microstructural features of interface zone in Ti6Al4V/AA1050/AA2519 and Ti6Al4V/AA2519 laminates produced by explosive welding

P. Bazarnik¹, B. Adamczyk-Cieślak¹, A. Gałka², B. Płonka³, L. Snieżek⁴, M. Cantoni⁵, M. Lewandowska¹

¹Warsaw University of Technology, Faculty of Materials Science, Woloska 141, 02-507 Warsaw, Poland
²ZTW Explomet GALKA, SZULC S.J., Oświęcimska 100H, 45-641 Opole, Poland
³Institute of Non-Ferrous Metals, Light Metals Division, Pilsudskiego 19, 32-050 Skawina, Poland
⁴Military University of Technology, Faculty of Mechanical Engineering, Kaliskiego 2, 00-908 Warsaw, Poland
⁵Electron Microscopy Center, EPFL-CIME, MXC-133, 1015 Lausanne, Switzerland

The aim of the work is to investigate the microstructure of Ti–6Al–4V alloy and AA 2519 plates cladded by the method of explosive welding with an emphasis on the role of an AA1050 interlayer. The results demonstrated that both Ti6Al4V/AA2519 and Ti6Al4V/AA1050/AA2519 composite plates exhibit good quality bonding without voids and major delamination. The explosive welding produced metallurgical bonding with a zone of Ti-Al nanoparticles embedded in aluminium matrix, as revealed by scanning electron microscopy observations and energy-dispersive X-ray spectrometry. This zone is significantly thicker in the joint with AA1050 interlayer when compared to the direct bonding of AA2519 and Ti6Al4V. In the latter, one can see the enrichment of grain boundaries in copper. In addition, the explosive welding introduces large plastic deformation which induces the process of grain refinement in aluminium plates. Good quality of joints are reflected in mechanical testing. The joints have never been the weakest element of the cladded plates and the failure occurred either in AA1050 interlayer or inside AA2519 plate.
Different routes of synthesis to new composite nanomaterials

Jingying Yao¹, Matthias Schelter¹, Jens Zosel¹, Evgeni Sperling², Michael Mertig¹,²

yao@ksi-meinsberg.de

¹ Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V. Meinsberg, 04736 Waldheim, Germany
² Physikalische Chemie, Mess- und Sensortechnik, Technische Universität Dresden, 01062 Dresden, Germany

Abstract: In this study, nano-sized gadolinium-doped ceria powder as solid electrolyte and MgO powder with similar diameter as isolator material are synthesized by different methods. The structures of the prepared nano-sized powders have been characterized by X-ray diffraction and transmission electron microscopy.

Keywords: composite nanomaterials, gadolinium-doped ceria, magnesia

Introduction
The development and the testing of novel nanostructured materials for solid electrolyte cells are required in the field of innovative energy storage technologies. Ceria-based nanocomposites have been chosen as electrolyte candidates due to their high ionic conductivity. According to results from [1], the grain boundaries between electrolyte and isolator particles can have even higher ionic conductivities than the electrolyte itself. Thus, the conductivity of 3D compounds shall increase with decreasing grain size. Therefore, there is a need for synthesis methods to obtain homogeneous nanoparticles of both components.

Results and Discussion
Via a carbonate co-precipitation process [2], gadolinium-doped ceria (GDC) nanoparticles with a diameter of about 10 nm and a narrow particle-size distribution were prepared, but a strong aggregation was observed after their preparation. Furthermore, a self-propagating high temperature method [3] was used for the synthesis of GDC and MgO nanoparticles utilizing nitrate salts as sources of metal ions and citric acid as complexing agent.

![Fig. 1: TEM image of the mixture of GDC and MgO nanoparticles prepared by self-propagating high temperature synthesis.](image)

The nanoparticles prepared by self-propagating high temperature synthesis have diameters between 10 and 20 nm. They show a narrow particle-size distribution (Fig. 1). In this case, no aggregation was observed.

![Fig. 2: XRD pattern of the sample shown in Fig. 1.](image)

As shown in Fig. 2, the XRD pattern of the same sample proves that it consists of the two pure phases GDC and MgO.

Conclusions
The nanoparticles of GDC and MgO with diameters of 10-20 nm were prepared by different methods. The TEM image and XRD pattern show that self-propagating high temperature synthesis is suitable for the preparation because of the narrow particle-size distribution and the absence of aggregation of the nanoparticles.

References
[2] A.I.Y. Tok et al., Consolidation and properties of Gd0.1Ce0.9O1.95 nanoparticles for solid-oxide fuel cell electrolytes, Materials Research Society 21 (2006), 119-124.

Acknowledgements
The presented work is financially supported by the German Federal Ministry of Education and Research (grant: 03EK3029C) and the Sächsische Aufbaubank (grant: 100243804/3235).
Oxygen Vacancies in the Ultrathin SiO$_2$ Interfacial Layer of High-k/Metal Gate CMOS Devices

Florian Lazarevic$^{1,2,3}$, Roman Leitsmann$^{1,2,3}$, Philipp Plänitz$^{1}$, Maximilian Drescher$^{4}$, and Michael Schreiber$^{2,3}$

$^1$MATcalc, AQcomputare GmbH, Annaberger Str. 240, 09125 Chemnitz, Germany
$^2$Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany
$^3$Dresden Center for Computational Material Science (DCMS), TU Dresden, 01069 Dresden, Germany
$^4$Fraunhofer IPMS-CNT, Königsbrückerstr. 178, 01099 Dresden, Germany

Abstract: We study oxygen vacancy defect levels in ultrathin SiO$_2$ layers in metal-oxide-semiconductor devices. First principles calculations were performed to model a Si/SiO$_2$/HfO$_2$ gate stack and a SiO$_2$ bulk reference system. The extremely thin SiO$_2$ layer thickness and dissimilar structural and electronic properties of the adjacent layers (namely Si and HfO$_2$) result in a degeneration and stabilization of certain SiO$_2$ bulk defects. We find that partial H passivation of the vacancies additionally stabilizes defects energetically which are related to the leakage current in CMOS devices. Furthermore the incorporation of F atoms has a large influence on the stability of H passivated SiO$_2$ defects.
High-resolution liquid AFM of P3(EO)$_3$T-DNA origami hybrid structures

F. Fischer$^1$, J. Zessin$^{1,2}$, A. Heerwig$^{1,3}$, M. Stamm$^2$, A. Kiriy$^2$, M. Mertig$^{1,3}$

$^1$Phys. Chemie, Mess- und Sensortechnik, Technische Universität Dresden, 01062 Dresden, Germany
$^2$Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany
$^3$Kurt-Schwabe Institut für Mess- und Sensortechnik e.V. Meinsberg, 04736 Waldheim, Germany

Abstract: We have performed high-resolution liquid AFM in tapping mode to investigate the structure of surface-bound hybrids of DNA origami and poly(3-tri(ethylene glycol)-thiophene – oligodeoxynucleotide (ODN) block copolymers (P3(EO)$_3$T-b-ODN). As DNA origami template, a 2D rectangular pad was used. From the pad 40 single-stranded overhangs (handles) protrude in four parallel lines of 10 handles each. Thereby, they form a regular 100 nm x 15 nm pattern with handle distances of ~ 6 nm. To each handle, one P3(EO)$_3$T-b-ODN can bind through hybridization of the handle and the ODN.

In the AFM images, bound block copolymers appear as roughly circular objects on the pads. They can be placed adjacently or reveal gaps. Using the ImageJ software [1,2], an image analysis routine was performed to localize, count and characterize the objects. Comparing the experimentally found positions to the theoretically expected revealed that handles on the inner lines are occupied about four times more frequently than handles on the outer lines. Furthermore, a mean object height of 5 nm and a mean diameter of 8 nm could be determined.

Systematic investigation of energy conversion efficiency in plasmonic waveguides by electromagnetic finite element simulations

Tobias A.F. König, Thorsten-Lars Schmidt, Andreas Fery

Leibniz-Institut für Polymerforschung Dresden e. V., Institute of Physical Chemistry and Polymer Physics, Hohe Straße 6, 01069 Dresden and Cluster of Excellence Centre for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, 01062 Dresden, DNA Chemistry group, Center for Advancing Electronics Dresden (cfaed), TU Dresden, 01062 Dresden
Department of Physical Chemistry of Polymeric Materials, Technische Universität Dresden, Hohe Str. 6, 01069 Dresden

Figure: (a) Schematic representation of the energy conversion setup from green to red light at well-spaced gold nanoparticle line. (b) Electric field distribution plotted in logarithmic scale for waveguide excitation perpendicular (S1) and parallel (S2) to the particle surface, respectively. Lower plot shows the surface charge plot to identify the plasmonic mode from case S1. (c) Energy loss along the particle line observed at various parameters such as dipole excitation orientations, diameters, inter-particle distances and environments.

We aim the energy down-conversion from green to red light for possible applications in integrating and multiplexing subwavelength optical nanosystems. This rational optical design is in close agreement with possible experimental realization through DNA origami templates and template-assisted self-assembly methods.\(^1\)\(^2\) We use the finite-difference time-domain (FDTD) method (Lumerical Solutions, Inc.) to determine the energy transfer and energy conversion efficiency of assembled gold nanoparticle waveguides (Figure). The energy transfer efficiency at a 300 nm plasmonic waveguide range between $5.6 \times 10^{-5}$ (-98 dB) at a weak coupling conditions (transversal mode, S2) and $6.2 \times 10^{-3}$ (-51 dB) at best coupling conditions (longitudinal mode, S1). Consequently, a rational optical design could result in an improvement of 3 orders of magnitude. Furthermore, we used the modelling method (surface charge plots) to discuss the physical nature of the waveguide modes for alternative propagation methods such as magnetic modes propagations or dark mode propagations.

Analysis of DNA origami gold hybrids by electron microscopy
Alexander Herms¹, Katrin Günther¹, Evgeni Sperling¹ and Michael Mertig¹,²

¹Physikalische Chemie, Mess- und Sensortechnik, Technische Universität Dresden, Dresden, Germany
²Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V. Meinsberg, Meinsberg, Germany

Very recently, self-propelling microswimmers have attracted scientific interest, because they allow studying active transport or assembly processes in fluids at the microscale.

Thermophoresis is a long known effect since SORET and LUDWIG discovered the movement of ions because of a temperature gradient. Since then, this effect has also been proven for particles such as polystyrene beads and biomolecules such as DNA [1]. BREGULLA et al. have used this effect to move and steer polystyrene beads with one hemisphere coated with a thin gold layer, so called Janus particles, by pulsed laser heating [2]. BRAUN et al. trapped single DNA molecules in a laser-driven thermophoretic trap [3].

Here we built a Janus particle-like structures consisting of gold nanoparticles (AuNPs) and DNA origami structures, so called six-helix bundles (6HBs). The DNA origami technique is a powerful tool to arrange nano objects in a controlled fashion with a nanometer precision and it is utilized to build the nanoswimmer.

Both, the DNA origami structures and the nanoswimmers were characterized by advanced microscopic methods. To image the DNA origami structure under natural conditions, AFM in liquid is used (Figure 1a). However, it is not possible to characterize the composition of the nanoswimmer sample by AFM due to the large difference in height of the two components of the hybrid (50 nm vs. 6 nm). For this reason, electron microscopy is deployed to determine morphology and assembly yield of different nanoswimmer species (Figure 1b and c).

Figure 1: (a) AFM image of the DNA origami structure (6HB), (b) TEM image of a nanoswimmer, (c) SEM image of a nanoswimmer, scale bars: 100 nm.

References


High-resolution transmission electron microscopy characterization of 3D DNA origami objects

Andreas Heerwig1,2, Mathias Lakatos1, Jan Erfkamp1, Evgeni Sperling1, Petr Formanek3, Michael Mertig1,2

1Technische Universität Dresden, Physikalische Chemie, Mess- und Sensortechnik, 01062, Dresden, Germany
2Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V. Meinsberg, 04736 Waldheim, Germany
3Leibniz-Institut für Polymerforschung, Physikalische Chemie/Polymerphysik, Nanostrukturierte Materialien, 01069, Dresden, Germany

The concept that DNA can be folded into various 1D and 2D nanoobjects was already shown in 2006 by Rothemund[1]. He used a long single-stranded DNA – the scaffold strand – and many short single-stranded DNA oligonucleotides – the staple strands – to form constructs of predefined shape with nanometer size. In the past decade, multitudinous structures were folded for diverse applications like artificial light harvesting antennas[2], drug delivery vehicles[3] or artificial ion channels[4]. Nevertheless, the synthesis of appropriate complex 3D DNA origami structures is still challenging due to low yields[5]. Here, we report of three different 3D DNA origami objects. The structures were designed with the software caDNAno[6] and the structure formation was modelled by the software CanDo[7]. The yield of well-formed structures after synthesis was in the range of 90 to 95 %. The formed complex structures were characterized by gel electrophoresis, TEM and cryo-EM. By using negative staining with uranyl acetate, we were able to study the inner core structure and to monitor the facets of the origami structures. By cryo-EM of the pristine 3D DNA origami objects, we were able to show that the structures are well formed (Fig. 1). These nanoobjects can be used as 3D template for binding and growing of nanoparticles to build up nanodevices like transistors or near-field sensors.

Fig. 1: 3D DNA origami “hourglass”, (a) Design, (b) cryo-EM and (c) TEM.

DNA-based assembly of plasmonic nanoantennas

Andreas Heerwig\textsuperscript{1,2}, Mathias Lakatos\textsuperscript{1}, Hanna Brunner\textsuperscript{1}, Evgeni Sperling\textsuperscript{1}, Michael Mertig\textsuperscript{1,2}

\textsuperscript{1}Technische Universität Dresden, Physikalische Chemie, Mess- und Sensortechnik, 01062, Dresden, Germany
\textsuperscript{2}Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V. Meinsberg, 04736 Waldheim, Germany

Conventional semi-conductor based data processing architectures in nanometer dimensions can cause parasitic capacities and electrical interface barriers. To circumvent these problems energy conversion of freely propagating optical radiation into localized energy and vice versa becomes favorable. The necessary plasmonic nanostructures for this purpose can be generated by DNA-assisted self-assembly processes. We used the so-called DNA origami method, first presented by Rothemund in 2006\textsuperscript{[1]}, to synthesize 2D nanoobjects (Fig. 1a): A long single-stranded DNA, the scaffold strand, is folded into a designed form by short single-stranded oligonucleotides, the staple strands. The resulting constructs additionally provide single-stranded DNA overhangs. Gold nanorods were covered with single-stranded thiol-oligonucleotides with a sequence complementary to the before mentioned overhangs (Fig. 1b). A rational design of the binding points on the DNA origami constructs directs the gold nanorods to a predestined location in a further hybridization step (Fig. 1c).

Figure 1: a) Folding a long single-stranded DNA with short oligonucleotides to a 2D object; b) functionalization of gold nanorods with thiol-oligonucleotides; c) positioning of gold nanorods.

The dimerization of the gold-DNA origami hybrid structures results in the aimed slot-dipole antenna (Fig. 2a). The formation of the entity was proven by TEM measurements (Fig. 2b). The variation of the slot width, which is easily accessible using DNA origami templates, as well as the implementation of nanoparticles – electronically switchable polymers or dielectrics – opens a wide range of possible optical manipulation opportunities.

Figure 2: a) Design scheme of the target structure; b) TEM micrograph of synthesized slot antennas.

Quantifying the magnetism of individual nanomagnets: EMCD on FePt nanoparticles

Sebastian Schneider¹,², Darius Pohl¹, Stefan Löfler³,⁴, Deepa Kasinathan⁵, Ján Rusz⁶, Peter Schattschneider³,⁷, Ludwig Schultz¹,² and Bernd Rellinghaus¹

¹IFW Dresden, Institute for Metallic Materials, Dresden, Germany
²TU Dresden, Institut für Festkörperphysik, Dresden, Germany
³Vienna University of Technology, USTEM, Vienna, Austria
⁴McMaster University, Dept. of Materials Science and Engineering, Hamilton, Canada
⁵MPI CPfS, Department Physics of Correlated Matter, Dresden, Germany
⁶Uppsala University, Department of Physics and Astronomy, Uppsala, Sweden
⁷Vienna University of Technology, Institute of Solid State Physics, Vienna, Austria
E-mail: sebastian.schneider@ifw-dresden.de

Electron energy-loss magnetic chiral dichroism (EMCD) [1], which is the electron wave analogue of X-ray magnetic circular dichroism (XMCD), offers the possibility to study magnetic properties at the nanoscale in a TEM. The method was already refined to such an extent that it is possible to probe magnetic moments of thin films of a variety of ferromagnets [2, 3]. However, quantitative EMCD measurements are so far only reported on thin films rather than on nanoparticles, which are expected to reveal distinct magnetic properties due to their reduced dimensions and enhanced surface to volume ratio.

We report on EMCD measurements on a single L₁₀ ordered FePt nanoparticle. Our experiments are supported by simulations of electron energy-loss spectra utilizing the WIEN2k program package in combination with Bloch-wave (BW) methods. These simulations are used to (pre-)determine optimal experimental parameters, that provide for the highest EMCD signals [4, 5]. From the experimental spectra, a ratio of orbital to spin magnetic moment $m_l/m_s = 0.08 \pm 0.02$ is for the first time quantitatively derived for individual FePt nanoparticles, which agrees well with the XMCD result $m_l/m_s = 0.09$ for a large ensemble of L₁₀ ordered FePt nanoparticles [6].

References

Non-Damaging Characterization of ULK Materials With Low Voltage Scanning Electron Microscopy (LVSEM) and the EsB detector

Aránzazu Garitagoitia Cid\textsuperscript{1, 2}, Rüdiger Rosenkranz\textsuperscript{2}, and Ehrenfried Zschech\textsuperscript{1, 2}

\textsuperscript{1} Dresden Center for Nanoanalysis (DCN), TU Dresden, 01062 Dresden, Germany
\textsuperscript{2} Fraunhofer Institute for Ceramic Technologies and Systems, Maria-Reiche-Str. 2, 01109 Dresden, Germany

Abstract: In addition to high-resolution imaging, the application of Scanning Electron Microscopy (SEM) in semiconductor industry confronts two challenges: the detection of small differences in the composition of layers and structures in microelectronic products, and a low damage when imaging the structures. In this paper, we will focus on the application of Low Voltage Scanning Electron Microscopy (LVSEM), i.e., using lower values of primary beam voltage ($E_p$), for the studying of Cu/low-k on-chip interconnect stacks, and particularly on the study of dense and porous organosilicate glass (OSG) thin films which are used as insulating material with low permittivity between the metal interconnects. Since the beam/specimen interaction volume is significantly reduced for LVSEM compared to high voltage operation, essential information originated at the sample surface is obtained. The differentiation between OSG and etch stop layers, with different chemical compositions, and the exact determination of geometrical data of the Cu/low-k structures at a cross-sectioned samples are important tasks for analytical labs in semiconductor industry, for both process control and physical failure analysis. In this study we will show that SEM at low acceleration voltages in combination with an Energy selective Backscattered (EsB) electron detector improves the compositional contrast and mitigates the shrinkage of the OSG caused by electron beam-induced material damage. The mitigation of sample damage is of particular interest for organic samples, as well as for some types of hybrid materials. In the case of OSG, the glass network is densified during the electron beam/sample interaction which phenomenologically causes a significant shrinkage of the material [1]. The spatial resolution and OSG thin film degradation during SEM imaging are studied systematically as a function of the $E_p$. By combining the advantages of using a low accelerating voltage with the EsB detector, the compositional contrast is increased and the shrinkage phenomena is significantly mitigated, as shown in Figure 1d).

FIGURE 1. In-lens images of shrinkage (a), (b), (c) in a OSG thin film on Si substrate after 3 min. scan with high magnification at $E_p$ values of 20, 10 and 5 kV respectively. The EsB image (d) shows no shrinkage with $E_p = 1$ kV.

Advanced characterization methods for materials properties of composite BEoL stacks for multi-scale simulation

Christoph Sander*, Martin Gall, André Clausner, Yvonne Standke, Rüdiger Rosenkranz, Ehrenfried Zschech

Fraunhofer Institute for Ceramic Technologies and Systems - IKTS, Maria-Reiche-Str. 2, 01109 Dresden, Germany

Meeting both the challenges of "More Moore" as well as "More than Moore", three dimensional (3D) integration has been identified as one of the key enablers for the future of the IC industry. Managing the emerging internal mechanical stress in chips particularly if they are 3D stacked is a key task to maintain performance and reliability of microelectronic products in advanced CMOS technology nodes, and it is a highly ranked concern for 3D TSV technologies. The stress management in complex systems starts during the design process and therefore requires multi-scale modelling, including accurate multi-scale materials data as input data for simulation and model validation and calibration [1]. This study shows advanced techniques to measure FEA- and design relevant properties and accumulates the results in a condensed database for effective composite materials properties. The shown methods are focused on the "Back End of Line" (BEoL) related materials, whereas the essential principle is applicable in all phases and scales of the design process. The techniques developed and applied on 3D ICs during this study include the characterization of the Young's modulus, Poisson's ratio and coefficient of thermal expansion (Fig. 1). Combined with adhesion experiments a complete assessment of design relevant materials properties with focus on the BEoL has been conducted. In conclusion, all shown methods lead to a complete materials properties investigation of the BEoL to allow IC designers an increased throughput of pre-manufacturing simulations.

Fig. 1: SEM micrograph of a CTE test structure

References

*corresponding author e-mail: christoph.sander@ikts.fraunhofer.de
Crack imaging in composite materials using high-resolution nano-XCT

Kristina Kutukova¹, Jürgen Gluch¹, Ehrenfried Zschech¹

¹ Fraunhofer-Institut für Keramische Technologien und Systeme (IKTS), 01109 Dresden, Germany

Abstract: The combination of high-resolution X-ray microscopy and nano X-ray computed tomography (XCT) with in-situ micromechanical experiments merges the advantage of the nondestructive high-resolution three-dimensional imaging of the microstructure of materials with the observation of microstructural changes under loading. Phenomena like crack initiation, crack propagation and in case of composites also delamination can be visualized. Therefore, an experimental micro-indentation set-up is suitable to study damage mechanisms in advanced materials like composites.

In this study, an Xradia nanoXCT-100 laboratory X-ray microscope is used, applying a rotating X-ray tube with Cu anode (monochromatic Cu Kα radiation). Using a Fresnel zone plate as focusing lens provides a resolution of 50 nm. To be transparent for photons with an energy of 8 keV, the samples have to have to be prepared to a maximum thickness of about 50 μm. The customized micro-mechanical test rig presented in this study allows in-situ mechanical studies of composites in a laboratory X-ray microscope, particularly micro-indentation experiments. The loading device had to be stiff enough to perform experiments with the desired accuracy, and it has to include sensors for an accurate force measurement. For the in-situ experiments, it needs to fit to the existing nano-XCT setup. The indenter geometry was chosen in such a way that the indenter tip and the sample fit within the field of view of the X-ray microscope (Xradia nanoXCT-100, FOV width: 65μm or 16μm). The operating range of forces is up to 1000 mN and the force resolution is better than 0.25 mN, what is required for studies of composite material with a hardness in the range from several GPa to several tens of GPa.

The performance of the customized indenter device was compared to a commercial standalone device (Hysitron PI950, micro indenter head) performing hardness measurements with Berkovich tip geometry on flat polished aluminum alloy plate. These results are in good agreement, i. e., the performance and accuracy of the measurements prove that the customized loading stage can be reliably used to characterize the materials studied.

This setup is well suited to perform tests at various composite materials, like carbon fibers reinforced composites with metallic, ceramic or polymer matrix. Studies at carbon fibre reinforced Aluminum matrix composites demonstrate a weak fibre/matrix interface, adhesive failure and push-out phenomena.