0002 - Invited talk

invited talk

Valence- and core-level EELS from low-dimensional materials

*K. Suenaga[1], Y.-C. Lin[1], J. Lin[1], L. Tizei[1], R. Senga[1]
[1]AIST - National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

In this presentation, single atom spectroscopy by means of core-level EELS will be first demonstrated to discriminate individual atoms in low-dimensional materials at their interrupted periodicities. It is emphasized here that information of the bonding/electronic states has become accessible for single atoms through the EELS fine-structure analysis [1] as well as the spin state [2]. Large variations of local electronic properties of 1D and 2D materials with different atomic coordinates will be shown [3]. Such an analysis was applied to understand catalytic behavior of Co doped MoS2 for hydrodeoxygenation reaction [4]. Furthermore, a high-energy resolution valence-EELS offers us possibilities to obtain local optical/vibrational properties. Some of the recent examples for such experiments on low-dimensional nanomaterials will be also presented [5].

[1] Y.-C. Lin et al., *Nano Letters,* **15** (2015) 7408-7413, L. Tizei et al., *Phys. Rev. Lett.*, 114 (2015) 197602, R. Senga et al., *Nature Mat.,* **13** (2014) 1050

[2] Y.-C. Lin et al., *Phys. Rev. Lett.*, **115** (2015) 206803

[3] Y.-C. Lin et al., *Nano Lett.,* **17** (2017) 494-500, R. Senga and K. Suenaga, *Nature Communications,* (2015) 6:7943

[4] G. Liu et al., *Nature Chem.* **9** (2017) 810

[5] J. Lin et al., *Nano Lett.*, **16**, (2016), 7198-7202, L. Tizei et al., *Phys. Rev. Lett.,* **114** (2015) 107601, R. Senga et al., *Nano Lett.*, **16**, (2016) 3661-3667

[6] This research was supported by JSPS KAKENHI (JP16H06333 and JP25107003).

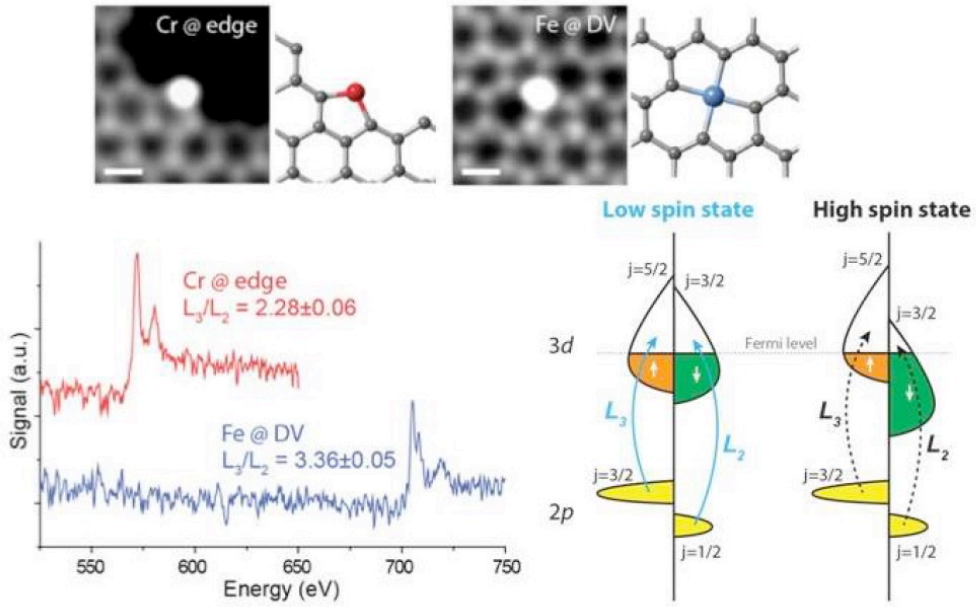


Figure: Single atom spectroscopy of dopants in graphene. *L2,3* core-level EELS clearly indicates that both Cr atom at edge (left) and Fe atom at di-vacancy (right) show a high-spin state.

0003 - Poster presentation

Spectroscopic methods in TEM and scanning electron microscopy (SEM): energy dispersive X-ray (EDX) spectroscopy, electron energy loss spectroscopy (EELS), simulation tools

Inelastic Momentum Transfer Measurement of a Surface Plasmon Mode

*J. Krehl[1], G. Guzzinati[2], J. Schultz[1], P. Potapov[1], D. Pohl[3], J. Verbeeck[2], A. Lubk[1]
[1]*IFW Dresden, IFF, Dresden, Germany*
[2]*University of Antwerp, Antwerp, Belgium*
[3]*IFW Dresden, IMW, Dresden, Germany*

Surface plasmons are excitations of the electron gas inside a nanoparticle which, due to the spatial confinement of the particle, have a discrete spectrum. They are created by an external time-dependent field, which couples strongly to resonant modes of the internal field, whose emanated field can reach much higher peak field strengths than the exciting field. This local field enhancement effect is a major motivation behind plasmonics research since it promises a great boost in the efficiency of photovoltaics and optical sensors. To further such ambitious goals new analytical tools are needed for the characterisation of such transient phenomena at the nanoscale. Here, we present a method for mapping the components of the electrical field inside a single plasmon mode by means of energy-filtered low-angle electron nanodiffraction.

Our basic approach consists of scanning a nanometer size electron beam over a plasmonic particle, where excited plasmons deflect the beam both laterally, creating a shift in a diffraction plane, and longitudinally, causing an energy loss. Accordingly, this inelastic momentum transfer (IMT) corresponds to the induced field integrated over the electron's trajectory. Our novel experimental setup enables measuring both the lateral and longitudinal mean momentum transfer at each scanning point by evaluating the sum and the center of mass (CoM) of the energy filtered electron beam. Due to the small deflection angles (in the order of microradians) these experiments have to be done in a low-magnification STEM mode, while the low intensity in the energy-filtered beam demands care for a very stable monochromator and filter setup.

We recordend such energy-filtered diffraction patterns (Fig 1b) of a dipole mode at 1.05 eV (see spectrum in Fig 1c) of an aluminium nanorod (Fig. 1a) with a variation of the sum of the diffraction patterns (Fig 2a) and a shift the CoM (Fig 2c) near the particle. These are spectral components of the projected induced field. We simulated these fields (with the MNPBEM toolbox and an effective medium correction) and achieved reasonable agreement between the experimental and simulated spectra (Fig. 1c), loss probabilities (Fig 2 a and b) as well as the induced lateral fields (Fig 2 c and d).

Our measurement of the IMT represents the first quantitative measurement of the transient lateral fields of surface plasmons. For this setup, both theory and simulation indicate that the lateral components can be related much more meaningfully to the local field strengths than the longitudinal, i.e. the EELS, signal.

Fig 1: (a) HAADF image (grayscale) and overall loss probability (color), (b) subset of inelastic diffraction patterns with indicated centers-of-mass, and (c) experimental (solid) and simulated (dashed) overall EEL spectra with employed energy slit indicated.

Fig 2: Energy-filtered experimental (a) and simulated (b) energy loss probabilities within the energy interval indicated in the spectra (Fig. 1c) and the experimental (c) and simulated (d) electrical field maps of the Al nanorod.

Figure 1

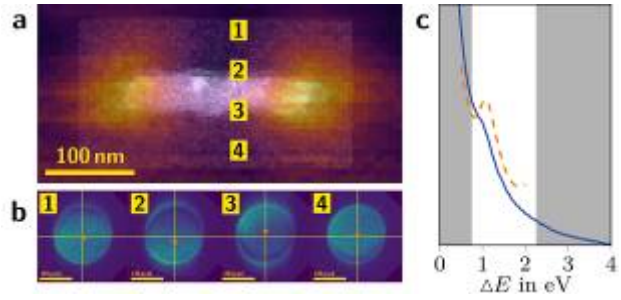
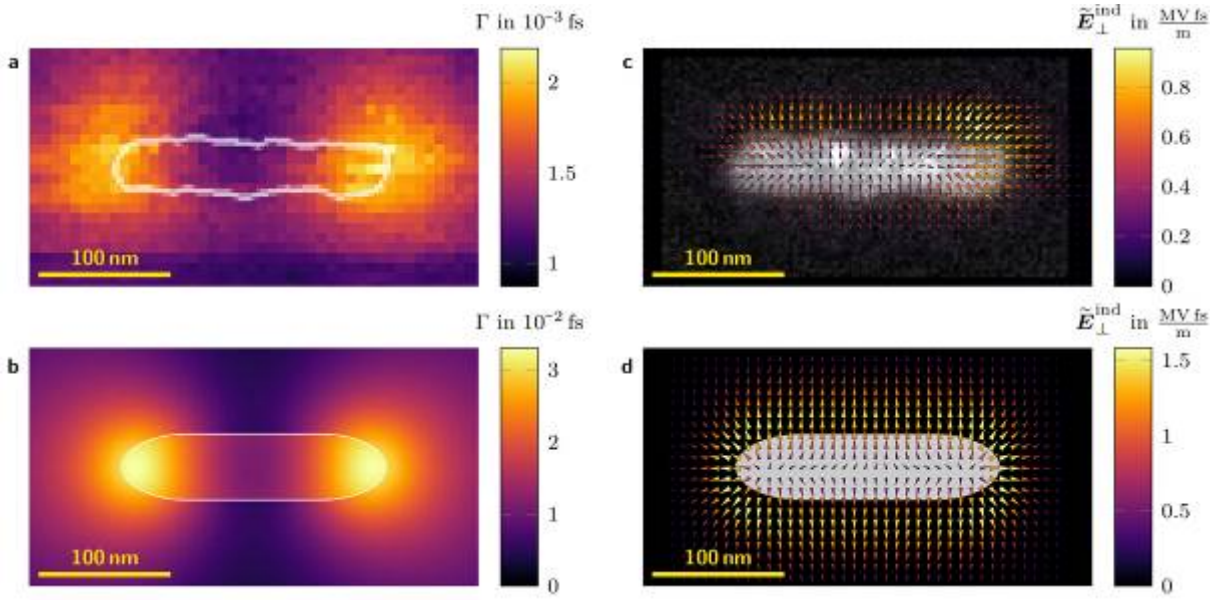


Figure 2


a
Γ in 10^{-3} fs
2
1.5
1
100 nm
c
$\tilde{E}_{\perp}^{\mathrm{ind}}$ in $\frac{\mathrm{MV\,fs}}{\mathrm{m}}$
0.8
0.6
0.4
0.2
0
100 nm
b
Γ in 10^{-2} fs
3
2
1
0
100 nm
d
$\tilde{E}_{\perp}^{\mathrm{ind}}$ in $\frac{\mathrm{MV\,fs}}{\mathrm{m}}$
1.5
1
0.5
0
100 nm

0004 - Poster presentation

Applications to characterizations of functional nanomaterials and devices, materials for energy, materials for information technology, catalysts, soft matter, biomaterials

Microstructure and Functionality of Cathode/Electrolyte Interfaces in Solid Oxide Fuel Cells

*H. Störmer[1], V. Wilde[1], F. Wankmüller[1], J. Szász[1], E. Ivers-Tiffée[1], D. Gerthsen[1]
[1]Karlsruher Institut für Technologie, Laboratorium für Elektronenmikroskopie, Karlsruhe, Germany

Future demands on solid oxide fuel cells with respect to long lifetime and high efficiency at low operating temperatures require a distinct selection of materials for the different components cathode material, electrolyte and anode. The mixed ionic and electronic conducting $(La_{0.58}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_{3-\delta}$ (LSCF) cathode material is best suited for high power densities, however, application is hampered due to formation of an insulating $SrZrO_3$ (SZO) blocking layer if the LSCF cathode material is directly deposited on the Y_2O_3-doped ZrO2 (YDZ) electrolyte. One option to prevent SZO formation is the insertion of a dense Gd_2O_3-doped Ceria (GDC) diffusion-barrier layer between LSCF cathode and YDZ electrolyte. Understanding the nature of this interface, which is composed of the mixed conducting LSCF cathode and the bilayer YDZ-GDC electrolyte, is still challenging since changes in microstructure and/or chemical composition dramatically affects the cell performance.

Symmetric cell samples were fabricated by screen-printing a GDC layer on both sides of YDZ substrates, followed by sintering at different temperatures ranging from 1100 °C to 1400 °C. Subsequently LSCF was screen-printed on top of the GDC layer and sintered at 1080 °C, irrespective of the former GDC sintering temperature. The LSCF/GDC/YDZ interfaces were studied in detail by means of (scanning) transmission electron microscopy ((S)TEM)) in combination with energy-dispersive X-ray spectroscopy (EDXS). Moreover, a correlative focused-ion-beam/scanning-electron-microscopy (FIB/SEM) tomography approach allowed identification and visualization of primary and secondary phases in a 3D volume [1]. The corresponding cell performance was measured by means of electrochemical impedance spectroscopy.

Formation of the secondary phase SZO dominates interface resistance and cell performance, depending on volume and local distribution. A gradual decrease in SZO phase formation is observed from low to high GDC sintering temperatures. Hence, it can be concluded that the barrier layer functionality is determined by the applied GDC sintering temperature, although no densification of GDC with increasing temperature can be monitored [1]. Instead, an interdiffusion layer (IDL) with varying thickness is formed between porous GDC and YDZ upon sintering at temperatures exceeding 1100 °C. No IDL is found at low GDC sintering temperature (1100 °C) which could impede SZO formation. Consequently, a continuous SZO layer is formed, leading to an increase of the interface resistance by three orders of magnitude. In contrast, after sintering at 1400 °C a thick IDL is formed and only single SZO grains predominantly at pores or grain boundaries are found. Therefore, "free" pathways for oxygen ions to migrate from LSCF though GDC into YDZ are present, resulting in a high-performing interface with minor losses. This findings demonstrate the importance to understand the correlation between processing parameters, resulting microstructure and performance.

[1] F. Wankmüller et al., Journal of Power Sources, 360 (2017) 399-408

0005 - Poster presentation

Applications to characterizations of functional nanomaterials and devices, materials for energy, materials for information technology, catalysts, soft matter, biomaterials

TEM analysis of multi-shell upconverting nanocrystals

*R. Popescu[1], D. Hudry[2], B. S. Richards[2], D. Gerthsen[1]
[1]*Karlsruher Institute für Technologie, Laboratorium für Elektronenmikroskopie, Karlsruhe, Germany*
[2]*Karlsruher Institut für Technologie, Institute of Microstructure Technology , Karlsruhe, Germany*

Over the last decade, numerous promising investigations on the practical utilization of lanthanide-doped upconverting nanocrystals (UCNC) are reported. Then, the structure–property relationships of UCNC gain in interest, as the energy migration pathways that are used to control UCNCs" optical properties depend on the, yet unclear, chemical and structural order of core-shell (CS) and core-shell-shell (C2S) interfaces.

Transmission electron microscopy (TEM) (FEI Titan^3 80-300 at 300keV) and high-angle annular dark-field (HAADF) scanning TEM (STEM) combined with energy-dispersive X-ray spectroscopy (EDXS) (FEI Osiris ChemiSTEM at 200 keV) are used for the structural and chemical characterization of UCNCs. Samples are prepared by drop-casting of a UCNCs suspension onto a thin amorphous carbon film. The chemical composition of the UCNCs is reconstructed by using an iterative algorithm [1].

Different UCNC architectures are synthesized [2] and investigated starting with the heavily doped optically active core (C), followed by the CS and C2S morphologies, where C are surrounded by one/two optically inert shells with compositions of $NaYF_4$ (inner) and $NaGdF_4$ (outer). TEM reveals that pure C have a relatively homogeneous distribution of Er and Yb cations without evidence of segregation with average composition $NaEr_{0.87}Yb_{0.13}F_4$ and average size of 18±2 nm. After deposition of the first Y-based shell not only the size slightly increases (26±3 nm), but also the chemical composition is strongly modified. The size of the Er/Yb core decreases down to 12 nm. It is surrounded by a non-homogeneous and relatively thick shell, whose chemical composition changes from an (Er/Yb)-rich solid-solution to an Y-rich one within 4 to 6 nm from the surface of the pure core region. The non-homogeneous interface is surrounded by a thin homogeneous pure Y shell. This clearly shows that the optically active elements (Er/Yb) are partially diluted during the growth of the first shell. After the growth of the second Gd-based shell, the size of the C2S architecture increases up to 42±4 nm. Interestingly, despite the growth of the primary Y-shell the whole chemical composition is once again modified. The size of the pure Er/Yb C shrinks to 8 nm. A thick (7.5 – 9 nm) (Er/Yb)/Y interface is formed with two different regions with different compositions. The thin pure Y-shell that characterized the outer region of the CS completely disappeared and is replaced by a second interface of 2.5 nm mainly composed of Y and Gd in various proportions. The second interface is surrounded by a 5 – 6 nm thick pure Gd-shell.

In conclusion, the TEM and STEM/EDXS analyses of CS and C2S UCNC reveal a significant disorder at their inner interfaces. By proper consideration of intermixing during shell growth, a structural and chemical model is established that allows the comprehensive understanding of the structure–property relationships of multi-shell UCNCs.

References

[1] C. Kind et al., RSC Advances, 2, 9473 (2012)

[2] G.S. Yi et al., Chemistry of Materials, 19, 341 (2007)

0006 - Poster presentation

Spectroscopic methods in TEM and scanning electron microscopy (SEM): energy dispersive X-ray (EDX) spectroscopy, electron energy loss spectroscopy (EELS), simulation tools

Structural and Chemical Analysis of Ca and Mn doped Bismuth Ferrite Thin Films

*U. Haselmann[1], G. Haberfehlner[2], Z. Zhang[1,3]
[1]*Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*
[2]*Institute for Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz, Austria*
[3]*Institute of Material Physics, Montanuniversität Leoben, Leoben, Austria*

Bismuth Iron Oxide (BiFeO3) has been a material of great interest in the past years, especially for its magnetoelectric coupling [1].

In this study, we investigated a **Ca and Mn co-doped** thin film with $Bi_{0.9}Ca_{0.1}Fe_{0.95}Mn_{0.05}O_{3-\delta}$ (**BCFMO**) as the intended composition grown epitaxially via pulsed laser deposition (PLD) on a SrTiO3 (**STO**) substrate. Additionally, **Mn doped** films, which have an intended composition of $BiFe_{0.95}Mn_{0.05}O_{3-\delta}$ (**BFMO**) and were deposited directly on STO substrate or on a Strontium-Ruthenium-Oxide (**SRO**) intermediate layer, were investigated. Selected area electron diffraction and geometric phase analysis of HRTEM images were used to analyze the film strains. Aberration-corrected scanning transmission electron microscopy (STEM) was conducted including analytical characterization via EELS and EDX.

The films grown directly on the STO substrate both show a substantial out-of-plane strain between 2.0±0.3% and 3.7±0.3% but no in-plane strain, which is expected for perfect epitaxial growth (see Fig. 1a and b). However, the SRO intermediate layer, grown for electrical characterization, shows an out-of-plain strain of 0.9±0.3% as well as a significant in-plane strain of 1.1±0.3%. As a result, the film (BFMO) grown on top also shows, beside an out-of-plane strain of 1.2±0.3%, an in-plane strain of 0.7±0.3% compared to the STO substrate.

For the Ca and Mn co-doped BFO film, chemical information with atomic resolution could be gained and the analysis showed very interesting results. The data suggest a single atomic layer at the A-side position at the interface between STO and doped BFO, where there is a significantly higher Ca content, which is dropping below the limits of detectability within several atomic layers of the film (see Fig. 1c and d). The reason for the formation of this unusual film structure and its effect on the electrical property are not clear at the moment.

In summary, this means that while the films deposited directly on the substrate showed almost perfectly epitaxial growth with an enlarged out-of-plane lattice parameter, this was prevented by the SRO intermediate layer. Chemical analysis of the Ca and Mn co-doped film showed that the Ca is concentrated at the interface and vanishes further into the film.

[1] T. Zhao *et al.*, "Electrical control of antiferromagnetic domains in multiferroic BiFeO3 films at room temperature.," *Nat. Mater.*, vol. 5, no. 10, pp. 823–9, 2006.

Our big gratitude goes to Univ.-Prof. Dr. Gerald Kothleitner and Univ.-Prof. Dr. Ferdinand Hofer at the Austrian Center for Electron Microscopy and Nanoanalysis (FELMI-ZFE) for enabling the aberration-corrected STEM measurements. We also like to thank Prof. Yunbin He from Hubei University in China for providing the samples. We gratefully acknowledge the financial support by the Austrian Science Fund (FWF): No. P29148-N36.

Figure 1

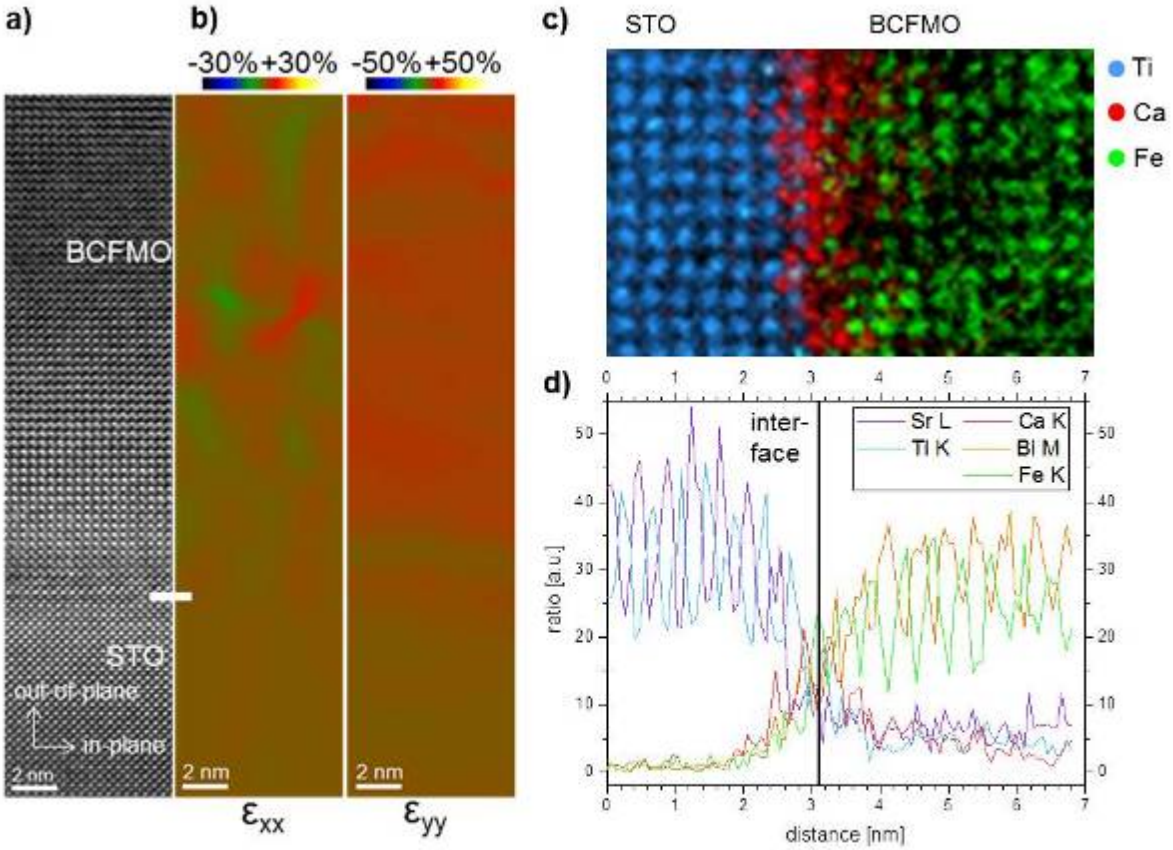


Fig. 1: a) HRTEM image of the BCFMO-STO interface. b) In-plane (ε_{xx}) and out-of-plane (ε_{yy}) strain. c) EELS signal map of Ti, Ca and Fe at the interface. d) EDX line profile across the same interface.

0007 - Invited talk

invited talk

Electron Holographyof Nanoscale Electric and Magnetic Fields

*M. McCartney[1]
[1]*Arizona State University, Department of Physics, Tempe, United States*

Off-axis electron holography in the transmission electron microscope provides a unique and powerful approach to visualizing electric and magnetic fields within materials with resolutions approaching the nanometer scale. The ability to image phase shifts at medium resolution opens up a wide field of interesting and important materials problems. The technique is potentially quantitative, given specific optimum sample geometries. The technique has been successfully used to quantify electrostatic and magnetic fields in and around deep-submicron devices and patterned nanomagnets. An important extension of this work has involved *in situ*applications, such as monitoring the lithiation of a Ge nanowire. One of the practical difficulties for expanding the use of the technique is lack of precision in the phase measurement. The requirement for high signal-to-noise is particularly important for measurements of magnetic fields since the measurement of the projected magnetic field involves a measurement of the gradient of the phase. In addition, magnetic domain wall positions are indicated by changes in these gradients. Another application requiring very high signal-to-noise in phase images is the *in situ*monitoring of magnetic hysteresis loops.

Holographic imaging at atomic dimensions for studying individual electrostatic charge is becoming feasible. The inherent weakness of measuring a small number of Bohr magnetons will, however, make atomic scale magnetic imaging more difficult. Future improvements will entail improved software, better detectors, and sample preparation.

0008 - Invited talk

invited talk

Electron spectroscopy of interfaces in cuprate superconductors

*W. Sigle[1], Y. Wang[1], Y. E. Suyolcu[1], U. Salzberger[1], F. Baiutti[2], G. Cristiani[3], G. Gregori[2], G. Logvenov[3], J. Maier[2], P. A. van Aken[1]
[1]Max Planck Institute for Solid State Research, Stuttgart Center for Electron Microscopy, Stuttgart, Germany
[2]Max Planck Institute for Solid State Research, Physical Chemistry of Solids, Stuttgart, Germany
[3]Max Planck Institute for Solid State Research, Thin Film Technology, Stuttgart, Germany

If two complex oxides are joined, the interface region can show physical properties that are different from those of the constituting single phases, thus allowing for new functionalities of these hetero-structure materials. This phenomenon has stimulated intensive research in recent years. In the case of interface superconductivity, the interatomic structure relaxation and charge transfer play a key role [1, 2]. We will present work, where we combine atomic-resolved quantitative STEM imaging with analytical STEM-EELS/EDX analysis to investigate the origin of superconductivity in superlattices of two-dimensionally Sr-doped La2CuO4. We use quantitative STEM analysis to understand cation and electron hole redistribution, as well as local lattice and oxygen octahedral distortion [3].

These measurements are possible due to the marked progress of the instrumentation hardware, which makes chemical analysis at atomic resolution readily possible nowadays. However, very often data quality and interpretation of atomically resolved EELS data suffers from image distortions and poor signal-to-noise ratio of individual spectra. By combining multi-frame spectrum imaging and automatic energy-offset correction, we developed a spectrum imaging technique, implemented into customized DigitalMicrograph scripts, which distinctly suppresses these deleterious effects [4].

References:

[1] A.Gozar, G. Logvenov, L. Fitting Kourkoutis, A. T. Bollinger, L. A. Giannuzzi, D. A. Muller, I. Bozovic, Nature 455, 782 (2008).

[2] F.Baiutti, G. Logvenov, G. Gregori, G. Cristiani, Y. Wang, W. Sigle, P. A. van Aken, P. A. van Aken, J. Maier, Nat. Commun. 6, 8586 (2015).

[3] Y.Wang, F. Baiutti, G. Gregori, G. Cristiani, U. Salzberger, G. Logvenov, J. Maier, P. A. van Aken, ACS Appl. Mater. Interfaces 8, 6763 (2016).

[4] Y. Wang, M. R. S. Huang, U. Salzberger, K. Hahn, W. Sigle, P. A. van Aken, Ultramicroscopy 184, 98 (2018).

0009 - Invited talk

invited talk

X-ray Microanalysis of Nanostructures and Soft Matter in the AEM

*N. J. Zaluzec[1]
[1]Argonne National Laboratory, Photon Sciences Division, Argonne, United States

Increasing sensitivity and collection efficiencies of detectors in the modern AEM have allowed unprecidented imaging to become possible. While electron imaging has advanced significantly with the advent of both direct electron and pixellated array detectors, a slow but equally important improvement to solid state detectors for spectroscopy is continuing to evolve. Combining low dose operations, large collection efficiencies (~ 2 sR), cryo-modes and temporally resolved hyperspectral imaging is permitting microanalysis using x-ray energy dispersive spectroscopy (XEDS) of nanostructures and soft matter, particularly at lower accelerating voltages (Figure 1 & 2). Experimental measurements of the minimum detectable mass show the expected improvement with decreasing accelerating voltage, while the minimum mass fraction has a relatively large nearly flat operating regime from ~ 40-300 kV. Experimental work from studies of single particles, organic/inorganic membranes, polymers as well as recent development of XEDS using cryo-enabled systems and the future prospects will be discussed.

Acknowledgements

This work was supported by the Photon Science Division and Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357. Some of the measurements in this study were conducted using instruments in the Center for Nanoscale Materials at Argonne National Laboratory as well as at the Thermo-Fisher - NanoPorts in the US & NL.

Figure 1

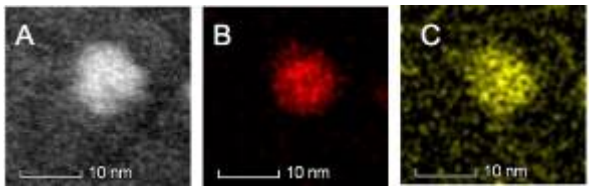
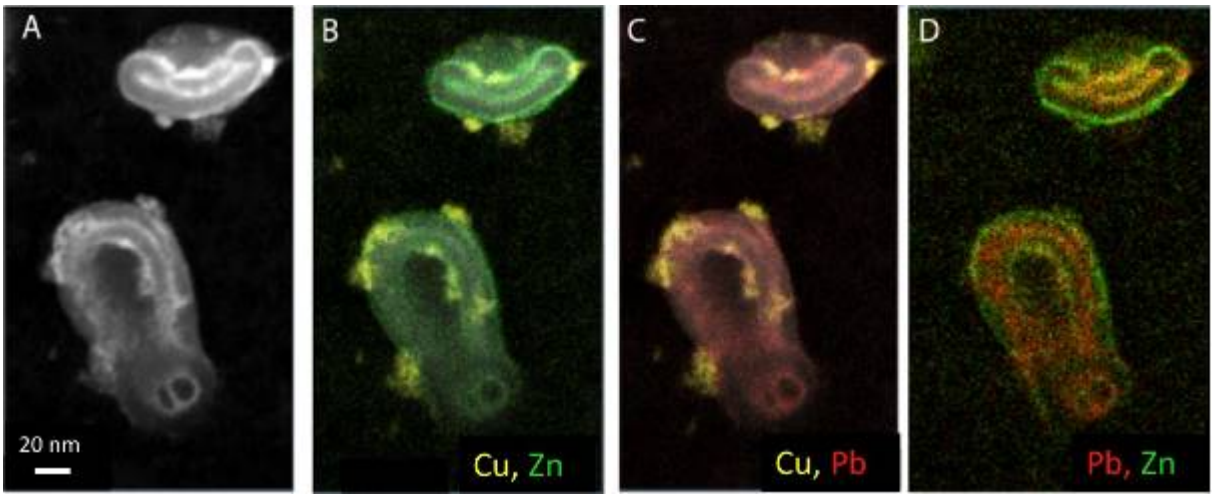


Figure 2



0010 - Invited talk

invited talk

High-resolution Electron Energy Loss Spectroscopy of Functional Oxides

*G. Botton[1], H. Liu[1], R. Safari[1], S. Cheng[1], M. Chatzidakis[1], A. Carranco[1]
[1]McMaster University, Hamilton, Canada

Electron energy loss spectroscopy (EELS) can provide useful information on materials at high spatial resolution. Combined with electron sources equipped with monochromators and electron-optics components such as direct electron detectors in spectrometers, this technique can provide detailed insight on chemical bonding and composition of materials down to the atomic column level. Today, the technique has been used to probe surface termination, bonding changes at interfaces in heterostructures, and the local chemistry of defects. Given the sensitivity to the local unoccupied states, EELS also has the potential to provide insight on the local electronic structure of materials with atomic column resolution.

In our work, we used a FEI *Titan* 80-300 scanning transmission microscope equipped with a monochromator and a Gatan *Quantum* spectrometer recently fitted with a retractable direct electron detector [1]. This detector has significant benefits in terms of quality of the spectra due to the improved point spread function and noise level.

We have probed several materials to highlight the capabilities of this technique to solve significant scientific and technological problems. The first example covers the use of atomic-resolved EELS to map bulk phases and defects in Li-Ion Batteries. With our instrumentation, we have shown compositional fluctuations at the surfaces of pristine Li-rich high-energy Li1.2Ni0.13Mn0.54Co0.13O2 (HENMC) materials with surface segregation as thin as two atomic planes[2] and we have demonstrated the local changes in composition in extended defects in the same materials. In commercial materials on the same family (Li1.2Ni1/3Mn1/3Co1/3O2), we have also demonstrated the presence of surface layers with reduced valence visible only after electrochemical exposure and voltage cycling including evidence of clustering of Li[3].

Oxides also provide the ideal test bed for atomic column level spectroscopy. At the more fundamental level, we also demonstrate that the presence of holes in high-temperature superconductors can be mapped [4] including with high precision, accounting for electron beam propagation [5] and even real-space mapping orbitals[6].

Further examples to be discussed also highlight the use of neural network methods to provide more robust interpretation of spectroscopic data. These developments open the prospects of more automated data analysis of much larger datasets and thus broader impact of EELS in applications related to functional oxides. [7]

[1] J. L. Hart, A. C. Lang, A. C. Leff, P. Longo, C. Trevor, R. D. Twesten, M. L. Taheri, Sci. Rep. **7**, 8243 (2017)

[2] H. Liu, K. Harris, M. Jiang, *et al.*, ACS Nano (2018) DOI: 10.1021/acsnano.7b08945

[3] H. Liu, M. Bugnet, M. Tessaro, *et al.*, Phys. Chem. Chem. Phys. **18** (2016), 29064.

[4] N. Gauquelin, *et al.*, *Nature Communications* **5**, 4275 (2014)

[5] M. Bugnet, *et al.*, *Science Advances* 2016; **2**:e1501652 (2016).

[6] S. Loeffler, M. Bugnet, N. Gauquelin, et al. , *Ultramicroscopy*, (2017), 177, 26-29

[7] This work is supported by NSERC, CFI.

0011 - Invited talk

invited talk

Solving Materials Science Problems by Imaging and Analysis with Cs-corrected STEM

*J. H. Neethling[1], E. J. Olivier[1], J. H. O'Connell[1], A. Janse van Vuuren[1]
[1]Nelson Mandela University, Centre for HRTEM, Port Elizabeth, South Africa

The development of the Cs-corrected STEM with HAADF imaging mode has provided a powerful technique for determining structural and chemical information at atomic resolution. This paper presents examples of long-standing materials problems that were solved by using a double Cs-corrected JEOL ARM200F.

The nature of small dislocation loops in proton, electron and neutron irradiated n-type GaAs may be determined unambiguously by Cs-corrected HAADF STEM since the image characteristics do not depend on foil thickness and defocus values as is the case for HRTEM imaging. Cs-corrected HAADF STEM imaging of {110} and {111} dislocation loops in neutron irradiated and annealed (600°C for 20 minutes) n-type GaAs revealed that the extra half-plane of the {110} loop consists of two layers of GaAs atoms, which is consistent with the model for a {110} pure-edge interstitial dislocation loop in GaAs. The extra half-plane of the {111} interstitial loop consists of one layer of GaAs atoms while the stacking sequence across the loop is consistent with that of an extrinsic stacking fault.

The finding, more than three decades years ago, that silver (a radioactive fission product) can be released by reputedly intact TRISO nuclear fuel particles has led to significant research efforts to determine the silver transport mechanism in SiC. Neethling and co-workers discovered that palladium, another high yield fission product, significantly enhances the transport of silver along grain boundaries in SiC [1]. The Pd assisted Ag transport mechanism was confirmed in a recent paper by Van Rooyen, Olivier and Neethling [2]. In this paper high resolution STEM was used to determine the location of fission products (Pd and Ag) in SiC from a neutron irradiated TRISO particle. It was found that Pd formed a palladium silicide layer of thickness about 2 nm along the SiC grain boundaries and that this silicide creates fast diffusion paths for Ag.

The nitrogen containing {001} platelet defect in type 1a diamond has been studied for more than 60 years. A spatial resolution better than 89 pm is required to resolve the atomic columns of the platelet defect. Comparisons of the HAADF STEM images with simulated platelet model images revealed that it agrees closely with a structural model called the zigzag model [3].

Despite many years of research on the silver-platinum system, it was until recently not well understood [4]. By using HAADF STEM, we were able to show that the Ag-Pt alloy consists of nanometre-sized domains with $L1_1$ ordering surrounded by disordered FCC domains [4].

References

[1] JH Neethling, JH O"Connell and EJ Olivier, Nucl. Eng. and Design **251** (2012), p. 230.

[2] IJ Van Rooyen, EJ Olivier and JH Neethling, J. Nucl. Mater. **476** (2016), p. 93.

[3] EJ Olivier *et al*, Nature Materials, **17** (2018), p. 243.

[4] GLW Hart *et al*, Acta Materialia, **124** (2017), p. 325

[5] The Department of Science and Technology and the NRF are acknowledged for financial support.

0012 - Invited talk

invited talk

EELS applied to plasmonics: wave effects, plasmons' phase measurement and self-hybridization

*H. Lourenço Martins[1], P. Das[1], L. Tizei[1], J. Verbeeck[2], G. Guzzinati[2], M. Kociak[1]
[1]*Laboratoire de Physique des Solides, Orsay, France*
[2]*EMAT, Antwerp, Belgium*

Surface plasmons resonances are collective oscillations of free electrons localized at an interface between a metal and a dielectric. Electron energy loss spectroscopy (EELS) in the low-loss region has attracted a large interest due to its efficiency in resolving plasmonic resonance at the nanometer scale [1]. In this talk, I will tackle two different problems of EELS applied to plasmonics.

In a first part, I will use conventional EELS to study exotic non-Hermitian effects in plasmonic systems. Within the quasi-static limit, Ouyang and Isaacson [2] have shown that the plasmon modes are the solutions of an eigenvalue problem. This boundary element equation has been extensively used to compute nano-particle plasmon resonances. Depending on the geometry of the particle, the solutions of this eigenproblem can form a bi-orthogonal basis but this property has always been considered as a mere computation detail. However, in a recent paper [3], we have demonstrated that, far from being a simple mathematical curiosity, plasmonic bi-orthogonality has dramatic physical consequences. Particularly, it enables eigenmodes of different orders within a single particle to interact. This phenomenon of self-hybridization is particularly non-intuitive because eigenmodes of a system are usually not overlapping and therefore unable to interact. In this talk, I will present a numerical and experimental realization of a self-hybridization in a silver dagger system.

However, despite its remarkable efficiency, EELS remains intrinsically unable to detect plasmon phase which can lead to dramatic experimental difficulties. In a second part of this talk, I will show that phase shaped electron probes constitute a perfect candidate to overcome this limitation and measure the surface plasmons" phase in an electron microscope - as recently pointed out through simulations by Asenjo-Garcia and García de Abajo [4]. In a recent paper [5], we developed a semi-classical formalism describing the interaction between an electron probe with an arbitrary phase profile and a plasmonic mode. We showed that the equation ruling this interaction takes the elegant form of a transition matrix between two electron states mediated by the eigen-potentials of the plasmon modes. In this talk, I will present the theoretical formalism and a wide variety of numerical studies of interactions between different nano-structures (e.g. square, rod) and phase shaped electron probes (e.g. vortex beams, HG-like beams...). Finally, I will show that vortex beams can even be used to probe the optical chirality flow which is a fundamental property of the electromagnetic field.

[1] Nelayah et al., Nature Physics, 3 (5), 348-353 (2007)

[2] Ouyang and Isaacson, Philo. Mag. B, 60 (4), 481-492 (1989)

[3] Lourenço-Martins et al., Nature Physics, 14 (4), 360-364 (2018)

[4] Asenjo-Garcia and García de Abajo, Phys. Rev. Lett. 113, 066102 (2014)

[5] Guzzinati et al., Nature Communication, 8, 14999 (2017)

0013 - Poster presentation

In-situ transmission electron microscopy techniques

Investigation on the cobalt-based catalysts used for Fischer-Trospch synthesis by *operando* TEM

*K. Dembélé[1,2,3], M. Bahri[2,3], C. Hirlimann[2], G. Melinte[2], A. Berliet[3], A. S. Gay[3], S. Maury[3], O. Ersen[2,4,5]
[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft , Department of Inorganic Chemistry, Berlin, Germany*
[2]*IPCMS/CNRS, Strasbourg, France*
[3]*IFPEN, Solaize, France*
[4]*Institut Universitaire de France, Paris, France*
[5]*USIAS, Strasbourg, France*

The Fischer-Tropsch synthesis (FTS) is an efficient process to produce high quality hydrocarbon molecules from the conversion of natural gas, biomass or coal [1]. In this synthesis, heterogeneous catalysts, made out of metallic nanoparticles (Fe, Co, Ni, Ru) dispersed onto alumina, silica or titania supports, are generally used. To improve the catalytic performances (activity, selectivity, stability), there is a need to better understand their behaviour during time on stream. To understand mechanisms such as the activation of the catalysts and their stability/deactivation, numerous studies using *in situ* and *ex situ* techniques have been used. Here, we present an *operando* TEM approach that associates an *in situ* TEM and a residual gas analyser (RGA), to probe catalysts under experimental conditions simulating their activation, operation, and deactivation.

Using these *operando* tools, cobalt oxide nanoparticles (NPs) supported onto alumina and silica supports have been submitted to different atmospheres and temperatures to gather a complete knowledge of their stability during the reaction and to perform a mass spectrometry analysis of the products formed. To this end, the systems are firstly observed under inert argon atmosphere at 200 °C, then activated under pure hydrogen with increasing the temperature up to 430 °C, followed by the operation under syngas (CO/H2 = 2) at 220 °C and 300-650 °C.

During the catalysts activation, different processes simultaneously occurred as a result of the oxygen removal: the disappearance of the cavities in the Co aggregates; the NPs densification with the decrease of their global size. In addition, the reduction phenomena were faster in the silica support compared to the alumina one, due to a weaker NPs-support interaction with the silica support.

In the subsequent operation under syngas, we have shown that with the silica support the Co active phase is relatively stable in the Fischer-Tropsch (FT) regime (220°C) for 2h. Whereas, in the case of the alumina support, the reduction of the NP was still on-going. In addition, the residual gas analysis has confirmed the formation of methane and others C2-C4+. By increasing the temperature to 400 °C, the NPs were encapsulated by graphitic carbon layers. This was related to the high dissociation of CO which can lead to the CO disproportionation reaction as observed by mass spectrometry. An additional increase of the temperature to 450 -650 °C showed the catalysts activation toward the growth of carbon nanotubes.

In conclusion, by using the *operando* TEM, we have developed a novel approach to follow the reactivity behaviour of Co-based FT catalysts under different atmospheres and temperatures. This way we could correlate the modification to the synthesised products. More generally, this method can be extended to the study of other important catalytic reactions such as the CO2 methanation or the CO oxidation by *operando* TEM.

References

[1] M. E. Dry, Catalysis Today, 71, 227–241 (2002)

[2] Andrei Y. Khodakov et al., Chem. Rev., 107, 1692-1744 (2007)

0014 - Poster presentation

Imaging with advanced methods of conventional and aberration-corrected electron microscopy: high-resolution transmission and scanning transmission electron microscopy (HRTEM and HRSTEM)

TEM investigations of disorder in o-Co4Al13

*I. Zelenina[1], P. Simon[1], W. Carrillo-Cabrera[1], U. Burkhardt[1], P. Gille[2], Y. Grin[1]
[1]Max Planck Institute for Chemical Physics of Solids, Chemical Metals Science , Dresden, Germany
[2]2Ludwig-Maximilians-Universität München, Department of Earth and Environmental Sciences, München, Germany

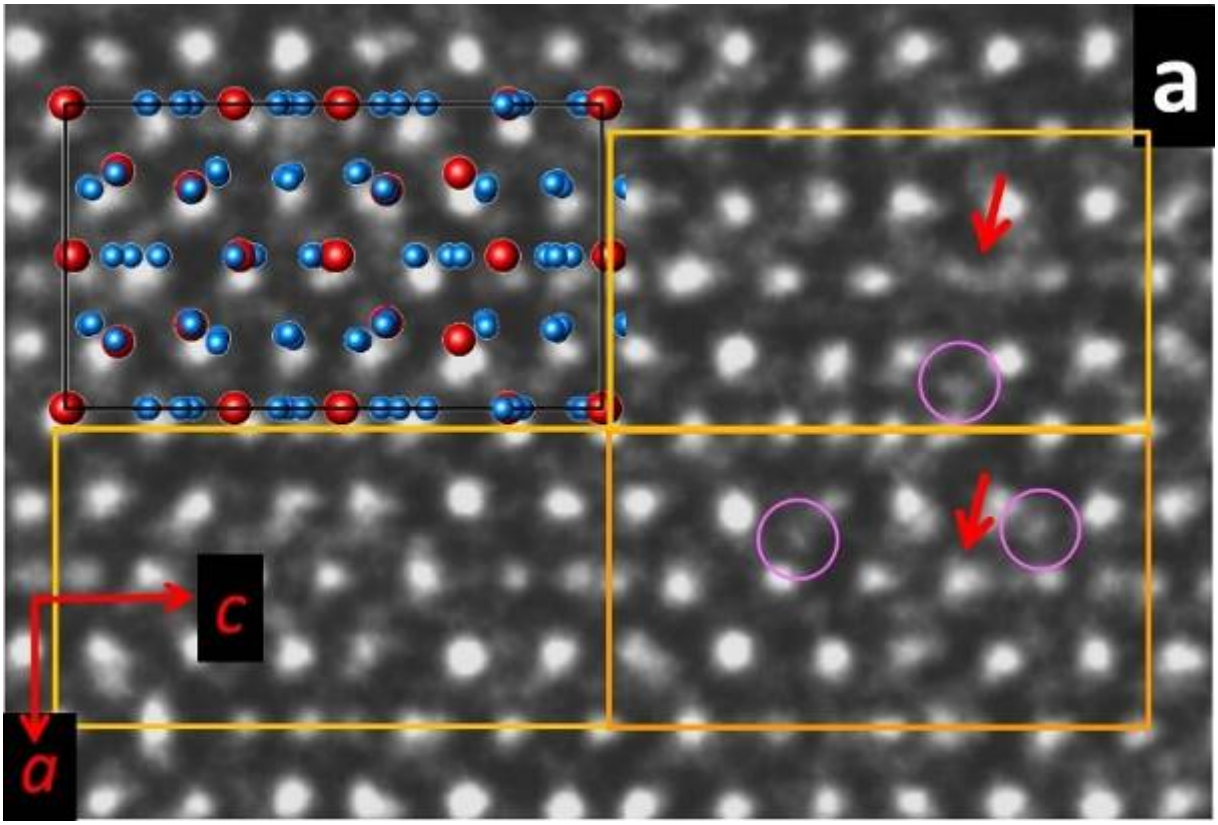
Complex intermetallic phases such as orthorhombic-Co4Al13 are promising candidates for in-situ stable, low cost heterogeneous catalysis. O-Co4 Al13 has the space group Pmn21 and the lattice parameters a=8.2 Å, b=12.3 Å, c= 14.5 Å [1]. In [100] zone, polyhedrons such as icosahedra of cobalt atoms are present, at the same time aluminum shows more complicated pattern. [1,2].

Single crystal of o-Al13Co4 was grown by the Czochralski technique. For TEM investigations focused ion beam (FIB) lift-out lamella were prepared with cuts parallel to (100) and (010) zones.

Fig. a) Overview TEM micrograph HRTEM of [010] zone with four unit cells indicated by orange rectangles. The model of the regular structure is overlaid at top left indicating the appearance of five layers along the *a*-axis. Upper red arrow indicates a smearing out of the aluminum positions whereas in the bottom unit cell below the same position appears clearly, see lower red arrow. The striking feature of the observed structure is the appearance of off-layer interstitial positions of aluminum marked by pink circles.

1. J. Grin, U. Burkhardt, M. Ellner, K. Peters. Crystal structure of orthorhombic Co4Al13. *J. Alloy. Compd*. 206 (1994) 243-247.
2. J. Grin, U. Burkhardt, M. Ellner and K. Peters. Refinement of the Fe4Al13 structure and its relationship to the quasihomological homeotypical structures. *Z. Kristall*. 209 (1994) 479-487.

Figure 1



0015 - Poster presentation

Applications to characterizations of functional nanomaterials and devices, materials for energy, materials for information technology, catalysts, soft matter, biomaterials

TEM Characterization and Synthesis of Cu Nanoparticles: Stability and Conversion into Cu2S Nanoparticles by Decomposition of Alkanethiolate

*C. Rohner[1], A. Pekkari[2], H. Härelind[2], K. Moth-Poulsen[2]
[1]*Fritz Haber Institute of the Max Planck Society, Inorganic Chemistry, Berlin, Germany*
[2]*Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Gothenburg, Sweden*

A lean synthesis of copper nanoparticles (Cu NP) from CuCl2 in dodecane via formation of Cu(I)-dodecanethiolate and their decomposition paths including spontaneous C-S bond cleavage of the alkanethiol on the surface of Cu NP is presented (Scheme 1).[1] Alkanethiols, widely used in noble metal nanoparticle synthesis, are considered a promising candidate for the oxidation protection of Cu NP, as several electrochemical studies on self-assembled monolayers on Cu electrodes show a stabilizing effect.[2] At the same time, a partial decomposition of alkanethiols has been reported when the thiolate is bound to a Cu surface or cluster by scission of the C-S bond at room temperature.[3]

Scheme 1 (Top) Reaction scheme of the neat reaction of CuCl2 and DDT yielding Cu(I)-DDT and didodecyl disulfide. (Bottom) Formation of metastable thiolate protected Cu NP and their decomposition paths in the presence of excess thiol under ambient conditions or N2 atmosphere, respectively.

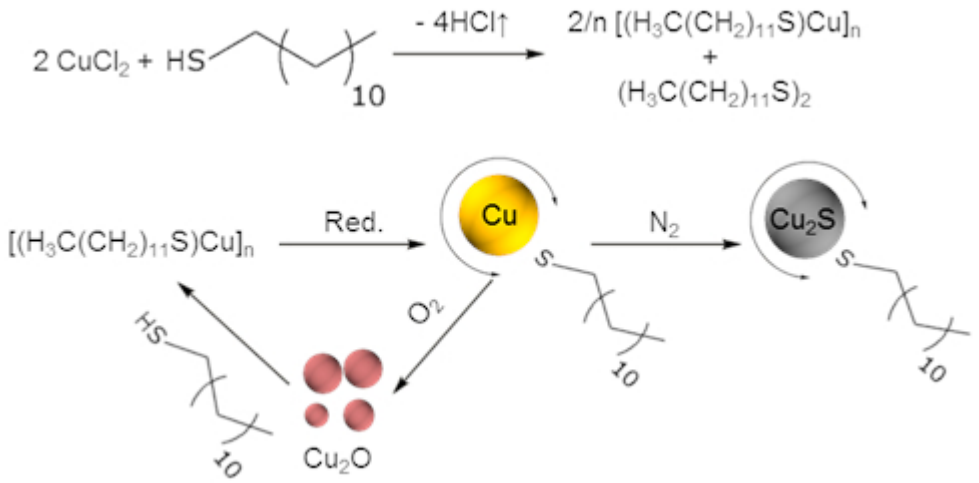
TEM measurements of the product Cu NP show the dependence of the average particle size, size distribution and NP morphology on the reaction parameters. Nevertheless, it was found that storage of NP solutions for more than a few hours lead to irreversible aggregation of the purified Cu NP colloid or the disappearance of the plasmon resonance band even under inert atmosphere. Interestingly, we observe that the thiol stabilized Cu NP are partially transformed to Cu2S and can be fully converted to Cu2S NP by heating the reaction mixture to ≥ 145 °C for an extended period of time, which is observed in SAED and in EDX measurements. The decomposition of Cu NP and conversion into Cu2S was systematically studied by variation of the reaction parameters, the isolation procedures and the postsynthetic treatment of the products, which were characterized by a set of complementary analytical techniques in addition to TEM (XRD, UV-Vis, ICP-MS). We envision that the decomposition of the alkanethiolate shell could be utilized when depositing the Cu NP on mesoporous supports followed by removal of the alkyl moieties for applications where sulfur impurities are not an obstacle or desired.

[1] C. Rohner, A. Pekkari, H. Härelind, K. Moth-Poulsen, *Langmuir* **2017**, *33*, 13272–13276.

[2] P. Wang, C. Liang, B. Wu, N. Huang, J. Li, *Electrochim. Acta* **2010**, *55*, 878–883.

[3] S. Vollmer, G. Witte, C. Wöll, *Langmuir* **2001**, *17*, 7560–7565.

Figure 1



0016 - Invited talk

invited talk

Quantitative energy dispersive X-ray spectrometry in the TEM using a multi detector system

*W. Grogger[1], J. Lammer[2], R. Krisper[2], G. Haberfehlner[1], M. Zakhozheva[3], G. Kothleitner[1], F. Hofer[1]
[1]Graz University of Technology, FELMI, Graz, Austria
[2]Graz Center for Electron Microscopy, Graz, Austria
[3]DENSsolutions, Delft, Netherlands

Thanks to the recent advent of very large area detectors and multi-detector systems, energy-dispersive X-ray spectrometry (EDXS) in analytical electron microscopes received a substantial boost. In particular, the combination of 2 or 4 detectors has proven to obtain such a good sensitivity that the detection of single atoms is feasible and atomically resolved mapping can be performed [e.g. 1, 2]. However, if it comes to quantitative work several issues regained importance, which need to be considered in order to obtain reliable elemental results.

In this work, we will explain the parameters that contribute to the EDX signal and influence quantitative analysis. In particular, we will describe how the geometry of the detector-microscope configuration affects the X-ray signals. As soon as more than one EDX detector is used, tilting of the specimen will change the illuminated area on the detectors and consequently, the measured X-ray intensities. Mainly the specimen holder causes this shadowing, and it turns out that the amount of shadowing depends on the X-ray"s energy. We will show how this can be simulated and that this approach can yield the detector"s positions in space for an FEI Titan³ TEM equipped with a Super-X detector [3]. Once the positions are known, the shadowing effects can be taken into account and the experimental setup of an analytical experiment can be optimized (fig. 1). In addition, we will also discuss the influence of the detector geometry on quantitative results.

When performing heating experiments, EDXS may also play an important role for the chemical characterization of a sample. Using DENSsolutions MEMS based heating holders, we did extensive research on the EDXS performance at elevated temperatures. First, we characterize different holders with respect to their geometry and the shadows cast on the detectors (fig. 2). On the other hand, infrared radiation is the main signal at elevated temperatures (fig. 3) and strongly influences the detector"s response. Therefore, we will show how to find suitable conditions for proper EDXS analysis from heated samples.

References

[1] TC Lovejoy, QM Ramasse, M Falke, A Kaeppel, R Terborg, R Zan, N Dellby, OL Krivanek, Appl. Phys. Lett. 100, 154101 (2012)

[2] G Kothleitner, MJ Neish, NR Lugg, SD Findlay, W Grogger, F Hofer, LJ Allen, Phys. Rev. Lett., 112, 085501 (2014)

[3] J Kraxner, M Schäfer, O Röschel, G Kothleitner, G Haberfehlner, M Paller, W Grogger, Ultramicroscopy 172, 30 (2017)

[∞] The authors thank the Austrian Research Promotion Agency FFG for funding.

fig. 1: effect of sample position (x, y, α) on the geometric detector efficiency (Super-X system, 2 detectors); the red surface indicates an illumination of greater than 98%

fig.2: geometric detector efficiency for a single-tilt heating holder (Super-X system)

fig.3: temperature dependence of detected infrared radiation (Super-X system, 2 detectors, 25° tilt towards detectors)

Figure 1

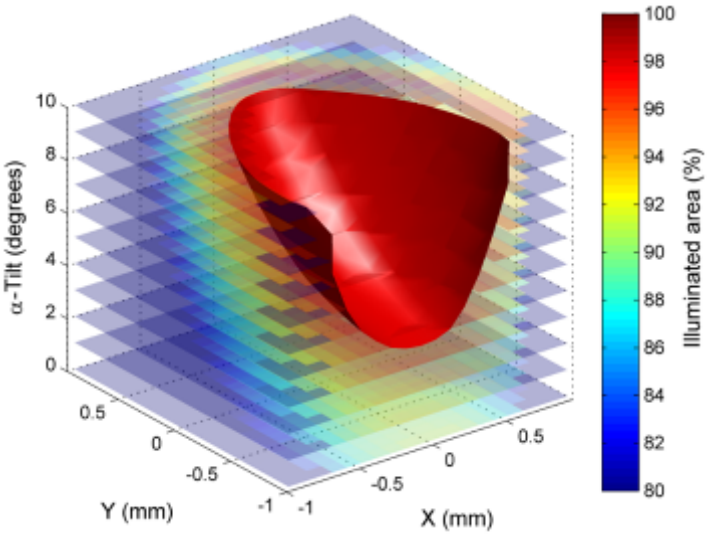


Figure 2

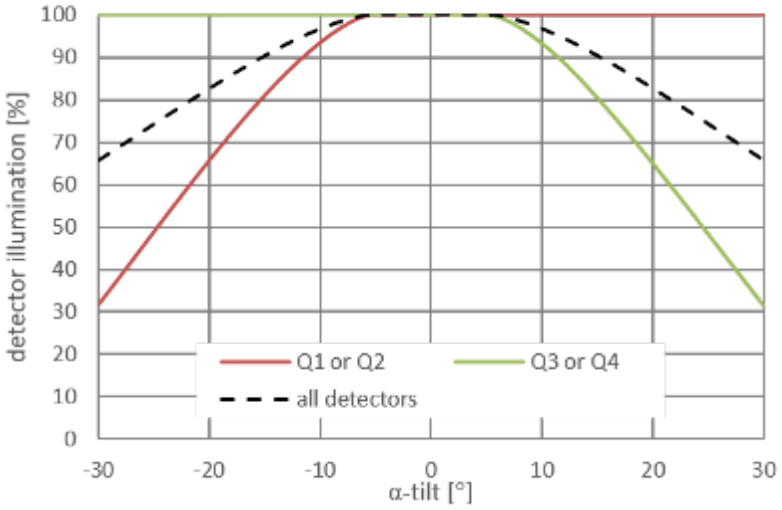
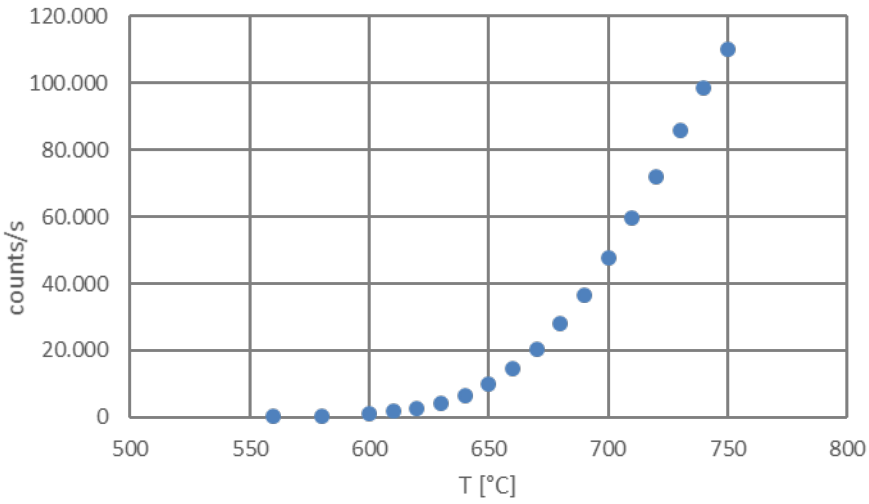


Figure 3



0017 - Poster presentation

Imaging with advanced methods of conventional and aberration-corrected electron microscopy: high-resolution transmission and scanning transmission electron microscopy (HRTEM and HRSTEM)

STEM characterisation of Ni single atom catalysts

*G. Algara-Siller[1], M. M. Millet[1], S. Wrabetz[1], A. Mazheika[1], F. Girgsdies[1], D. Teschner[1], F. Seitz[1], A. Tarasov[1], S. V. Levchenko[1], R. Schlögl[1], E. Frei[1]
[1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The understanding of CO_2 activation reactions has become a topic undergoing intense study because of environmental considerations. Among the transition metals efficient for CO_2 activation and hydrogenation reactions, supported Ni catalysts are prominently represented. Interestingly, for the methanation reaction, the size of the metal particles has shown to have a large influence on the selectivity of the reaction. Larger particles are leading to more CH_4 selective catalysts, while small particles are more selective towards CO [1,2]. As a consequence, we have focused our interest on the preparation of Ni single atom catalysts.

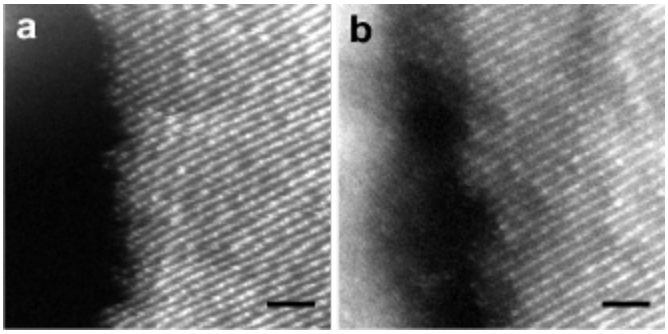
$Ni_xMg_{1-x}O$ catalysts were synthesized with a Ni concentration of 10 at.-% and characterized before and after catalysis. Among other methods the sample was firstly characterized with X-ray diffraction (XRD). The XRD results after Rietveld refinement show that the sample is phase pure. To further characterize the initial sample we used a JEOL ARM 200F operated at 200 kV with emission of 5 uA and a probe current of 1 nA operated in STEM mode. The sample was transferred from the synthesis oven to the glove box and from there to the microscope using a vacuum transfer holder in order to avoid exposure to air, i.e. to maintain the pristine structure. The STEM characterization of the initial 10 at.-% Ni shows a distribution of Ni atoms on the MgO, moreover Ni clusters or particles were not found on the sample (Figure 1a). This observation corroborates the successful incorporation of single Ni atoms into MgO. Catalytic testing was performed on the sample at 30 bar, 300°C and a gas mixture of H_2:CO_2 of 4:1 for 40 hours. During this period no deactivation of the catalyst was observed. Moreover the sample retained the distribution of Ni atoms without clusters or particles as seen by STEM image (Figure 1b). These results assert the stability of the single Ni atoms on the MgO and their involvement on the activation of CO2, through reverse-water-gas-shift reaction, and their activity.

Figure 1. High resolution STEM images of NiMgO (Ni 10at.-%) (a) in pristine state and (b) after catalytic testing

[1] Lu, B.; Kawamoto, K. *Materials Research Bulletin* **2014**, *53*, 70.

[2] Lu, B.; Kawamoto, K. *RSC Adv.* **2012**, *2*, 6800.

Figure 1



0018 - Poster presentation

Applications to characterizations of functional nanomaterials and devices, materials for energy, materials for information technology, catalysts, soft matter, biomaterials

Towards the metal distribution in complex mixed metal oxide catalysts

*L. Masliuk[1], W. Hetaba[1], A. Trunschke[1], R. Schlögl[1,2], T. Lunkenbein[1]
[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft , Department of Inorganic Chemistry, Berlin, Germany*
[2]*MPI for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*

The properties of functional materials can be crucially influenced by local alterations of their composition. Examples are p- and n- type dopants in semiconductors or promoters in heterogeneous catalysts. Meanwhile these local alterations can be easily overseen by common bulk or surface averaging methods. Structural and compositional analysis down to the nanoscale can be provided by (scanning) transmission electron microscopy ((S)TEM) coupled with chemical analytical techniques, such as energy dispersive X-ray spectroscopy (EDS) or electron energy loss spectroscopy (EELS). [1-2]

It has been shown that average the surface composition of catalytic materials can significantly differ from the bulk composition and depends on the feed composition.[3] Here we use an orthorhombic mixed (Mo,V) oxide as an example of a structure with a broad local variability even in the pristine state.[4] We explore local compositional differences between bulk, surface, and defects via STEM-EELS line scans (Figure 1).

The compositional variations, which occur within the bulk framework, are related to local unit cell inhomogeneities and reflect differences in the metal site occupancies within the unit cell. Additionally, the analysis of extended defects confirms the relation between local morphology and composition. Furthermore, our results suggest a preferential Mo enrichment of the surface which is interrupted partially by V-enriched surface facets. The present study can pinpoint local compositional variations of the catalyst surface and therefore provide a background for establishing novel activity-composition correlations.

Figure 1: a) HAADF-STEM image of (Mo,V)O_x rod. b) Qualitative Mo/V ratio based on STEM-EELS measurements. Color lines indicate line scan positions that correspond to the colored squares in b); white arrow – [001] crystallographic direction.

References

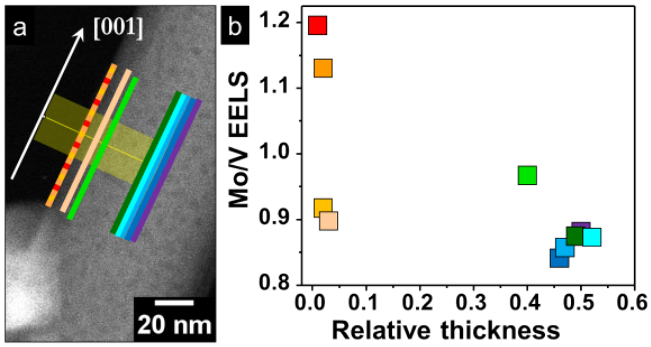
[1] P. E. Batson, Nature, 366, 727-728 (1993).

[2] D. B. Williams, C. B. Carter, in Transmission Electron Microscopy: A Textbook for Materials Science (Eds.: D. B. Williams, C. B. Carter), Springer US, Boston, MA, 581-603, (2009).

[3] A. Trunschke, J. Noack, S. Trojanov, F. Girgsdies, T. Lunkenbein, V. Pfeifer, M. Hävecker, P. Kube, C. Sprung, F. Rosowski, R. Schlögl, ACS Catal., 7, 3061-3071 (2017).

[4] L. Masliuk, M. Heggen, J. Noack, F. Girgsdies, A. Trunschke, K. E. Hermann, M.-G. Willinger, R. Schloegl, T. Lunkenbein, J. Phys. Chem. C, 121, 24093-24103 (2017).

Figure 1



0019 - Invited talk

invited talk

Electron Beam Driven Dynamics in Experiment and Simulation

*F. Hofer[1], D. Knez[1], G. Haberfehlner[1], W. Grogger[1], G. Kothleitner[1]
[1]Graz University of Technology, Institute for Electron Microscopy and Nanoanalysis, Graz, Austria

Metallic clusters, with diameters of a few nanometres or less, are of high interest for potential applications such as catalysis, optics or magnetism. The properties of these clusters depend on their crystallographic structure and chemistry at the sub-nanometre scale. To characterise these clusters thoroughly, aberration corrected scanning transmission electron microscopy (STEM) plays a pivotal role. Due to the high current densities occurring in a highly focused electron beam, however, interpretation of STEM data is often impeded by continuous beam induced specimen changes. Despite its significance, knowledge about beam induced dynamics is still very limited.

In this paper we report STEM investigations performed on supported clusters grown inside superfluid He-nanodroplets [1]. This method allows the synthesis of high purity clusters in UHV conditions without templates or stabilisers, providing an ideal basis for studying interaction mechanisms without the influence of organic contaminants.

We apply both experimental and computational methods to elucidate the electron beam induced dynamics down to the single atom level. On the one hand, we performed time resolved STEM experiments, which allow observing the dynamics of clusters and single atoms under the controlled influence of the electron beam. To evaluate image series consisting of several hundred images we use automatic image processing techniques. On the other hand, we developed a computational framework to simulate elastic electron damage processes in solids and to obtain deeper insights into the observed dynamics. Our approach is based on the combination of molecular dynamics and Monte Carlo techniques [2], which has been applied to a STEM HAADF image series of a Janus type Ag-Au cluster on an amorphous carbon support. The two cluster phases show highly different dynamics under electron irradiation, due to differences in atomic mass and binding energies between Ag and Au. While the Au cluster mostly retains its size during the experiment, the Ag cluster exhibits significant mass loss due to surface sputtering. This behaviour is reproducible using the above mentioned simulations [3].

To study the effect of the electron beam on atomic motion we recorded an atomically-resolved STEM HAADF image series of Pt atoms on the surface of a thin silicon crystal. Using a novel image processing approach the dynamics of the silicon substrate is separated from that of the adatoms and automated particle tracking enables the detailed analysis of the diffusive motion of the Pt adatoms [4].

References

[1] D. Knez, P. Thaler, A. Volk, G. Kothleitner, W.E. Ernst, F. Hofer, Ultramicroscopy 176 (2017) 105.

[2] D. Knez, M. Schnedlitz, M. Lasserus, A. Schiffmann, W.E. Ernst, F. Hofer, Ultramicroscopy 192 (2018) 69.

[3] M. Lasserus, M. Schnedlitz, D. Knez et al., Nanoscale 10 (2018) 2017.

[4] T. Furnival, D. Knez, E. Schmidt, R. W. Leary, F. Hofer, P.D. Bristowe, P.A. Midgley, submitted.

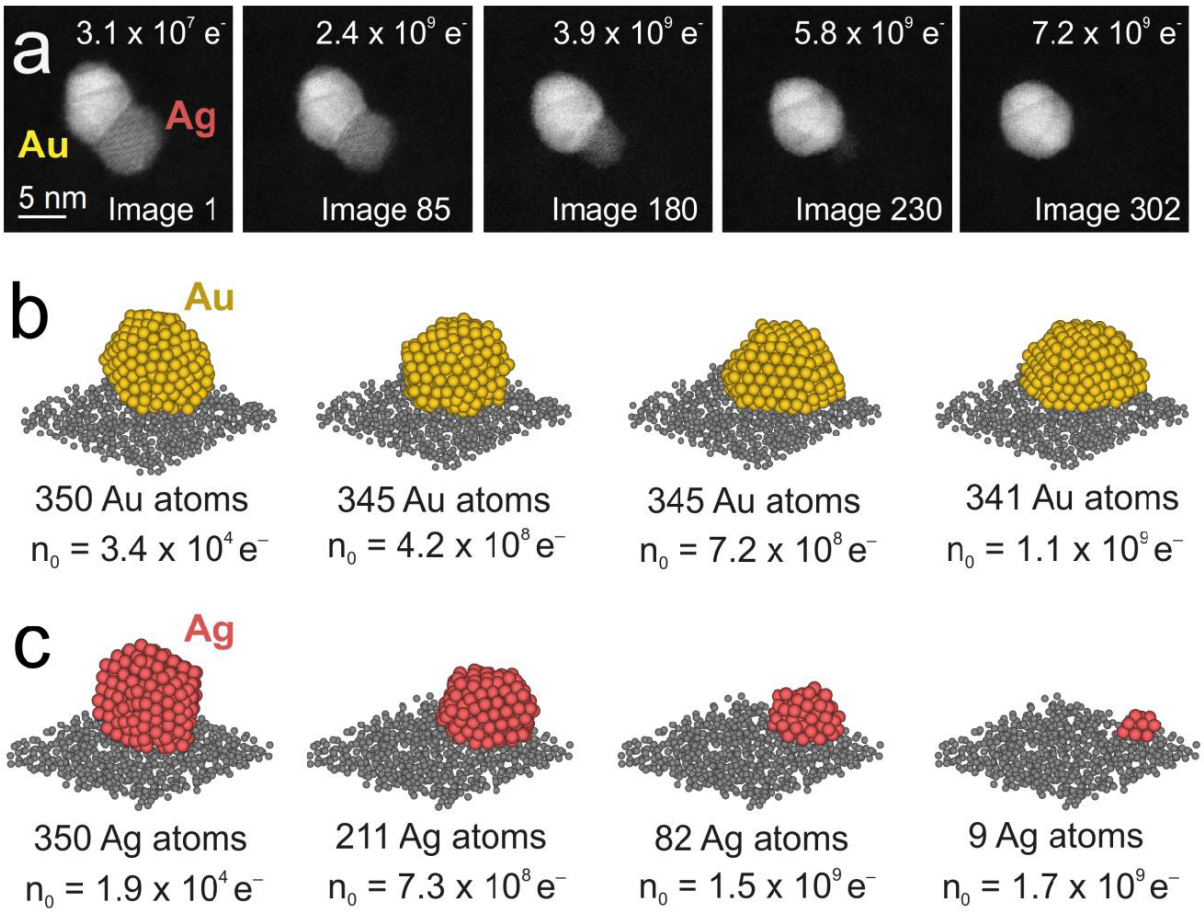


Figure 1 (a) Experimental STEM HAADF image series of a Ag-Au nanoparticle showing the effect of selective Ag sputtering, dependent on the applied dose in number of electrons; (b, c) simulation of beam induced dynamics in carbon supported clusters initially comprised of either 350 Au or Ag atoms, demonstrating significant surface sputtering of Ag atoms at 300 keV electron energy.

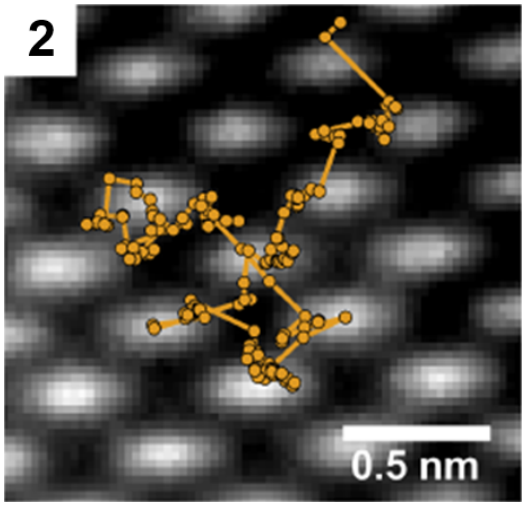


Figure 2 Tracking of a Pt adatom on the surface of a thin Si-crystal with [110] orientation; image sequences were denoised and aligned; a robust principal component analysis (RPCA) revealed the low-rank component (Si lattice) and the high rank component (mobile Pt adatoms).

0020 - Poster presentation

In-situ transmission electron microscopy techniques

In situ TEM Studies of Transitions and Unusual Transrotational Crystal Growth in Amorphous Films Under the Influence of Electron Beam

*V. Kolosov[1]
[1]*Ural Federal University, Research Institute of Physics & Applied Mathematics , Ekaterinburg, Russian Federation*

In this paper we present our *in situ* TEM studies of thin-film transformations initiated by electron beam primarily for initially amorphous layers of several oxides and chalcogen-based materials. To change electron beam illumination we change condenser apertures and condensers currents with different beam focusing and beam currents. For some in-situ studies thermal heating of the sample in the TEM holder was added. Annealing of some similar TEM samples outside TEM column was performed to control any specific influence of e-beam. Most experiments have been done for 100KV and 200 KV in different Philips/FEI, JEOL and Tesla TEMs but higher (300Kv) and lower (5 Kv, using LVEM-5) accelerating voltages were also used. Special attention is paid to the growth of unusual transrotational crystals and corresponding reversible transformations amorphous - crystalline important for memory devices that use PCMs (phase-change materials)

To be continued and supported images to be downloaded

0021 - Invited talk

invited talk

Watching Things Fail: In-Situ Electron Microscopy of Fracture and Flow

A. Kelling[1], B. Kapelle[1], G. Richter[2], *C. Volkert[1]
[1]University of Göttingen, Institute of Materials Physics, Göttingen, Germany
[2]Max-Plank-Institute for Intelligent Systems, Stuttgart, Germany

Deformation and fracture are complex and highly non-equilibrium processes which determine the strength of materials. Gaining insights into the mechanisms which control these dynamic processes requires dynamic methods. This presentation will describe in-situ electron microscopy studies of deformation and fracture in nanoscale specimens where we have performed dynamic observations at length scales down to Angstroms and time scales between 0.1 seconds and several hours.

Our studies on deformation have been primarily focused on tensile loading of high quality Au nanowires using in-situ testing in the TEM and the SEM, where we observe the creation of dislocations by surface nucleation. Both the evolution of the defect morphology and the stress-strain behavior of the 20 nm to 300 nm diameter nanowires have been studied. We show that surface structure, stress state, and initial defects are more important in determining the deformation mode in nanoscale samples than the actual sample size. We also discuss evidence for reversible dislocation storage and the role of dislocation nucleation in the deformation of bulk metals.

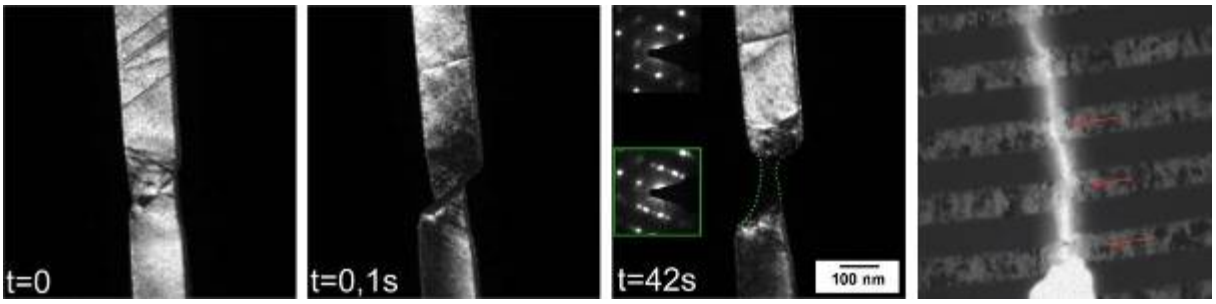
Our studies on fracture have focused on crack propagation in nanolaminates, where we attempt to decipher the roles of surfaces and interfaces by propagating cracks parallel and perpendicular to the layer interfaces. We can directly observe the extent of the plastic zone in the TEM, which allows a qualitative connection between plasticity, fracture toughness values, and the selection of the crack propagation path. Furthermore, we observe changes in the crack path with layer thickness that we attribute to a size-dependent flow stress. The implications of such size dependent effects on the fracture toughness and recycling of nanocomposites will be discussed.

References

[1] Roos, B., Kapelle, B., Richter, G., Volkert, C.A. *Appl. Phys. Lett.* ***105***, 201908 (2014).

[2] Kelling, A., Mangipudi, K.R., Knorr, I., Liese, T., Krebs, H.U., Volkert, C.A. *Scripta Mat.* ***115***, 42-45 (2016).

Figure 1



0022 - Invited talk

invited talk

Unraveling catalyst growth and degradation mechanisms via STEM

K. Hengge[1], *C. Scheu[1]
[1]Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

Polymer electrolyte membrane fuel cells find application in the transportation and stationary sector. The lifetime of these fuel cells is limited by various operation related degradation effects. In order to minimize such effects, new materials need to be developed and tested. In our work, we replaced the standardly used Pt catalyst in the anode by a Pt/Ru catalyst alloy and analysed its aging behaviour during various fuel cell operation conditions in detail [1,2].

Cyclic voltammetry and scanning transmission electron microscopy (STEM) experiments were performed on identical catalyst nanoparticles located on their carbon support material. These experiments included energy-dispersive X-ray spectroscopy (EDX) to study the change in chemical composition and electron tomography to track the surface and volume changes of the individual nanoparticles in 3D. The results show that dissolution and agglomeration are the main degradation mechanisms in the dynamic fuel cell operation mode [1]. It was also found that both phenomena depend strongly on the applied voltage with dissolution and agglomeration increasing when the upper potential is increased. Figure 1 shows the 3D reconstruction of a network of Pt/Ru catalyst particles before and after potential cycling between 0 and 1.2 VRHE. Especially the catalyst dissolution has consequence on the real stack performance and we observed the formation of a catalyst band within the polymer membrane after continuous fuel cell operation [2].

Another electrode type was investigated where novel Pt networks were grown on tungsten oxide support materials with an electroless deposition method and subsequent thermal reduction [3]. For this system, we were able to determine the growth mechanism by analyzing the network after different deposition stages via STEM EDX mapping and electron tomography. During the initial growth stage, the Pt network has only formed at the outer part of octahedral-shaped µm-sized morphologies while the inner part consists of Pt nanoparticles embedded in a reduced form of the Pt-Cl precursor. With increasing time of the thermal reduction process, the Cl of the interior is released as hydrogen chloride (HCl) and only Pt nanocrystals remain which assemble to a network [3]. The high stability of the Pt catalyst networks on tungsten oxide leads to a lower degradation rate during fuel cell operation compared to the standardly used Pt nanoparticles on carbon support.

Figure 1: Electron tomography of a network of Pt/Ru catalyst nanoparticles before (left), after 2000 (middle) and 7000 cycles (right) in the potential range of 0–1.2 VRHE. Images taken from [1].

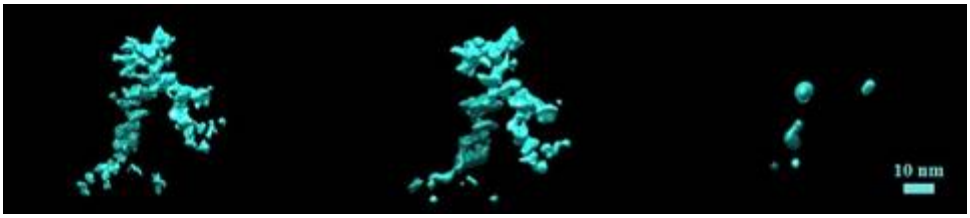
References

[1] K. Hengge, T. Gänsler, E. Pizzutilo, C. Heinzl, M. Beetz, K. J. J. Mayhofer, and C. Scheu, International Journal of Hydrogen Energy 42 (40), 25359-25371 (2017)

[2] K. Hengge, C. Heinzl, M. Perchthaler, D. Varley, T. Lochner, and C. Scheu, Journal of Power Sources, 364, 437-448 (2017)

[3] K. Hengge, C. Heinzl, M. Perchthaler, S. Geiger, K. J. J. Mayrhofer, C. Scheu, Crystal Growth & Design, 17, 1661-1668 (2017)

Figure 1



0023 - Poster presentation

Applications to characterizations of functional nanomaterials and devices, materials for energy, materials for information technology, catalysts, soft matter, biomaterials

Re-Distribution of Elements in α_2/O-Phase Lamellae of Ti-42Al-8.5 Nb

*H. Gabrisch[1], T. Krekeler[2], U. Lorenz[1], M. W. Rackel[1], M. Ritter[2], F. Pyczak[1]
[1]*Helmholtz-Zentrum Geesthacht, Metal Physics, Geesthacht, Germany*
[2]*Technical University of Hamburg, BEEM, Hamburg, Germany*

Gamma-Titanium aluminides are promising, structural light-weight materials for applications in aircraft engines. They are often alloyed with beta-stabilizing elements for improved creep strength and oxidation resistance, e.g. with Nb [1].

The addition of Nb in combination with an annealing treatment leads to the formation of a new constituent, the orthorhombic O-phase that was previously described in Nb-rich α2-based Ti-aluminides [2, 3]. TEM imaging shows that the O-phase is located inside α2 lamellae of lamellar (α2+γ)-colonies [4]. An example is shown in Fig. 1a, where the orthorhombic distortion (indicated by arrows) of the hexagonal α2-lattice can be observed directly by atomically resolved STEM imageing. In this presentation, we monitor the distribution of Ti, Al and Nb by EDX mapping after different annealing times to explore whether Nb agglomeration is required for the formation of O-phase. In all annealing states, high amounts of O-phase were identified by HERXD.

We find that after 168 h of annealing Ti and Al (not shown) segregate to the bright lines in Fig. 1b. In Fig. 1c the regions enclosed by this line pattern are identified as regions of increased Nb concentrations. For comparison, no elemental segregation is observed after 8h of annealing time, where already substantial amounts of O-phase are present within the alloy"s microstructure.

Therefore, we conclude that Nb diffusion only sets in after O-phase has formed and is no requirement for its formation.

a.) b.) c.)

Fig. 1 : Images of specimen annealed for 168 h at 550°C. A section of a a2/O-phase lamella is shown in α2-[0001] viewing direction. a.) STEM image at atomic resolution illustrating orthorhombic distortion in brighter regions. b, c.) EDX maps using the signals Ti-Ka and Nb-La.

Acknowledgement

Atomic resolution HAADF STEM imaging was conducted using the Nion UltraSTEM 100 (U100) dedicated aberration-corrected STEM at the Center for Nanophase Materials Sciences at Oakridge National Laboratory, which is a DOE Office of Science User Facility.

References

[1] F. Appel, M. Oehring, and R. Wagner, Intermetallics **8**, 1283-1312 (2000).

[2] D. Banerjee, et al., Acta metall. **36** 4, 871-882 (1988).

[3] M.W. Rackel, et al., Acta Materialia **121,** 343-351 (2016).

[4] H. Gabrisch, et al., Acta Materialia **135** 304-313 (2017).

Figure 1

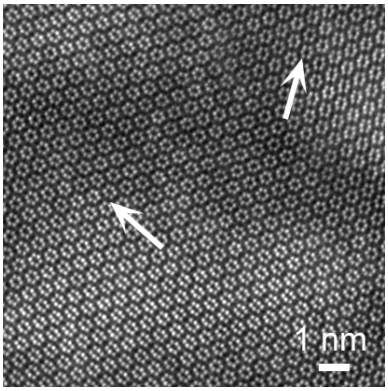


Figure 2

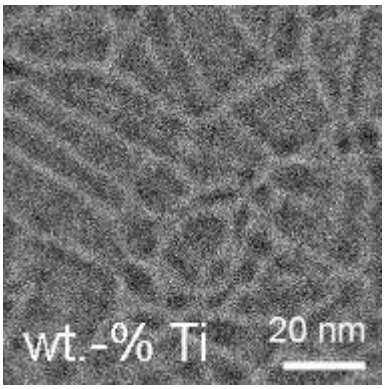
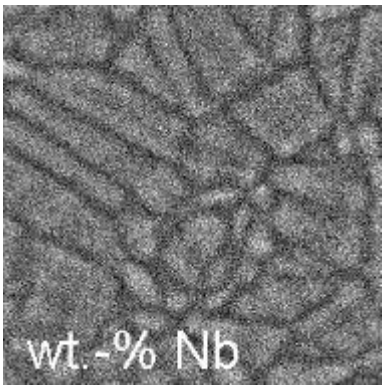


Figure 3



0024 - Invited talk

invited talk

Geometric Phase Analysis for measuring elastic stresses and strains in nanocrystals and across grain boundaries and heterostructures

*M. Hytch[1], N. Cherkashin[1], F. Houdellier[1], A. Ishizuka[1], K. Ishizuka[1]
[1]HREM Research Inc., Higashimatsuyama, Japan

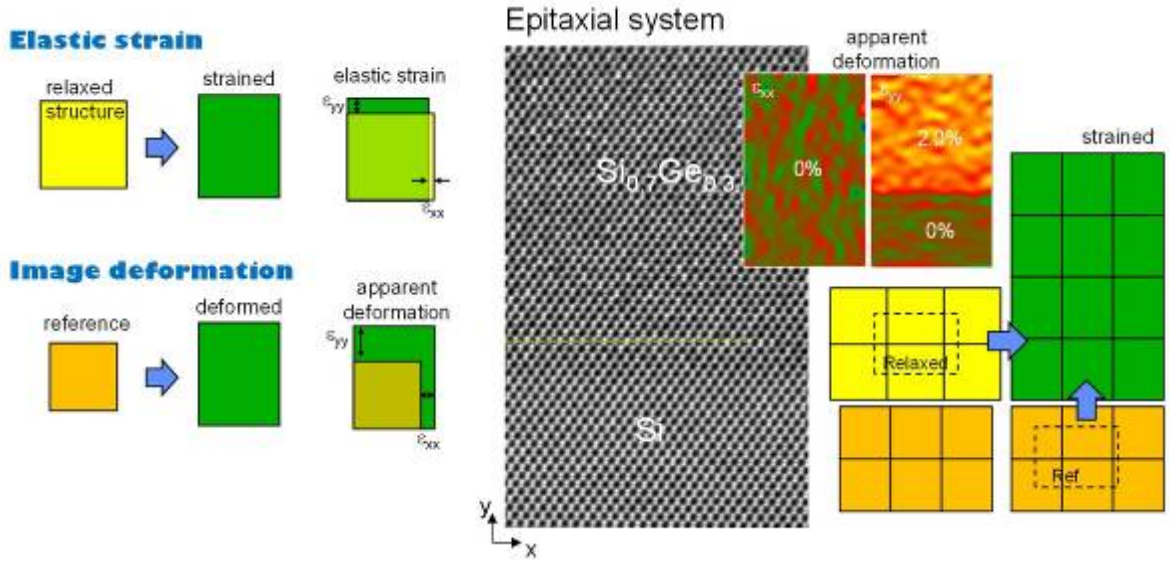
Geometric phase analysis (GPA) of HR(S)TEM images has become a standard technique for strain mapping over the years [1]. Whilst successful, the approach is not without limitations (Figure 1). An internal reference of undisturbed crystal must be present within the field of view and the regions of crystal to be analysed must have common, or closely related, reciprocal lattice vectors. Here, we present a major extension of GPA that overcomes these problems allowing the study of nanocrystals, where no reference region is generally present, grain boundaries and epitaxial heterostructures. The new theory has the added advantage of correcting errors due to global optical distortions and is general to any stain mapping technique based on images. It is little known, for example, that a global shear applied to an image will disturb conventional strain analysis.

We start from the principle that elastic strain is measured with respect to the relaxed crystal structure. By introducing the notion of crystallography to GPA, we will show how a reference image of known uniform crystal can be used to define the optical distortions and absolute magnification. An experimental image taken under identical conditions can then be analysed to determine the local elastic strain, independently of the in-plane orientation of the crystal. Large rotations across grain boundaries and domain walls will be accommodated by the new procedure. The local stresses can then be determined from elastic theory. We will implement the theory, which has been incorporated in the latest version of GPA from HREM Research Inc., for some representative examples.

[1] M.J. Hÿtch, E. Snoeck and R. Kilaas, Ultramicroscopy 74 (1998) 131–146.

Figure 1. Illustration of the reference problem: elastic strains are measured with respect to the relaxed (unstrained) crystal whereas GPA measures the image deformation with respect to an internal reference, often the substrate (as here). The new theory addresses this and other problems.

Figure 1



0025 - Poster presentation

Electron diffraction techniques, simulation tools, multi-scale techniques

Crystal structure determination of single nanocrystals by dynamical refinement of precession electron diffraction tomography data

*C. Antunes Correa[1,2], V. Drinek[3], J. Kopecek[4], L. Palatinus[2]
[1]*Charles University in Prague, Physics of Materials, Prague, Czech Republic*
[2]*Czech Academy of Sciences, Structure Analysis, Prague, Czech Republic*
[3]*Institute of Chemical Process Fundamentals, Prague, Czech Republic*
[4]*Czech Academy of Sciences, Prague, Czech Republic*

Electron diffraction has recently achieved the possibility to obtain the crystal structure of single nanocrystals with the accuracy approaching that of single crystal X-ray diffraction [1,2]. This increase of accuracy could only be obtained using the dynamical theory of diffraction for the calculated intensities during the crystal structure refinement (called dynamical refinement, for brevity). In this communication, we will present the results of the dynamical refinement against precession electron diffraction tomography data [3-5] and compare them to that of single crystal X-ray diffraction, which is the standard technique used to obtain the crystal structure of micrometer-sized crystals. The dynamical refinement was implemented in the crystallographic software JANA2006 [6] and has been applied to a range of materials [7-10], paving the way for the accurate crystal structure of nanocrystals.

References

[1] L. Palatinus, V. Petříček, C. A. Corrêa. Acta Crystallographica A71, 235-244 (2015).

[2] L. Palatinus, C. A. Corrêa, G. Steciuk, D. Jacob, P. Roussel, P. Boullay, M. Klementová, M. Gemmi, J. Kopeček, M. C. Domeneghetti, F. Camara, V. Petříček. Acta Crystallographica B71, 740-751 (2015).

[3] U. Kolb, T. Gorelik, C. Kuebel, M.T. Otten, D. Hubert. Ultramicroscopy 107 (6-7), 507-513 (2007).

[4] R. Vincent, P.A. Midgley. Ultramicroscopy 53 (3), 271-282 (1994).

[5] E. Mugnaioli, T. Gorelik, U. Kolb. Ultramicroscopy 109 (6), 758-765 (2009).

[6] V. Petříček, M. Dušek, L. Palatinus. Z. Kristallogr. 229 (5), 345-352 (2014).

[7] L. Palatinus, P. Brázda, F. Boullay, O. Perez, M. Klementová, S. Petit, V. Eigner, M. Zaarour, S. Mintova. Science 355, 166-169 (2017).

[8] C. A. Corrêa, M. Klementová, V. Dřínek, J. Kopeček, L. Palatinus. Journal of Alloys and Compounds 672, 505-509 (2016).

[9] Z. Zhou, Y. Qiu, F. Liang, L. Palatinus, M. Poupon, T. Yang, R. Cong, Z. Lin, J. Sun. Chem. Mater. 30, 2203-2207 (2018).

[10] C. C. Mayorga-Martinez, Z. Sofer, J. Luxa, Š. Huber, D. Sedmidubský, P. Brázda, L. Palatinus, M. Mikulics, P. Lazar, R. Medlín, M. Pumera. ACS Nano 12, 464-473 (2018).

0026 - Poster presentation

In-situ transmission electron microscopy techniques

Atomic Scale Characterisation of Pt-Re/CeO_2 for the Water Gas Shift Reaction

*R. Martin[1], P. Kooyman[1]
[1]University of Cape Town, Centre for Catalysis, Cape Town, South Africa

The water gas shift (WGS) reaction reacts carbon monoxide and water to form carbon dioxide and hydrogen. This is used in fuel processing for hydrogen fuel cells to reduce the amount of carbon monoxide present in the hydrogen feed line. Carbon monoxide poisons the platinum catalyst used in hydrogen fuel cells [1], therefore it is important that as much of the carbon monoxide be removed before the feed stream enters the fuel cell.

The traditional Cu/ZnO/Al2O3 catalyst used for the WGS reaction cannot be used at this scale as it is pyrophoric when exposed to air and requires reduction before use, which is undesirable for long-term use in fuel cells [2]. Platinum supported on metal oxides has been identified as an alternative catalyst for the WGS reaction, showing high activity, due to the bifunctional nature of the support. However, this leads to reduced stability [1, 2].

When platinum is promoted with rhenium, the activity and stability of the catalyst increases significantly [2]. The mechanism of this promotion is not yet fully understood, however it has been shown that bimetallic clusters of platinum and rhenium form during synthesis which are a possible promotion route. It is also thought that the addition of rhenium adds an additional pathway for the WGS reaction to occur, increasing activity and stability [1, 2].

Traditionally prepared catalysts using impregnation techniques have poor control over particle and lead to inhomogeneous alloying. Organic solution synthesis methods are able to produce Pt3Re nanoparticles which are then supported on CeO2 [3]. With rhenium being inactive for the WGS reaction on its own [4], it is therefore hypothesised that a more homogeneous Pt-Re catalyst will lead to higher activity and stability.

References

[1] Y. Sato, K. Terada, S. Hasegawa, T. Miyao and S. Naito, *Applied Catalysis A: General,* vol. 296, pp. 80-89 (2005)

[2] Y. Sato, K. Terada, Y. Soma, T. Miyao and S. Naito, *Catalysis Communications,* vol. 7, pp. 91-95 (2006)

[3] D. Raciti, J. Kubal, C. Ma, M. Barclay, M. Gonzalez, M. Chi, J. Greeley, K. L. More and C. Wang, *Nano Energy,* vol. 20, pp. 202-211 (2016)

[4] K. Azzam, I. Babich, K. Seshan and L. Lefferts, *Applied Catalysis B: Environmental,* vol. 80, pp. 129-140 (2008)

0027 - Poster presentation

In-situ transmission electron microscopy techniques

In-Situ TEM investigation of dynamics and relaxation in amorphous NiTi

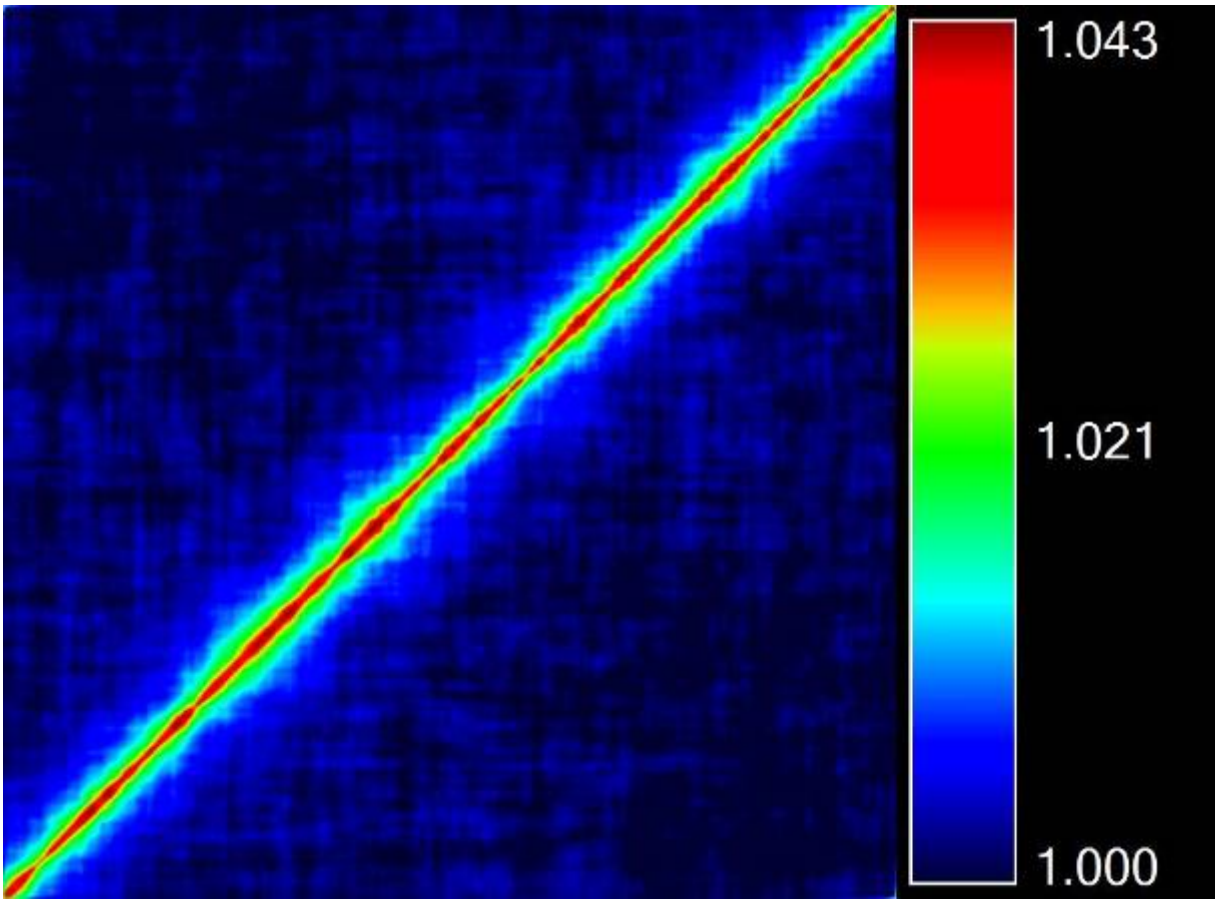
*S. Hilke[1], F. Abdollahzadeh Davani[1], G. Wilde[1], M. Peterlechner[1]
[1]University of Münster, Institute of Materials Physics, Münster, Germany

In transmission electron microscopy (TEM) the method of electron correlation microscopy (ECM) has been introduced by He et al. [1] to investigate dynamics and relaxation phenomena at the atomic scale. Recently, the great ability has been shown using tilted dark-field in TEM in the super-cooled liquid of a metallic glass by Zhang et al. [2]. In this work we extended this approach to a wide range of temperatures (room temperature to 400 °C) using repeated cold rolled (RCR) amorphized NiTi. At all temperatures we found a two-step decay process of the autocorrelation function g2(Δt) which can be fitted using a double Kohlrausch-Williams-Watt (KWW) expression. Additionally we analyzed locally for each temperature the two-time-correlation-function (TTCF) (exemplarily shown for 4000 frames in Fig. 1 at 100 °C) as mostly used in the x-ray equivalent technique of x-ray photon correlation spectroscopy (XPCS) and found aging phenomena as well as local temporal double KWW and areas which were in thermodynamic equilibrium. In 2017 Luo et al. [3] presented a decoupling of α and β relaxation in metallic glasses by following the stress decay under a constant strain. Until the glass transition they saw decoupled relaxation phenomena with two different activation energies. For the first time ECM data show a double KWW dependence in non-equilibrium dynamics. This is supported by the fact, that no glass transition was observed neither in differential scanning calorimetry (DSC) nor in the crossover of the ECM relaxation times before crystallization. This indicates that the glass transition temperature of amorphous RCR NiTi is to close or even above the crystallisation temperature.

References

[1] He, L., Zhang, P., Besser, M. F., Kramer, M. J., & Voyles, P. M.; Microscopy and Microanalysis, 21(4), 1026-1033, (2015).
[2] Zhang, P., Maldonis, J. J., Liu, Z., Schroers, J., & Voyles, P. M..; Nature communications, 9(1), 1129, (2018).
[3] Luo, P., Wen, P., Bai, H. Y., Ruta, B., & Wang, W. H.; Physical review letters, 118(22), 225901, (2017).

Figure 1



0028 - Poster presentation

In-situ transmission electron microscopy techniques

TEM in-situ investigation of relaxation and dynamics in amorphous FeNiP nanorods

*K. Spangenberg[1], S. Hilke[1], M. Peterlechner[1], G. Wilde[1]
[1]WWU Münster, Institut für Materialphysik, Münster, Germany

The method of electron correlation microscopy (ECM) using transmission electron microscopy (TEM) has been presented by He et al. [1] to investigate dynamics and relaxation phenomena at the atomic scale. Using conventional TEM tilted dark field, the method has the ability to spatially resolve the dynamical processes in the supercooled region of an amorphous alloy [2].

In the present study, the influence of dose rates, hollow-cone illumination with different precession times and non-equilibrium dynamics of amorphous FeNiP in nanostructured confinement are investigated. A minimum dose rate is estimated to ensure proper signal-to-noise ratio. First hollow-cone results show good signal-to-noise ratio but the averaging of diffracted intensity suggests a relation between precession time and results. Non-equilibrium dynamics were investigated and analysed using the time autocorrelation function $g_2(\Delta t)$ which can be fitted using a Kohlrausch-Williams-Watt (KWW) expression. ECM is used to calculate spatial distribution of relaxation times, represented by τ-maps.

The FeNiP glass exhibits a phase separation upon heat treatment [3]. EDX measurements reveal a transformation from a homogeneous composition towards a bamboo structure of Fe-rich and Ni-rich layers. By comparing the atomic fluctuation with the local phase composition, a relation between phase separation and time scales of the heterogeneous dynamics can be discussed.

References

[1] L. He, P. Zhang, M. F. Besser, M. J. Kramer & P. M. Voyles, *Microscopy and Microanalysis*, *21*(4), 1026-1033, (2015)

[2] P. Zhang, J. J. Maldonis, Z. Liu, J. Schroers, & P. M. Voyles, *Nature communications*, *9*(1), 1129, (2018)

[3] N. Winkler, M. Peterlechner & G. Wilde, *Journal of Materials Chemistry C*, 3, 7543-7551, (2015)

0029 - Invited talk

invited talk

The role of atomic resolution TEM in the development of novel high-strengths steels

*J. Mayer[1,2], M. Beigmohamadi[2], M. Lipinska-Chwalek[1,2], T. Hickel[3], T. Scheu[3], C. Liebscher[3], D. Raabe[3], J. E. Wittig[4]
[1]*RWTH University, Central Facility for Electron Microscopy, Aachen, Germany*
[2]*Forschungszentrum Jülich, Ernst Ruska Centre, Jülich, Germany*
[3]*Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany*
[4]*Vanderbilt University, Interdisciplinary Materials Science, Nashville, United States*

Recently developed high-manganese steels exhibit an exceptional combination of strength and ductility and show great promise e.g. for automotive applications. Understanding the relationships between manganese and carbon content, microstructure, temperature, defect formation and strain-hardening behavior is critical for further optimization of these steels. A combination of HRTEM, HRSTEM, atom probe and *ab initio*-modeling were used to investigate the influence of alloy content, temperature and deformation behavior on the alloy properties. Experimentally we investigated the microstructural evolution of an austenitic Fe-14Cr-16Mn-0.3C-0.3N alloy showing twinning induced plasticity (TWIP) and of a two-phase nanostructured Fe-30.5Mn-8Al-1.2C alloy exhibiting microband induced plasticity (MBIP). The twinning induced plasticity (TWIP) effect enables designing austenitic Fe-Mn-C based steels with >70% elongation at an ultimate tensile strength >1 GPa. High resolution TEM and STEM images of the planar defects will be presented and comparison to the modeling revealed insight in the atomistic structure of defects and defect/dislocation interaction. In the MBIP alloys, regularly spaced coherent precipitates of the κ-Phase were found, which cause the unique properties of these materials.

Figure 1

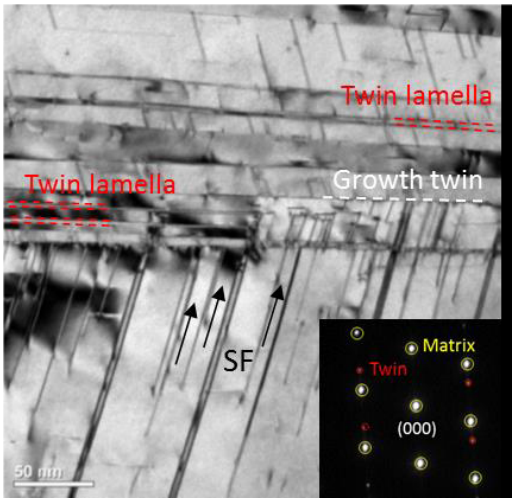
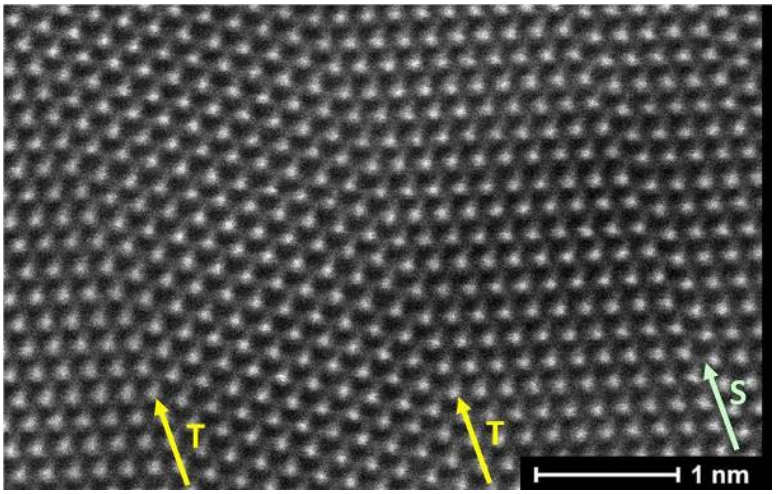


Figure 2



0030 - Oral presentation

invited talk

Biodegradable Mg implants: a multiscale problem

*R. Willumeit-Römer[1]
[1]Helmholtz Zentrum Geesthacht, Geesthacht, Germany

Mg and its alloys are a new class of load bearing metal implants because they degrade under physiological conditions. This amazing property offers significant advantages over classical, non-degrading implants which have to be removed upon the completion of the healing process. This is especially important for children but can offer also therapeutic potential for e.g. patents suffering from osteoporosis. However, it is not easy to deal with Mg-based implant materials.

One of the great challenges is to tailor the degradation in a manner that is acceptable for the biological environment. Here not only the alloy composition and microstructure is important but also the corrosion under physiological conditions. The correlated processes are highly complex in a living system and sufficient data describing the degradation *in vivo* is missing. Many chemical reactions take place in parallel and the living cellular environment can actively participate in the degradation process by altering not only the degradation rate but also the composition of the degradation layer underneath cells which is eventually remodeled into bone matrix. Therefore, we have to include the biological environment and response together with the microstructure and surface properties to tailor the degradation rate.

This presentation will outline how close the interplay is between microstructure, material degradation and biological response.

0031 - Oral presentation

invited talk

ZHM Young Professionals:
Design of a Nanometric AlTi Additive for MgB2 Based Reactive Hydride Composites with Superior Kinetic Properties

*T. T. Le[1], C. Pistidda[1], J. Puszkiel[1], M. V. Castro Riglos[1], A. Santoru[1], T. Klassen[1,2], M. Dornheim[1]
[1]Helmholtz-Zentrum Geesthacht, Nanotechnology Department, Geesthacht, Germany
[2]Helmut Schmidt University, Hamburg, Germany

Solid-state hydride compounds are a promising option for an efficient and safe hydrogen-storage systems. Lithium reactive hydride composite system 2LiBH4 + MgH2/2LiH + MgB2 (Li-RHC) has been widely investigated owing to its high theoretical hydrogen-storage capacity and low calculated reaction enthalpy (11.5 wt % H2 and 45.9 kJ/mol H2). In this work, a thorough investigation into the effect of the formation of nano-TiAl alloys on the hydrogen-storage properties of Li-RHC is presented. The additive titanium (III) chloride-aluminum chloride (3TiCl3·AlCl3) is used as the nanoparticle precursor. For the investigated temperatures and hydrogen pressures, the addition of ~5 wt % 3TiCl3·AlCl3 leads to hydrogenation/dehydrogenation times of only 30 min and a reversible hydrogen-storage capacity of 9.5 wt %. The material containing 3TiCl3·AlCl3 possesses superior hydrogen-storage properties in terms of sorption rates and a stable hydrogen capacity during several hydrogenation/dehydrogenation cycles. These enhancements are attributed to an in situ nanostructure and a hexagonal AlTi3 phase observed by high-resolution transmission electron microscopy. This phase acts in a 2-fold manner, first promoting the nucleation of MgB2 upon dehydrogenation and second suppressing the formation of Li2B12H12 upon hydrogenation/dehydrogenation cycling.

0032 - Invited talk

invited talk

Plasticity of topologically close packed phases – Characterisation of mobile defects from nanomechanics to HR-TEM

S. Schröders[1], S. Sandlöbes[1], J. Gibson[1], L. Peters[2], B. Berkels[3], *S. Korte-Kerzel[1,4]
[1]RWTH Aachen University, Institute for Physical Metallurgy and Metal Physics, Aachen, Germany
[2]RWTH Aachen University, Institut für Kristallographie, Aachen, Germany
[3]RWTH Aachen University, AICES, Aachen, Germany
[4]RWTH Aachen University, Aachen, Germany

The deformation behaviour of hard and brittle precipitates can have significant effects on the properties of metallic alloys. These may be advantageous, where an alloy is purposefully reinforced, but often the presence of hard precipitates is detrimental and can lead to stress concentrations, crack initiation and local dealloying of the matrix. In the case of topologically close packed phases in nickel-based superalloys all of these effects have been observed, but the underlying properties of these phases are largely unknown, impeding any purposeful discrimination between different precipitates or modelling of the mechanism by which they affect the surrounding material.

Here, we have employed nanomechanical testing to characterise the plastic deformation in the binary Fe7Mo6 μ-phase [1] to elucidate the phase"s anisotropy, determined by the active slip systems and respective critical resolved shear stresses, and the underlying defect structures. In particular, we confirmed by high resolution imaging of defects after plastic deformation that plasticity on the basal planes occurs in the Laves-layers of the stacked unit cell by the synchroshear mechanism.

References

[1] S. Schröders, S. Sandlöbes, C. Birke, M. Loeck, L. Peters, C. Tromas, S. Korte-Kerzel, International Journal of Plasticity 108, 125-143 (2018)

0033 - Invited talk

invited talk

Quantifying the 3D atomic structure of nanomaterials through dose-efficient scanning transmission electron microscopy

*S. Van Aert[1]
[1]EMAT - University of Antwerp, Antwerp, Belgium

Aberration-corrected scanning transmission electron microscopy (STEM) has become a powerful technique for materials characterisation of complex nanostructures. Recent progress in the development of quantitative methods enables us to extract reliable structural and chemical information in two dimensions (2D) as well as in three dimensions (3D) from experimental images. In a quantitative framework, images are treated as datasets from which structure parameters are determined by comparison with image simulations or by using parameter estimation based methods. In order to obtain precise atom counts along the viewing direction, scattering cross-sections are very useful. These cross-sections describe the total scattered intensity for each atomic column. Based on atom counts, an initial atomic model can be created that can be used as an input for energy minimisation to obtain a relaxed 3D reconstruction.

To reliably count atoms with single atom sensitivity, a minimum electron dose is necessary, while on the other hand beam damage, induced by the high energy electrons, puts a limit on the tolerable dose. An important challenge is therefore to develop experimental strategies to optimise the electron dose by balancing atom counting fidelity versus the risk of structural damage. To achieve this goal, a statistical framework combined with physics-based modeling of the dose-dependent processes is proposed and experimentally verified. This model enables the investigator to theoretically predict, in advance of an experimental measurement, the optimal electron dose resulting in an unambiguous quantification of nanostructures in their native state with the highest attainable precision.

For beam-sensitive materials, where the optimal electron dose can be very low, the resulting images will exhibit a limited signal-to-noise ratio. Especially for light-element nanostructures, where the contrast can be very weak, an automatic and objective method to reliably detect the presence or absence of an atom is of great importance. A combination of physics-based model fitting and model-order selection is proposed to quantify how more likely one atomic structure is as compared to another one. In this manner, the most probable atomic structure can be assigned.

Finally, developments to extend atom-counting from homogeneous to heterogeneous materials are presented. For heterogeneous materials, changes in atom ordering in the column have an effect on the cross-sections, significantly complicating the analysis. To circumvent the need for time-consuming image simulations to compute scattering cross-sections of mixed columns, a so-called atomic lensing model is introduced. In combination with energy dispersive X-ray spectroscopy or 4D STEM experiments, the benefits of this model to unravel thickness, composition and even the 3D ordering of atoms will be demonstrated.

0034 - Invited talk

invited talk

Probing the dynamics of nanomaterials using TEM: from *in situ* experiments to ultrafast TEM

*H. Florent[1], A. Arnaud[1], C. Giuseppe-Mario[1], W. Sebastien[1], G. Christophe[1], W. F. Bénédicte[1], H. Martin[1], S. Etienne[1]
[1]CNRS, CEMES, TOULOUSE, France

Investigating the dynamics of a physical system in the time domain inside a TEM requires (i) to be able to excite the sample, (ii) observe it with a controlled delay with respect to the excitation, and (iii) with an excitation and observation time much shorter than the characteristic duration of the physical process under scrutiny to avoid the information gained to be temporally averaged. With the variety of sample-holders available today, any kind of stimuli (electric current, magnetic field, mechanical stress, heat, etc.) can be applied to a sample directly inside the objective lens. *In-situ* TEM refers to the observation of a sample using conventional, high-resolution imaging, holography, diffraction or spectroscopy as it evolves in real-time after being perturbed inside the electron microscope. *In-situ* TEM techniques have provided invaluable information on dynamic microstructural changes [1], and I will show some examples performed in our laboratory mostly using *in situ* electron holography [2,3].

However, the timescale accessible in these experiments remains limited by the frame rate of the camera used for detection to typically a few milliseconds using CCD based devices to microseconds using modern direct electrons detectors. Time-resolved TEM experiments with temporal resolution in the nanosecond range or faster rely on strategies and tools inspired from ultrafast optical spectroscopy. They are pump-probe experiments involving an optical pulse and a delayed electron pulse. The beam from a first pulsed laser is sent to the electron source to trigger the emission of electrons. A second beam from a pulsed laser is sent inside the objective lens of the microscope and focused on the sample. The optical pump pulse brings the sample out of equilibrium and the electron probe pulse, delayed and synchronized with respect to the excitation, is used to probe the sample during its relaxation. By systematically changing the delay between pump and probe, it is possible to record the dynamical evolution of the sample as the latter goes back to equilibrium [4]. Recently in our laboratory we have developed a unique coherent time resolved FE-TEM based on this pump-probe approach [5]. I will present what are the greatest benefits of this new instrument for materials science within the general framework of *in situ* TEM.

[1]Dehm, G., Howe, J. M., & Zweck, J. (2012). Front matter. In In-situ electron microscopy (pp. I–XVIII). Wiley–VCH Verlag.

[2]L. De Knoop, F.Houdellier, C. Gatel, A. Masseboeuf, M. Monthioux, and M.J. Hÿtch. *Micron*, Elsevier, 2014, 63, pp.2--8.

[3]C. Gatel, B.Warot-Fonrose, N.Biziere, L.A. Rodríguez González, D. Reyes, R. Cours, M. Castiella and M.J. Casanove. *Nature Communications*, Nature Publishing Group, 2017, p 8.

[4]A. Arbouet, G.M. Caruso, F. Houdellier. *Advances in Electronics and Electron Physics*, 207, Elsevier, 2018, 1076-5670.

[5]F. Houdellier, G.M. Caruso, S. Weber, M. Kociak, A. Arbouet. *Ultramicroscopy*, Elsevier, 2018, 186, pp.128 - 138.

0035 - Invited talk

invited talk

Medium-range order of amorphous structures studied by nano-beam diffraction patterns and image simulations

*M. Peterlechner[1]
[1]*University of Münster, Institute of Materials Physics, Münster, Germany*

Keywords: Fluctuation Electron Microscopy (FEM), amorphous, simulation, Medium Range Order (MRO), diffraction mapping

The local structure of amorphous matter is not perfect topological disorder but may show preferred motives as icosahedral ordering or continuous random networks in the medium range order (MRO) length scale of about 0.5-3 nm. It is a question of long standing how to influence the MRO by synthesis, deformation and/or relaxation. Molecular dynamic (MD) simulations indicate differences in the MRO depending on the synthesis route, deformation processes and relaxation state. In this presentation the focus is set on methological aspects of measuring properties of MRO in an amorphous single component system (Si) and binary system (CuZr). Based on multislice simulations the sensitivity on structural changes is evaluated, and experiments were made to compare the simulations to real atomic configurations.

As a first reference system elementary Si was made amorphous by self-ion implantation [1], in a molecular dynamic (MD) simulation as well as in an experiment [2]. By scanning transmission electron microscopy (STEM) multislice simulations it can be shown, that the sensitivity of the high-angle annular dark field (HAADF) signal is able to statistically detect density changes within the amorphous phase in the order of less than a percent. The MRO was analyzed by nano-beam diffraction pattern (NBDP) series. NBDPs are most sensitive to coherently scattering domains in the order of the applied probe size. These NBDPs were analyzed by the amount of intensity variations at a constant scattering angle (thin dark field detectors), according to fluctuation electron microscopy (FEM). The amorphous Si samples show in simulations and experiments a probe size dependence with a maximum in the achieved FEM signals at probe sizes of 1.2 to 1.8 nm. By MD and image simulations of differently relaxed amorphous states, it is shown that FEM is sensitive to detect subtitle structural changes. Moreover this indicates, that electron correlation microscopy (ECM) during in-situ heating experiments is capable to measure relaxation phenomena in Si, either by a time correlation of dark-field images or NBDPs.

Moreover, a nanoscale multilayered compound of amorphous CuZr and crystalline Cu was processed by sputtering and plastic deformation was induced by cold rolling. Undeformed and deformed states were experimentally analyzed and compared to MD simulations [3]. By experimental deformation induced shear offsets, visible in the crystalline Cu layers, the position of shear bands in the amorphous CuZr layers can be identified in cross sectional samples. It must be emphasized, that neither in HAADF nor in bright-/dark-field images contrast differences between shear band and matrix could be detected. However, the FEM data show subtle structural changes in the MRO of the deformed amorphous phase, namely the sheared zones as well as the surrounding matrix. Since the experimental and the simulated HAADF shows no contrast variation between shear band and matrix, it is concluded that the density and chemistry does not change in a shear band with respect to the surrounding amorphous matrix. The experimental FEM characteristics must therefore stem from topological rearrangements of atoms in the MRO. The comparison with MD simulations and corresponding multislice image simulations indicates, that during and directly after the plastic deformation local relaxation/diffusion phenomena are active. It is to expect, that in multicomponent systems the diffusion/relaxation phenomena are slowed down, leading to more pronounced local structural changes stable (or metastable) after deformation (as e.g. periodic density variations already shown in deformed AlYFe glasses [4]).

[1] Collaboration with the groups of Prof. Larens, Prof. Bougeard, Posselt and Liedke, Prof. Bracht.

[2] Radek, M., Tenberge, J.-G., Hilke, S., Wilde, G. and Peterlechner, M. Ultramicroscopy 188, (2018).

[3] MD structure based on the thesis of Tobias Brink, group of Prof. Albe (TU Darmstadt).

[4] Rösner, H., Peterlechner, M., Kübel, C., Schmidt, V. and Wilde, G. Ultramicroscopy 142, 1–9 (2014).

Financial support by the DFG under grant number PE 2290/2-1 is gratefully acknowledged.

0036 - Invited talk

invited talk

Progress of STEM Imaging in a Scanning Electron Microscope

C. Sun[1], Y. Li[1], M. Hugenschmidt[1], M. Čalkovský[1], E. Müller[1], *D. Gerthsen[1]
[1]Karlsruher Institut für Technologie (KIT), Laboratorium für Elektronenmikroskopie, Karlsruhe, Germany

Transmission electron microscopy (TEM) with low-energy electrons has emerged as an important addition to electron microscopy to avoid knock-on damage and increase the contrast of weakly scattering objects. An alternative approach towards low-energy TEM is scanning transmission electron microscopy (STEM) in a scanning electron microscope with electron energies of 30 keV and below. Recently, the installation of an on-axis CCD camera in a scanning electron microscope became possible which is essential for structure analyses by transmission electron diffraction (TED). STEM, SEM and TED can be performed in a correlative manner, which gives comprehensive and simultaneous information on surface topography, bulk properties and qualitative information on the composition from material contrast of the same specimen region. Comparison of experimental and simulated STEM intensities are essential to support the interpretation low-energy STEM images and allow to extract quantitative data, e.g., on the local specimen thickness.

We use a Thermo Fisher Helios G4FX FIB/SEM instrument for this work, which is equipped with a multi-segmented STEM detector, double-tilt holder for electron transparent specimens and a CCD-camera for the acquisition of on-axis TED patterns. Bright-field STEM resolution is 0.34 nm. Simulations of the STEM intensity are performed with the in-house developed program CeTE1.4, which numerically solves the electron transport equation [1].

Results of low-energy STEM and correlative STEM/SEM/TED imaging from different material classes will be presented. Absorber layers of organic solar cells were investigated which consist of domains of donor and acceptor materials with similar scattering properties resulting in poor contrast at high electron energies. Strong contrast is also obtained for membranes and organelles in thin sections of plastic-embedded biological cells, which are only fixed with OsO4 without any additional staining. Catalytically active materials consisting of nanostructured ceramics with deposited nanoparticles particularly profit from correlative SEM/STEM imaging because the complex topography of these materials must be taken into account for the interpretation of STEM images. We will also show that prepared TEM specimens from bulk materials can be well analyzed at low electron energies. For example, bright-field STEM was utilized to determine the Burger vector b of dislocations in epitaxial GaN layers using two-beam imaging conditions with imaging vector g and applying the $g \circ b = 0$ extinction criterion.

STEM in SEM approaches the capabilities of STEM at high electron energies. A particular benefit is correlative STEM/SEM imaging of bulk and surface properties. The resolution has significantly improved in the past few years and is sufficient to answer numerous questions in materials and life sciences.

References

[1] S. Goudsmit and J.L. Saunderson, Phys. Rev 57, 24–29 (1940).

0037 - Poster presentation

Imaging with advanced methods of conventional and aberration-corrected electron microscopy: high-resolution transmission and scanning transmission electron microscopy (HRTEM and HRSTEM)

On a novel strain indicator based on uncorrelated misorientation angles for correlating dislocation density to local strength

*P. O. Guglielmi[1], M. Ziehmer[2], E. T. Lilleodden[1,2]
[1]Helmholtz Center Geesthacht, Institute of Materials Research, Materials Mechanics, Geesthacht, Germany
[2]Hamburg University of Technology, Institute of Advanced Ceramics, Hamburg, Germany

A new and non-destructive method based on Electron Backscattered Diffraction (EBSD) is proposed and used to characterize dislocation densities of site-specific areas selected on bulk samples prior to small-scale mechanical testing. Gold samples submitted to different degrees of pre-straining are analyzed. The method is based on the determination of a new scalar misorientation parameter called the Characteristic Misorientation Angle (CMA), which is derived from uncorrelated misorientation data obtained by Electron Backscattered Diffraction (EBSD). We show that CMA is virtually independent of the scan step size and is more sensitive to plastic deformation than the more conventional parameters Grain Average Misorientation (GAM) and Grain Orientation Spread (GOS). A coupled effect of local plastic strain and area size is observed on the measured values of CMA, based on which values of local GND density are determined. The strength of the characterized areas is subsequently measured by spherical nanoindentation and is defined as the hardness at the first pop-in observed on the load-displacement curves. Results show that the site-specific strength of gold decreases with increasing initial dislocation density. While previous studies have suggested the same trend, the present work offers a new approach to more quantitatively correlate local dislocation densities to the onset of plasticity, without the need for destructive TEM investigations or micro-sample fabrication.

0038 - Invited talk

invited talk

Quantitative magnetic imaging of skyrmions using off-axis electron holography

*A. Kovacs[1], F. Zheng[1], N. Kiselev[2], J. Caron[1], T. Denneulin[1], V. Migunov[1], S. Bluegel[2], R. Dunin-Borkowski[1]
[1]*Forschungszentrum Jülich, Ernst Ruska-Centre, Jülich, Germany*
[2]*Forschungszentrum Juelich, Institute for Advanced Simulation, Juelich, Germany*

Magnetic skyrmions are vortex-like spin textures that promise to provide significant advantages in racetrack-type memory applications, as the electric current densities that are required for their controlled motion are orders of magnitude smaller than those required for the motion of magnetic domain walls. Magnetic imaging in the transmission electron microscope (TEM) allows skyrmions to be imaged with high spatial resolution as a function of applied magnetic field, electrical bias and temperature. We are presently using off-axis electron holography to study the magnetic field distributions and stabilities of Bloch-type and Néel-type skyrmions in B20-type FeGe and thin film heterostructures. Focused Ga ion beam specimen preparation in a scanning electron microscope is used to control the three-dimensional morphologies of TEM specimens, in order to study the effect of geometrical confinement on skyrmion formation and motion. Experiments are performed in magnetic field free conditions (Lorentz mode) in an aberration-corrected TEM operated at 300 kV. An external magnetic field can be applied to samples using the conventional microscope objective lens. Liquid nitrogen cooled specimen holders are used to vary the sample temperature between 95 and 320 K. Fresnel defocus images and off-axis electron holograms are recorded using a direct electron detection camera.

In FeGe, *in situ* magnetization studies reveal that geometrically-confined Bloch-type skyrmions are able to adopt a wide range of sizes in a nanostripe [1] and to form flux-closed spin textures (target skyrmions) in nanodisks in the absence of externally applied magnetic fields [2]. Measurements of in-plane magnetization are used to reveal geometrical distortions in lattices of Bloch-type skyrmions and fine magnetic structures in interstitial regions between adjacent skyrmions [3]. They are also used to measure the saturation magnetizations of skyrmions and helical states [4]. Furthermore, the formation of chiral bobbers in thin films is studied using phase shift measurements and theoretical calculations [5].

In sputtered heavy metal/ferromagnetic multilayers, the sizes of Néel-type skyrmions, which are stable at room temperature, can be tuned by engineering the materials and deposition parameters. Unfortunately, magnetic imaging of Néel-type skyrmions in the TEM is challenging, as they result in zero phase shift when the incident electrons are parallel to their cores. Preliminary off-axis electron holography results obtained from studies of Néel-type skyrmions as a function of sample tilt angle and applied magnetic field will be presented.

1. C. Jin et al., Nature Communication 5, 15569 (2017)
2. F. Zheng et al., Physical Review Letters 119, 197205 (2017)
3. A. Kovács et al., Applied Physics Letters 111, 192410 (2017)
4. D. Song et al., Physical Review Letters 120, 167204 (2018)
5. F. Zheng et al., Nature Nanotechnology 13, 451 (2018)

0039 - Oral presentation

invited talk

Aerosol Spraying of Bismuth Vanadate for Hydrogen Technology

*C. Wolpert[1], F. Gärtner[1], M. Villa Vidaller[1], T. Klassen[1]
[1]Helmut-Schmidt-University, Department of Mechanical Engineering, Hamburg, Germany

Dense, nano-structured bismuth vanadate thin films were successfully deposited by Aerosol Deposition Method (AD) at room temperature. AD offers a low-cost alternative route for fabrication of photoactive thin film metal oxide coatings as no binders or sintering processes have to be applied A micron-sized bismuth vanadate powder was used to fabricate thin photoactive layers with thicknesses below 1 µm on FTO and titanium substrates. The thin films were photocatalytically active under solar light due to their nano-sized structure and thus resulting enlarged surface area and the exceptional band gap of bismuth vanadate which makes them ideal candidates for photoelectrochemical hydrogen production through water splitting. Obtained coatings were analysed in order to estimate adhesion properties, film thickness and morphology.

0040 - Invited talk

invited talk

Mechanical and Chemical Dynamics of Oxide Interfaces

*Y. Ikuhara[1,2,3]
[1]*The University of Tokyo, Institute of Engineering Innovation, Tokyo, Japan*
[2]*Japan Fine Ceramics Center, Nanostructures Res. Lab., Nagoya, Japan*
[3]*Tohoku University, WPI-AIMR Research Center, Sendai, Japan*

So far, many experimental investigations have been tried to understand the dislocation-grain boundary interaction in materials, but these experiments were mostly carried out statically, and the dynamic behavior is still not well understood yet. It has been known that several oxide crystals can be plastically deformed even at R.T. by dislocation slip like metals. In this study, the in-situ nanoindentation experiments were conducted for $SrTiO_3$ single crystal and its bicrystals inside TEM. For bicrystal experiments, various types of GBs including CSL (Coincidence Site Lattice) GBs and low angle tilt and twist GBs were prepared. It was found that whether dislocations can penetrate across GBs depends on the grain boundary characters (GB orientation and plane). Various interface phenomena such as dislocation pile-up at GBs, jog formation, jog-drag motion were dynamically observed. The dislocation-GB interaction and its dependence on the GB characters will be discussed in detail.

The properties of lithium ion battery cathodes strongly depend on the diffusion of lithium ions during charge/discharge process. Then, direct visualization of lithium site is required to understand the mechanism of the diffusion of lithium ions. In this study, aberration corrected STEM were applied to directly observe the {010} surface, which corresponded to perpendicular to the 1-D diffusion orientation, of the olivine Li_xFePO_4. The morphology of the interface between Li-rich and Li-poor phases of Li_xFePO_4 after chemical delithiation were observed with atomic resolution at fit intervals during half a year. It was found that orientation of boundary layers at the $FePO_4/Li_{2/3}FePO_4$ interface gradually changed from lower index planes to higher index planes. This indicates that intermediate phase plays an important role in healing crystal cracking by allowing the interface to remain coherent so that Li ions can diffuse back into regions depleted during delithiation. The mechanism of the lithiation/delithiation from and to the surface will be discussed based on the observation results.

References

(1) Kondo, T.Mitsuma, N. Shibata, Y. Ikuhara, *Sci.Adv.*, **2**: e1501926 (2016)

(2) Kobayashi, C.A.J.Fisher, T.Kato,Y.Ukyo,T.Hirayama and Y.Ikuhara, *Nano Lett.* **16**, 5409 (2016).

(3) S.Kobayashi, A. Kuwabara, C. A.J. Fisher, Y. Ukyo and Y. Ikuhara,*Nat. Commun*., 9, 2863 (2018)

0041 - Oral presentation

invited talk

Characterization of Water-splitting Photoelectrodes by Scanning Probe Microscopy

*R. Raudsepp[1,2], H. Kriegel[2], M. Schieda[2], M. Villa-Vidaller[1], T. Klassen[1,2]
[1]*Helmut Schmidt University, Hamburg, Germany*
[2]*Helmholtz-Zentrum Geesthacht, Geesthacht, Germany*

Semiconductor electrodes have an important application in the generation of hydrogen via photodriven water splitting. The photoelectrochemical performance of these materials is significantly affected by the microsctructure at the interface to the electrolyte, including the distribution of grains, grain boundaries and surface defects. Scanning Probe Microscopy (SPM) allows us to simultaneously obtain morphological, mechanical, electrical and electrochemical properties in the nanoscopic scale.

In this presentation, we show some examples of our current work on atomic-layer deposited metal oxide semiconductors, to illustrate the rich information provided by state of the art SPM, from high-resolution topography, to photoconductive AFM (pc-AFM) and Kelvin Probe Force Microscopy (KPFM) for photocurrent and surface photovoltage measurements respectively.

Furthermore, recent technological developments allow the measurement in situ of local electrochemical activity, enabling scanning photoelectrochemical microscopy with nanometer resolution (nanoSECM).

0042 - Invited talk

invited talk

In-situ TEM Study on Strengthening Mechanisms and Dislocation Plasticity of FeCoCrMnNi HEA

*S. Lee[1], M. Feuerbacher[2], C. Kirchlechner[1], C. Liebscher[1], S. H. Oh[3], G. Dehm[1]
[1]Max-Planck-Institut für Eisenforschung, Structure and Nano-/ Micromechanics of Materials, Düsseldorf, Germany
[2]Forschungszentrum Jülich, Jülich, Germany
[3]Sungkyunkwan University , Suwon, South Korea

In-situ TEM deformation testing is a unique and powerful experimental approach to quantify the mechanical properties of nanomaterials and their deformation behavior especially dislocation plasticity. Dislocation-based deformation mechanisms of high entropy alloys (HEAs) remain elusive and require a fundamental understanding in order to tailor their mechanical properties. Since HEAs have five or more constituent elements with a near-equiatomic ratio, their plastic deformation is expected to be different compared to conventional alloys.

In this talk, we present a study correlating the microstructure and dislocation plasticity of FeCrCoMnNi FCC single crystal HEA by in-situ transmission electron microscope (TEM) compression and tensile deformation. Moreover, an atomic-scale chemical analysis is conducted by aberration-corrected scanning TEM energy dispersive X-ray spectroscopy (STEM-EDS) and atom probe tomography (APT) to investigate chemical inhomogeneity, for example, precipitates or segregations. The aims of the study are 1) understanding of dislocation plasticity in HEA, 2) investigation of nanometer-scale elemental distribution and 3) measurement of mechanical properties of HEA submicron pillars.

1% yield stress of micro-and submicron-HEA pillars shows mechanical size effects with a size exponent of 0.55 which is smaller compared to other FCC metals suggesting the strong material"s inherent hardening processes. However, spectroscopic analysis with STEM-EDS and APT shows uniform elemental distribution without ordered structures or precipitates. Dislocation dynamics investigated by in-situ TEM straining tets shows the planar slip is the dominating deformation mechanism while cross-slip is rarely observed. The threshold shear stress for dislocation glide measured from the curvature of dislocations is around 500 MPa which is higher compared to that of other FCC metals suggesting the high lattice friction stress. Stacking fault width of gliding partial dislocations shows a periodic fluctuation; periodical increase in every four dislocations. It suggests the existence of short-range ordering with a spacing of four Burgers vector or 1 nm which might contribute to the high lattice friction stress.

0043 - Invited talk

invited talk

Investigating complex heterostructures using aberration-corrected STEM

*D. J. Smith[1], A. Gangopadhyay[2], S. Lu[2], B. D. Tracy[1], H. W. Wu[2], M. R. McCartney[1]
[1]Arizona State University, Department of Physics, Tempe, United States
[2]Arizona State University, School of Engineering for Matter, Transport and Energy, Tempe, United States

Complex heterostructures based on combinations of oxide/oxide, oxide/semiconductor and semiconductor/semiconductor potentially provide the bases for a wide variety of novel electronic and optoelectronic devices. This talk will present an overview some of our recent studies of complex heterostructures primarily using aberration-corrected scanning transmission electron microscopy (AC-STEM). The systems studied include various perovskite oxides grown either on strontium titanate (STO) or on Si(001) and Ge(001) substrates with thin oxide buffer layers, and several pairs of Group II-VI/Group III-V compound semiconductors with zincblende structure. For the oxides grown on STO, changes in the titanium oxidation state close to the interface result in the creation of a two-dimensional electron gas. For the oxide/semiconductor combinations, minimization of mismatch strain can be used as a strategy to control crystallographic orientation and hence the polarization direction. For semiconductor materials, lattice mismatch as well as valence mismatch play major roles in controlling the types of interfacial defects observed. Recent observations of isovalent (valence-matched) II-VI/II-VI and III-V/III-V structures such as GaAsSb/GaAs, ZnTe/CdTe and InSb/GaSb, and heterovalent (valence-mismatched) II-VI/III-V structures such as ZnSe/GaAs and CdTe/ InSb will be described.

Acknowledgments: We gratefully acknowledge ongoing collaborations with the groups of Alex Demkov and John Ekerdt (University of Texas-Austin), Nikolai Faleev and Christiana Honsberg (Arizona State University) and Yong-Hang Zhang (Arizona State University).

0044 - Invited talk

invited talk

Microstructure Evolution in Nanoscale Metal Networks – Highlighting the Link to Mechanical Behavior

*J. Weissmüller[1,2]
[1]*Hamburg University of Technology, Institute of Materials Physics and Technology, Hamburg, Germany*
[2]*Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Materials Mechanics, Geesthacht, Germany*

Size- and interface effects on the behavior of nanoscale objects are of interest both from a fundamental science point of view and with an eye on exploiting new handles for materials design towards functionality or mechanical behavior for possible technological application. While isolated nanoscale objects are readily synthesized, it remains challenging to assemble them into nano *materials*, that is, aggregates of nano objects that can be upscaled to macroscopic dimensions and that support shaping into engineering parts. 3D lithographic techniques are under consideration, yet the number of microstructural elements that can be assembled (in the order of 1000) fall well short of the 10^{15} objects per mm^3 that are required for a nanomaterial with 10 nm structure size. This emphasizes the power of dealloying, a controlled corrosion process that provides uniform network of struts or "ligaments" with a well-defined size in the low nanoscale regime in the form of monolithic, mm- or cm sized bodies. Making nanomaterials by dealloying thus underlines once more the versatility of a key strategy of materials science, namely exploiting the thermodynamics and kinetics of metallurgical microstructure evolution for shaping materials properties in essentially scalable processes. It is believed that the elementary processes of dealloying are identified – dissolution of the less noble element, vacancy island nucleation, and curvature-driven growth by surface diffusion. Yet, even with this simple set of processes, highly complex microstructures are found to evolve in a way that remains to be explored in full detail. The content in and distribution of residual less noble element are among these issues, as are the various stages in which the corrosion proceeds either in isolation or along with a coarsening of the network structure. Not all microstructural characteristics of the network have been explored in depth, as is exemplified by the ongoing search for suitable measures of the connectivity – and for the way in which the affect the material"s behavior – in the context of the strength and stiffness of nanoporous gold. The talk will address selected aspects of the state-of-the-art in microstructure evolution during dealloying and during ageing of dealloying-derived microstructures, with an eye on their impact for the effective mechanical materials behavior.

Related publications by the author

T. Krekeler, A.V. Straßer, M. Graf, K. Wang, C. Hartig, M. Ritter, J. Weissmüller, *Silver-Rich Clusters in Nanoporous Gold*, Mater. Res. Lett. 5 (2017) 314.

H.-J. Jin, J. Weissmüller, D. Farkas, *Mechanical Response of Nanoporous Metals: A Story of Size, Surface Stress, and Severed Struts*, MRS Bulletin 43 (2018) 35.

C. Soyarslan, S. Bargmann, M. Pradas, J. Weissmüller, *3d Stochastic Bicontinuous Microstructures: Generation, Topology and Elasticity*, Acta Materialia 149 (2018) 326-340.

L. Lührs, B. Zandersons, N. Huber, J. Weissmüller, *Plastic Poisson"s Ratio of Nanoporous Metals: A Macroscopic Signature of Tension–Compression Asymmetry at the Nanoscale;* Nano Letters 17 (2017) 6258.

0045 - Invited talk

invited talk

Understanding electron magnetic circular dichroism in a transition potential approach

*J. Barthel[1]
[1]Forschungszentrum Jülich GmbH, Ernst Ruska-Centrum (ER-C 2), Jülich, Germany

Electron magnetic circular dichroism (EMCD) is an effect seen in electron energy-loss spectroscopy (EELS) and one of the few techniques for studying the properties of magnetic materials in the electron microscope. By comparing spectra at a given energy loss, but for a detector placed sequentially at two different symmetry related positions in the diffraction plane, element specific information on the magnetic properties of the specimen can be accessed. Mapping spin states of a magnetic material with high spatial resolution is a key motivation for performing EMCD in an electron microscope and the matter of current research [1,2].

The EMCD effect is usually understood by drawing analogies with XMCD, as discussed in the seminal paper by Hébert and Schattschneider [3], with the first experimental confirmation following three years later [4]. An appeal is usually made to a picture involving "virtual photons" with specific circular polarization, resulting in spectral differences which are a maximum when a virtual photon with left circular polarization and one with right circular polarization are absorbed. By adopting an approach based on transition potentials for inelastic scattering of electrons, an alternative perspective is provided on the underlying physics of the EMCD effect [5]. Consideration of the localization of the transition potentials confirms that atomic scale EMCD is possible. The unequal occupation of spin-up and spin-down valence states, spin-orbit coupling, and the domination of dipole transitions are identified as the essential ingredients leading to strong EMCD signal observed for example at the $L_{2,3}$ edge of transition metals.

The cases of two-beam and three-beam systematic rows of reflections in the diffraction plane, usually employed in EMCD experiments with conventional transmission electron microscopy (CTEM), are discussed within the transition potential framework. Fundamental symmetries seen in the formalism in the CTEM three-beam case are shown to be consistent with experimental data taken on $NiFe_2O_4$. The acquisition of atomic-scale EMCD in STEM is discussed for two different setups based on simulations: (i) using a standard STEM probe for two symmetry-related off-axis detector positions to obtain a difference signal is compared to (ii) the use of two images recorded with vortex probes with opposite chirality for a detector symmetrically placed about the optical axis. Strong implications of the elastic scattering after the inelastic transitions are expected.

[1] J. Rusz *et al., Nature Communications* **7** (2016) 12672.

[2] Z. Wang *et al., Nature Materials* **17** (2018) 221.

[3] C. Hébert, P. Schattschneider, *Ultramicroscopy* **96** (2003) 463.

[4] P. Schattschneider *et al., Nature* **441** (2006) 486.

[5] J. Barthel et al., *Phys. Rev. B* **97** (2018) 144103.

0046 - Invited talk

invited talk

Quantitative STEM

*A. Rosenauer[1], K. Müller-Caspary[1], F. F. Krause[1], T. Grieb[1], J. Müßener[1], M. Eickhoff[1], M. Duchamp[2], V. Migunov[2], F. Winkler[2], R. E. Dunin-Borkowski[2], S. Van Aert[3], J. Verbeeck[3]
[1]Universität Bremen, Institut für Festkörperphysik, Bremen, Germany
[2]Jülich Research Centre, Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Jülich, Germany
[3]University of Antwerp, Electron Microscopy for Materials Science (EMAT), Antwerp, Belgium

This talk I shall start with an introduction to 4D STEM [1] using a pixelated detector, based on measurement of the center of mass in the diffraction pattern, which yields the expectation value of the lateral momentum transferred to the incident electron beam [2]. The lateral momentum represents the central measured quantity, from which the projected electric field and the projected charge density can be derived for sufficiently thin specimens. The suitable specimen thickness below approximately 5 nm is given by the condition that the intensity distribution of the electron probe should not change considerably as it propagates through the specimen. The measured momentum transfer is proportional to the gradient of the object phase within the limits of the phase object approximation. A simulation of Ronchigrams for 2.2 nm thick GaN will be used to compare the object phase from integration of the evaluated momentum transfer with results of ptychographic reconstruction [3,4].

The requirement of a small specimen thickness predestines this method for investigation of 2D materials such as MoS_2. Results of experiments in cooperation with the ERC Jülich using the ultrafast pnCCD camera with a frame time of 250 µs will be shown. The acquired 4D STEM dataset allowed to evaluate the projected charge density. These results were used to determine the stacking of two monolayers that form a bilayer in a part of the investigated area. As a second application I shall discuss measurement of polarization induced fields in a nanowire that contains a 40 x GaN/AlN heterostructure. Using these nanowires, modification of optical transitions by an externally applied bias was demonstrated [5]. The transitions are influenced by the quantum confined Stark effect (QCSE), caused by polarization induced electric fields with an amplitude of 3-6 MV/cm. The 4D STEM measurement was performed in collaboration with the EMAT center of the University of Antwerp. It will be demonstrated that measurement of the momentum transfers and averaging them over translationally invariant areas allows to evaluate the difference of the polarization induced electric fields in GaN and AlN. The influence of the mean inner potential varying along the heterostructure will be discussed. Finally, I shall briefly compare measurement of momentum transfer using pixelated and multi-segment detectors in a simulation study. Different methods to improve the accuracy of a multiple-segment detector measurement [6,7] will be discussed.

[1] Knut Müller et al., Nature comm. 5 (2014) 5653

[2] Knut Müller-Caspary et al., Ultramicroscopy 161 (2016) 146-160

[3] Hao Yang et al., Ultramicroscopy 180 (2017) 173–179

[4] Timothy J. Pennycook et al., Ultramicroscopy 151 (2015), 160-167

[5] J. Müßner et al. ACS nano 11 (2017) 8758-8767

[6] Takehito Seki et al., Ultramicroscopy 182 (2017) 258–263

[7] N. Shibata et al., Nature communications 8 (2017) 15631

0047 - Invited talk

invited talk

Atomic Electron Tomography Using Phase Contrast HRTEM – Measuring the Position and Species of Every Atom in Weakly-Scattering Samples

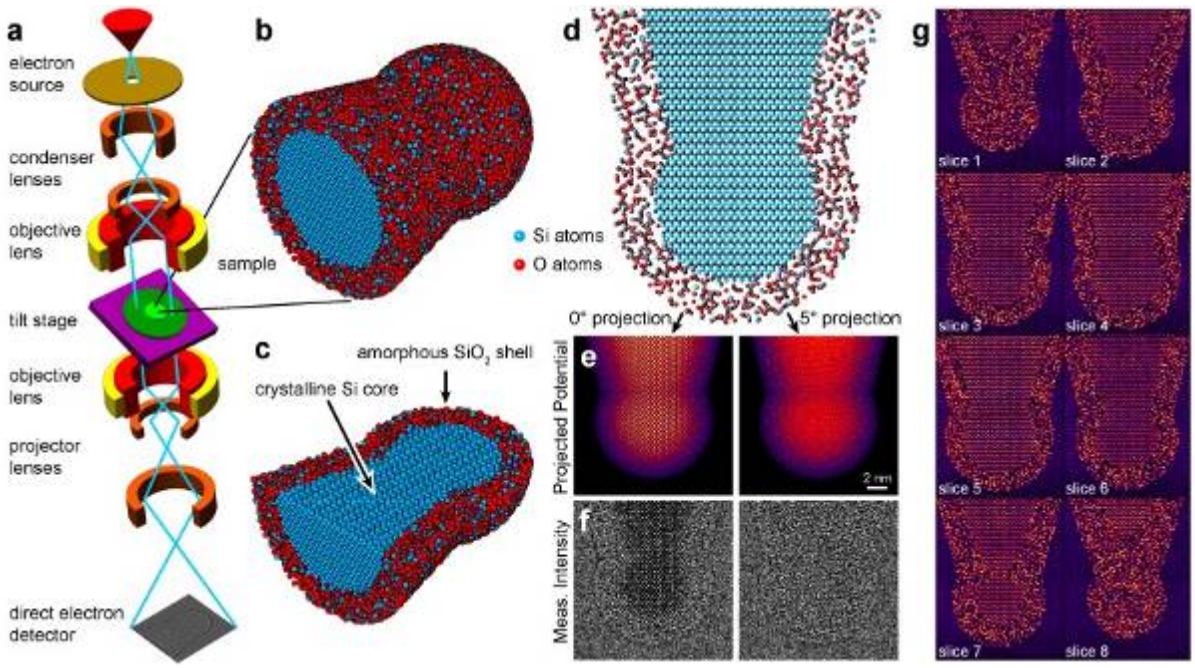
*C. Ophus[1]
[1]Lawrence Berkeley National Laboratory, NCEM, Molecular Foundry, Berkeley, United States

The past decade of development for transmission electron microscopy (TEM) and scanning TEM (STEM) have been enormously successful. In structural biology, cryo-TEM methods can solve the structure of proteins with sub-nanometer resolution. In materials science, hardware aberration correction has enabled routine atomic resolution imaging in two dimensions, as well as allowing 3D tomography that can identify the 3D position and species of every atom in a nanoscale sample. This technique, called atomic electron tomography (AET), has been applied using high angle annular dark field (HAADF)-STEM, which is a high dose imaging method that not sensitive to weakly scattering elements such as a carbon or oxygen. By contrast, cryo-TEM is used to reconstruct the 3D structure of biological structures which are composed of only weakly-scattering elements. This is accomplished by averaging hundreds or thousands of images of identical or near-identical samples, which is only possible because of biological replication of proteins. Thus, there is a need to solve the structure of unique, heterogeneous samples composed of weakly-scattering or beam-sensitive samples.

In this talk, I will present a practical method for reconstructing the electrostatic potential from a tomographic tilt series of HRTEM phase contrast measurements. Our method fully accounts for the non-linear scattering of the electron beam, including multiple scattering and strong phase shifts. We have tested the method using multislice simulations of a sample consisting of a crystalline silicon core, surrounded by an amorphous silicon dioxide shell. These simulations show that our method is robust to a restricted tilt angle range, uses much lower electron doses than existing AET studies, and can be used for a wide range of experimental parameters. The experimental geometry, a simulated test sample, projected images and reconstruction are shown in Figure 1, adapted from arXiv:1807.03886. I will also show our current progress in reconstructing experimental phase contrast HRTEM tilt series datasets at atomic resolution.

Figure 1 – HRTEM atomic electron tomography. (a) Experimental geometry, (b) sample, (c) sample cross section, (d) slice with (e) corresponding projected potential and (f) intensity measurement with 40 e/Å2. (g) Reconstruction from 60 tilts, 3 defocus values, 50 000 total e/Å2.

Figure 1



0048 - Invited talk

invited talk

Development of Time-Resolved Electron Holography for Measuring Periodically Changing Electric Potentials and Magnetic Fields

*M. Lehmann[1], T. Wagner[1], T. Niermann[1]
[1]Technische Universität Berlin, Institut für Optik und Atomare Physik, Berlin, Germany

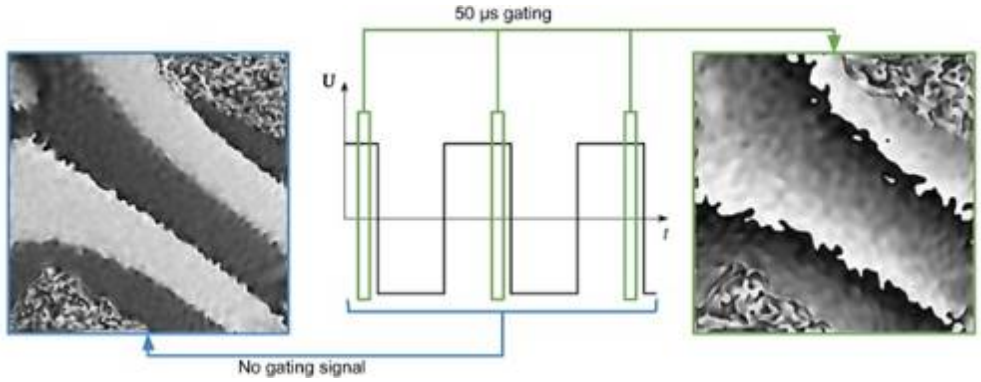
Electric potentials and magnetic fields of the object under investigation cause phase modulations of the electron wave, which can be measured by off-axis electron holography. Typical holography applications are e.g. the measurement of p-n junctions in semiconductors or imaging magnetic domains in nanoparticles and their stray fields. The recording time of such a hologram, however, ranges from a few seconds up to several minutes, when a series of holograms is taken for improved signal-to-noise ratio. Consequently, conventional electron holography is limited to highly constant electric potentials and magnetic fields during acquisition time.

Electron holography is extremely sensitive to any instrumental instabilities since a constant phase difference between object wave and reference wave is mandatory for recording stable interference fringes. Deliberately introduced instabilities, while leaving the instrument undisturbed for a short time, enable an interference gating as a stroboscopic technique of periodic signals. This allows, in principle, the measurement of periodically varying electric potentials and magnetic fields with the time resolution of the gate length.

As a demonstrator, the electric potential between the plates of a periodically switched capacitor is measured by interference gating. In first experiments [Niermann et al., Ultramicroscopy 182 (2017) 54], the instrumental instabilities has been introduced by modulating the biprism, which is used for forming the electron hologram. Due to limitations of the frequency generator (a conventional PC sound card) and artefacts in the hologram, the scanning coils of the TEM (see experimental results in figure 1) and lately a biprism in the condenser aperture is used for introducing the instabilities between object wave and reference wave. Using an advanced frequency generator, time-resolved electron holography with a time-resolution of a couple of 10 ns is within reach, most probably limited by the inappropriate high-frequency electric wiring to and within the biasing specimen TEM holder.

Figure 1: Middle: square wave signal of 1 kHz as applied to the plate capacitor. Left: phase image of a plate capacitor while its voltage was switched during hologram acquisition as known from double-exposure holography. Right: phase image of the same plate capacitor while applying the 50 µs gating. It clearly shows the gradient of potential between both capacitor plates as expected from a plate capacitor.

Figure 1



0049 - Invited talk

invited talk

Direct observations of the role of interfacial steps in microstructural evolution

*U. Dahmen[1], T. Radetic[2]
[1]*Lawrence Berkeley National Laboratory, National Center for Electron Microscopy/Molecular Foundry, Berkeley, Ca, United States*
[2]*University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia*

In this work, we study the structure and dynamic behavior of steps in Σ3 {112} grain boundaries by in-situ observation during island grain shrinkage in thin films of Au with the mazed bicrystal microstructure. Aberration-corrected TEM and STEM imaging along the <111> zone axis is used to characterize the atomic structure at steps and facet junctions. Complementing this mode of observation with lattice imaging using the forbidden 1/3{422} reflections allows us to observe the dynamic behavior of steps over larger areas of interest, including entire island grains that are bounded by three sets of {112} facets in the same <111> zone. The mechanism of interface motion and the rate of shrinkage of these island grains under the influence of capillary forces have been characterized in detail using in-situ observation at elevated temperature.

Nucleation events are observed to be stochastic in nature, and steps tend to fluctuate by moving back and forth rapidly over a distance of nanometers before suddenly propagating along an entire facet and being eliminated. Once all pre-existing steps have disappeared in this manner, a hexagonal island grain can remain stable for extended periods until the entire grain collapses precipitously within a single video frame.

In this presentation, we show that the formation of a step in a {112} interface facet is equivalent to the formation of an M facet, which was found to be a stable low-energy facet in Ag and Cu [1,2]. The M facet is inclined about 8° to the {112} facet, and its low energy has been show to be due to its dissociation, with a thin intermediate layer having the 9R structure. In Ag and Cu, this structure is stabilized by the low stacking fault energy. When viewed along the <111> direction, all {112} facets that enclose an island grain are seen edge-on, whereas the M facet would be inclined to the beam, corresponding to a series of buried steps similar to those observed previously during step coalescence in a different Au grain boundary [3].

While our previous observations have highlighted the importance of surfaces and other defects in the nucleation and motion of steps and kinks [3,4], the current work underscores the role of interface dissociation or phase transformation in the migration of flat or faceted interfaces in this material.

[1] T. Muschik, W. Laub, U. Wolf, M.W. Finnis, Acta Met Mat 41, 2163 (1993).

[2] F. Ernst, M.W. Finnis, *et al.*, PRL 69, 620 (1992).

[3] M.L. Bowers *et al.* PRL 11, 106102 (2016)

[4] T. Radetic *et al.*, Acta Mat 60, 7051 (2012).

0050 - Invited talk

invited talk

Investigation of novel Co-base superalloys using TEM techniques

*F. Pyczak[1]
[1]Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

By addition of Al and W to Co it is possible to form a $L1_2$ type precipitate phase in Co-base superalloys similar to the γ'-phase which acts very efficiently in hardening Ni-base superalloys. Nevertheless, many properties in this new type of Co-base superalloys are still unknown. Information about element partitioning between matrix and precipitates, site occupancy of alloying elements in the $L1_2$ phase and mechanisms of plastic deformation are examples for such unknown properties which are all accessible using transmission electron microscopy methods.

The talk shows examples about the characterisation of deformation structures using diffraction contrast, the determination of the composition of different phases and element partitioning between them using EDX as well as investigations of the site occupancy of different alloying elements in the $L1_2$ structure of precipitates using ALCHEMI. While these novel Co-base superalloys on first sight appear very similar to Ni-base superalloys, many important properties differ, which have to be understood fully for a knowledge based development of these new alloys.

0051 - Invited talk

invited talk

Nanomaterials for High Temperature Photonics

P. Dyachenko[1], S. Lang[1], G. Shang[1], Q. Y. Nguyen[2], M. Chirumamilla[1], K. Knopp[1], G. Vaidhyanathan[3], S. Molesky[4], H. Renner[1], A. Yu Petrov[1,4], Z. Jacob[5], M. Störmer[3], T. Krekeler[6], M. Ritter[6], G. Schneider[2], *M. Eich[1,3]
[1]Hamburg University of Technology, Institute of Optical and Electronic Materials, Hamburg, Germany
[2]Hamburg University of Technology, Institute of Advanced Ceramics, Hamburg, Germany
[3]Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Geesthacht, Germany
[4]ITMO University, St. Petersburg, Russian Federation
[5]Purdue University, Birck Nanotechnology Center, School of Electrical and Computer Engineering, West Lafayette, United States
[6]Hamburg University of Technology, Electron Microscopy Unit, Hamburg, Germany

Recent research results will be presented on nanomaterials as selective emitters and for near field radiative transfer for thermophotovoltaics and on tailored photonic glasses as non-iridescent structural colors.

Emission of thermal radiation is a fundamental physical process defined by the dielectric properties of the thermally excited materials. Radiation into far field is described by Planck"s law and is limited by the blackbody emission. In near field, additional thermal energy transfer can be achieved due to evanescent fields, which are orders of magnitude larger than in far field. In the far field, emission, e.g. of long wavelengths below the energy of a semiconductor receiver band gap, can be suppressed in band edge emitters from nanostructured hyperbolic optical metamaterials as well as with resonantly coupled dielectric particle layers on top of plasmonic substrates. We demonstrate selective band edge emitters for thermophotovoltaic devices stable up to 1400°C based on W-HfO_2 refractive metamaterials as well as ZrO_2 based ceramic particles on tungsten. We further report on ceramic photonic structures as high-temperature compatible structural colors. A careful choice of the interplay between lattice and motif parameters of the photonic glass allows for structural colors with strong color saturation.

References

1. Shang, G.; Maiwald, L.; Renner, H.; Jalas, D.; Dosta, M.; Heinrich, S.; Petrov, A.; & Eich, M.; Photonic glass for high contrast structural color, *Scientific* Reports, 8, 7804 (2018)

2. Dyachenko, P.N.; Molesky, S.; Petrov, A.Y.; Stormer, M.; Krekeler, T.; Lang, S.; Ritter, M.; Jacob, Z.; and Eich, M.; Controlling thermal emission with refractory epsilon-near-zero metamaterials via topological transitions, *Nature Communications*, vol. 7, no. 11809, pp. 1–8, June 2016

3. Lang, S.; Sharma, G.; Molesky, S.; Kränzien, P.U.; Jalas, T.; Jacob, Z.; Petrov, A.Y.; and Eich, M.; Dynamic measurement of near-field radiative heat transfer, *Scientific Reports*, vol. 7, no. 1, p. 13916–13916, October 2017

4. Leib, E.W.; Pasquarelli, R.M.; do Rosario, J.J.; Dyachenko, P.N.; Doring, S.; Puchert, A.; Petrov, A.Y.; Eich, M.; Schneider, G.A.; Janssen, R.; Weller, H.; and Vossmeyer, T.; Yttria-stabilized zirconia microspheres: novel building blocks for high-temperature photonics, *Journal of Materials Chemistry C*, vol. 4, no. 1, pp. 62–74, January 2016

5. Biehs, S.-A.; Lang, S.; Petrov, A.Y.; Eich, M.; and Ben-Abdallah, P.; Blackbody Theory for Hyperbolic Materials, *Physical Review Letters*, vol. 115, no. 17, p. 174301–174301, October 2015

6. Dyachenko, P.N.; do Rosário, J.J.; Leib, E.W.; Petrov, A.Y.; Störmer, M.; Weller, H.; Vossmeyer, T.; Schneider, G.A.; and Eich, M.; Tungsten band edge absorber/emitter based on a monolayer of ceramic microspheres, *Optics Express*, vol. 23, no. 19, pp. A1236, August 2015

0052 - Invited talk

invited talk

Instrumental developments for advanced in-situ Electron Microscopy

*M. Haider[1], M. Linck[1], H. Müller[1]
[1]CEOS GmbH, Heidelberg, Germany

The requirements and challenges for advanced in-situ electron microscopy are different compared to ultra-high resolution EM. For in-situ EM more space in the objective lens area is a prerequisite [1] in order to incorporate the equipment needed for the observation of the various processes of, for example, catalytic mechanisms of small particles. The electron optical performance, however, depends on the focal length of the objective lens and, therefore, the compensation of aberrations is mandatory to attain atomic resolution in such an in-situ microscope. With such aberration correctors the former contradiction of in-situ and ultra-high resolution microscopy can be circumvented. However, the exact knowledge of all of the resolution limiting aberrations is necessary. For this purpose not only the axial aberrations in TEM are important also the off-axial ones have to be considered if a large field of view has to be achieved. The same is true if sub-Angstrom resolution is required with a large pole-piece gap and not only the spherical aberration but also the chromatic aberration limits the attainable contrast at high spatial frequencies. In both cases appropriate correction systems have to be employed.

For example, with a 300 kV TEM equipped with a cold field emitter sub-Å resolution can be achieved even if the gap is 11 mm [2], as it is the case for in-situ microscopy. In the case of a Schottky-emitter with a larger energy spread of about 0.6 eV a monochromator is advantageous for high contrast below 1 Å. However, if one is interested in the observation of beam sensitive materials at low energies and electron microscopy is applied at 20 – 80 keV the compensation of Cc is mandatory [3]. A large pole-piece gap is also needed in the case of high resolution life-science applications because an appropriate stable cold stage requires sufficient space. In this case the contrast at high spatial frequencies plays an important role as well as the large field of view. Such a life science microscope has recently been developed and an information transfer down to about 0.7 Å could be demonstrated at 300 kV with a monochromator in operation and the so-called BCOR [4] for a large field of view.

The compensation of Cc is not only mandatory at low energies but can also be very beneficial at higher electron energies such as 300 keV. For an electron gun using a photo-emitter and short intense Laser pulses the energy spread can become very large: this energy spread depends on the number of emitted electrons per pulse and consequently depends on the Laser pulses. In this scenario, a Cc-correction system can be very advantageous because the energy width of such electron punches can go up to about 100 - 500 eV. With the CCOR as it was developed for the TEAM project [5, 6] and later advanced for PICO [7] the focus spread due to such high energy variations can be neglected. Such a setup would enable high resolution EM also with a pulsed electron gun.

References

[1] F. Börrnert, et al., Ultramicroscopy **151** (2015) 31-36,

[2] E. Snoeck, et al. Microsc. Microanal. 20 (2014) 932; doi:10.1017/S1431927614006382,

[3] M. Linck et al., PRL **117**, 076101 (2016),

[4] H. Müller et al., Nucl. Instr. and Meth. in Physics Res. A 645 (2011) 20–27,

[5] C. Kisielowski et al., Microsc. Microanal. **14** (2008) 469–477,

[6] M. Haider et al., Microsc. Microanal. **16** (2010) 393–408,

[7] Lei Jin et al., Ultramicroscopy 176 (2017) 99 – 104

0053 - Invited talk

invited talk

Diffusion and diffusion-assisted defect processes in compositionally complex superalloys studied by analytical and in situ TEM

*E. Spiecker[1], Y. Eggeler[1], M. Lenz[1], D. Kubaka[1]
[1]Universität Erlangen-Nürnberg, Institute of Micro- and Nanostructure Research & Center for Nanoanalysis and Electron Microscopy (CENEM), Erlangen, Germany

Superalloys exhibit outstanding high-temperature properties making them uniquely suitable for use in modern jet engines. Their superior properties arise from a two-phase microstructure composed of γ'-cubes coherently embedded in a γ-matrix. Modern superalloys are compositionally-complex materials containing up to ten alloying elements to improve creep strength, phase stability and oxidation resistance [1]. During processing and service diffusion of these elements lead to severe changes in the microstructure. Simulations so far mainly build on diffusion data obtained from diffusion-couples of simplified binary alloy systems. We present a new approach which directly uses the γ/γ'-microstructure in compositionally-complex superalloys as intrinsic nano diffusion couples. After establishing equilibrium at one temperature we follow the transition to a new equilibrium at a different temperature. We compare ex situ and in situ approaches and use STEM-EDXS for measuring diffusion profiles across γ-channels and γ'-cubes. This approach provides valuable insight into the high temperature diffusion of individual alloying elements and their interplay and paves the way to relevant diffusion data for compositionally complex superalloys.

Recent work in the literature has shown that diffusion of alloying elements also plays a prominent role to establish segregation at planar faults which form during creep of superalloys [2-6]. Segregation occurs in Ni-base superalloys in a certain temperature-stress regime but even more pronounced in Co-base superalloys which are more prone to planar fault formation owing to much lower fault energies. Segregation in Co-base superalloys has been observed for stacking faults, antiphase boundaries and microtwins and it has been proposed that diffusion towards leading partial dislocations might be rate limiting step for creep. Here, we report on high-resolution microscopic studies of segregation to planar faults in two types of Co-base superalloys. [7]

References

[1] R. C. Reed, Superalloys, 1st ed. New York: Camebridge University Press, 2006

[2] M.S. Titus, R.K. Rhein, P.B. Wells, P.C. Dodge, G.B. Viswanathan, M.J. Mills, A. Van der Ven, T.M. Pollock, Sci. Adv. 2, e1601796 (2016)

[3] D. Barba, T.M. Smith, J. Miao, M.J. Mills, R.C. Reed, Metall. Mater. Trans. A (2018)

[4] Y.M. Eggeler, J. Müller, M.S. Titus, A. Suzuki, T.M. Pollock, E. Spiecker, Acta Mater. 113, 335-349 (2016)

[5] L.P. Freund, O.M.D.M. Messé, J.S. Barnard, M. Göken, S. Neumeier, C.M.F. Rae, Acta Mater. 123, 295-304 (2017)

[6] S.K. Makineni, A. Kumar, M. Lenz, P. Kontis, T. Meiners, C. Zenk, S. Zaefferer, G. Eggeler, S. Neumeier, E. Spiecker, D. Raabe, B. Gault, Acta Mater. 155, 362-371 (2018)

[7] The authors gratefully acknowledge financial support from the German Research Foundation (DFG) through the collaborative research center SFB-TR 103 "From Atoms to Turbine Blades - a Scientific Approach for Developing the Next Generation of Single Crystal Superalloys".

0055 - Invited talk

invited talk

In Situ High Resolution and Environmental TEM Studies of Vacancy Ordering in Epitaxial Ceria Thin Films

*R. Sinclair[1], S. C. Lee[1], Y. Liu[1], Y. Zeng[1], Y. Shi[1,2], W. C. Chueh[1,2]
[1]Stanford University, Department of Materials Science and Engineering, Stanford, United States
[2]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, United States

We have applied aberration-corrected transmission electron microscopy (TEM) imaging and electron energy loss spectroscopy (EELS) to study the structure and chemistry of epitaxial ceria thin films, grown by pulsed laser deposition onto (001) yttria-stabilised zirconia (YSZ) substrates [1]. There are few observable defects apart from the expected mismatch interfacial dislocations and so the films would be expected to have good potential for applications. Particular attention is paid to the transition from fully to partially coherent interfacial structures, and this is correlated to x-ray diffraction measurements [2]. Under high electron beam dose rate (above about 6,000 e-/Å2s) domains of an ordered structure appear and these are interpreted as being created by oxygen vacancy ordering. The ordered structure does not appear at lower lose rates (ca. 2,600 e-/Å2s) and can be removed by imaging under 1 mbar oxygen gas in an environmental TEM. EELS confirms that there is both oxygen deficiency and the associated increase in Ce^{3+} versus Ce^{4+} cations in the ordered domains. *In situ* high resolution TEM recordings show the formation of the ordered domains, which can be analyzed by the classical Avrami approach, as well as atomic migration along the ceria thin film (001) surface. The influence of thin film strain, by using different substrates, will also be considered [3].

[1] R. Sinclair, S. C. Lee, Y. Shi, W. C. Chueh, Ultramicroscopy, 176, 200 (2017).

[2] Y. Shi, S. C. Lee, M. Monti, C. Wang, Z. A. Feng, W. D. Nix, M. F. Toney, R. Sinclair, W. C. Chueh, ACS Nano, 10, 9938 (2016).

[3] C. B. Gopal, M. Garcia-Melchor, S. C. Lee, Y. Shi, A. Shavorsky, M. Monti, Z. Guan, R. Sinclair, H. Bluhm, A. Vojvodic, W. C. Chueh, Nature Comm., 8, 15360 (2017).

0056 - Invited talk

invited talk

Model-Based Reconstruction of Charge Density and Electric Field using Electron Holography

F. Zheng[1], J. Caron[1], V. Migunov[1], *R. Dunin-Borkowski[1]
[1]Forschungszentrum Jülich, Ernst Ruska-Centre and Peter Grünberg Institute, Jülich, Germany

The ability to measure local variations in charge density would provide a valuable tool for the study of functional materials, including ferroelectrics and semiconductors. Similarly, the ability to measure local variations in electric field outside electrically-biased samples would be of great importance for understanding the fidelity of reconstructions of microstructure and chemical composition achieved using atom probe tomography. Off-axis electron holography provides direct access to the phase of the high energy electron wave that has passed through a sample in the transmission electron microscope. In the absence of magnetic fields, the phase is sensitive to the electrostatic potential in the specimen projected in the electron beam direction. The local projected charge density in the specimen can in principle be determined directly from the Laplacian of a recorded phase image. However, such a model-independent approach suffers from poor signal-to-noise, as well as from artefacts associated with local variations in mean inner potential and specimen thickness. We have developed a model-based iterative technique that can be used to reconstruct the projected charge density inside a specimen from a single electron optical phase image recorded using off-axis electron holography, or alternatively the three-dimensional charge density distribution from a tomographic tilt series of phase images [1]. We use a forward model in an iterative algorithm to solve the inverse problem of reconstructing the charge density in the specimen, as shown in Fig. 1. Additional constraints and physical laws can be incorporated in the algorithm. For the three-dimensional problem, the use of such a model-based approach avoids many of the artifacts that are associated with the use of backprojection-based tomographic techniques. The projected or three-dimensional electric field can be determined numerically from the reconstructed charge density [2].

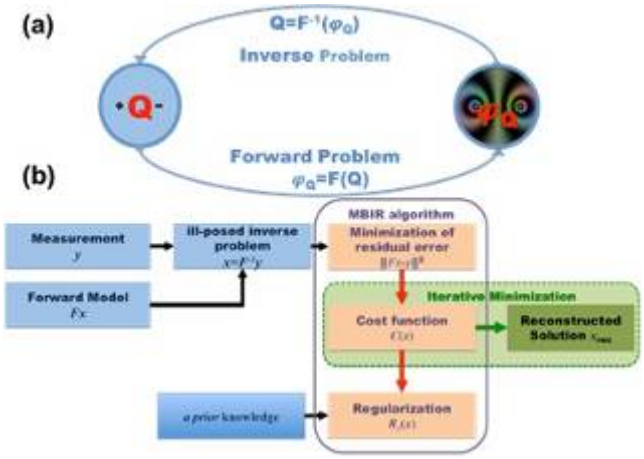
Figure 1. (a) Illustration of the forward and inverse problems that link the charge distribution Q in a specimen with the recorded phase shift φ_Q. (b) Workflow of the reconstruction process.

References

[1] J Caron, Ph.D. dissertation, RWTH Aachen University (2017).

[2] We are grateful to J Ungermann, M Riese , M Beleggia and G Pozzi for valuable contributions.

Figure 1



0057 - Invited talk

invited talk

Materials under the microscope: the atomic origin of functionality

*S. J. Pennycook[1], X. Zhao[1], J. Dan[1], H. Wu[1], M. Li[1], C. Tang[1], C. Li[1], S. Ning[1]
[1]National University of Singapore, Department of Materials Science and Engineering, Singapore, Singapore

Keywords: scanning transmission electron microscopy, electron energy loss spectroscopy, 2D materials, piezoelectrics, thermoelectrics

The aberration-corrected scanning transmission electron microscope (STEM) provides real space imaging and spectroscopy with unprecedented sensitivity down to the single atom level. Thoroughly understanding and tailoring structural defects is extremely significant for understanding the structure-property relations of existing high-performance materials, and more importantly, guiding the design of new materials with improved properties. Several representative studies will be presented. In 2D materials, sub-Ångstrom information transfer can be achieved at only 40 kV, and point defects and their local environments directly identified to correlate with properties. New edge structures in nanoporous MoS2 are found to exhibit excellent catalytic properties [1], and 2D Mo metal membranes can be fabricated from MoSe2 films via beam induced sputtering of Se [2]. In addition, beam induced healing of holes can also be observed under certain conditions.

In piezoelectrics, owing to growing environmental concerns, the development of lead-free materials with enhanced properties is urgently required. Precise mapping of atomic displacements reveals a hierarchical nanodomain structure as the origin of excellent properties, the coexistence of ferroelectric phases inside nanodomains and gradual polarization rotation between them (Fig. 2). Density functional calculations and phase field modelling confirm this scenario [3,4]. Similarly, in thermoelectrics, a hierarchical structure ranging from point defects through nanoscale and microscale precipitates results in a high-performance material with lattice thermal conductivity approaching the theoretical minimum [5].

[1] X. Zhao, *et al., Nano Lett*, **18** (2017) 482–490.

[2] X. Zhao, *et al., Adv. Mater.* (2018) 1707281.

[3] T. Zheng, *et al., Energy Environ. Sci*, **10** (2017) 528–537.

[4] B. Wu, *et al., J Am Chem Soc*, **138** (2016)15459–15464.

[5] Y. Xiao, *et al., J Am Chem Soc*, **139** (2017) 18732–18738.

0058 - Invited talk

invited talk

Nanostructured Materials for Hydrogen Technology

*T. Klassen[1,2], R. Raudsepp[1], C. Wolpert[1], C. Borchers[1], S. Boerries[1], H. Cao[1], J. Jepsen[1], G. Capurso[1], J. Bellosta von Colbe[1], K. Taube[1], C. Pistidda[1], T. Emmler[1], M. Villa-Vidaller[1], M. Schieda[1], F. Gärtner[1], M. Dornheim[1]
[1]Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Geesthacht, Germany
[2]Helmut Schmidt University, University of the Federal Armed Forces Hamburg, Hamburg, Germany

Hydrogen is the ideal clean energy carrier for our future sustainable energy economy as well as for zero-emission mobility. Recent research on nanostructured materials for efficient renewable production and reversible storage of hydrogen will be presented. Different aspects from basic materials development to systematic science-based scale-up and system design will be covered. Certain nanocrystalline semiconductors are photocatalytically active and can be used for water splitting in photo-electrochemical cells. For this study, nanocrystalline TiO_2, $BiVO_4$, and WO_3 coatings were produced by cold spraying. In cold spraying, particles are accelerated in a gas stream to velocities of more than 800 m/s and bind to the substrate upon impact. Binder agents are not required, and TEM micrographs show that the nanocrystalline microstructure is retained. The initially present secondary structure of the nanoparticles bursts on impact leaving behind the primary nanocrystals and resulting in a large active surface area. The coatings show high photo-currents for hydrogen production by solar water splitting. With respect to hydrogen storage, solid nanostructured hydrides offer a safe and energy efficient solution for stationary as well as mobile applications. Highest energy efficiencies can be achieved, if working temperature and reaction enthalpy of the respective hydrogen releasing process can be tailored for the particular system integration, e.g. with a fuel cell. Tuning of reaction enthalpies can be facilitated using Reactive Hydride Composites (RHC), which release or store hydrogen by redox reactions between at least two hydrides. Up to 11 wt.% hydrogen may be stored reversibly at technically relevant temperatures. Recent progress in tailoring reaction enthalpies and optimizing reaction kinetics will be presented. In particular, microscopical methods contributed to clarify the microscopic phase reaction mechanisms. In view of application, the design of larger storage tanks can be optimized via neutron radiography and tomography.

0059 - Invited talk

invited talk

Hierarchically Structured Biomaterials Investigated *in situ* with X-Ray and Neutron Scattering on Multiple Length and Time Scales

*M. Müller[1,2]
[1]*Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Geesthacht, Germany*
[2]*Kiel University, Institute of Experimental and Applied Physics, Kiel, Germany*

Synchrotron radiation X-ray and neutron scattering techniques are extremely useful tools for the non-destructive analysis of the structure of structural biological materials such as wood and silk, making the *in situ* investigation of structural changes upon mechanical stress possible – across many length and time scales.

The low-divergence synchrotron radiation X-rays can be focused down to sub-micrometer size, enabling e. g. scanning studies of the wood nanostructure with (sub-)microscopic position resolution [1]. Molecular time and length scales are addressed using neutron spectroscopy.

I will highlight recent advances in the understanding of the micro- and nanostructure of wood, silk and spider adhesive hairs in relation to their unique mechanical properties. Examples include the local breakdown of cellulose fibre texture in wood cell walls [2], the deformation mechanism of a single wood cell [3], the viscoelastic properties of silk [4] and insight into molecular mechanisms in silk and spider silk upon mechanical deformation [5,6]. The most recent study reveals orientational changes upon attachment and detachment of spider hairs investigated *in situ* [7].

References

[1] M. Müller. *Materials Science Forum* **599**, 107–125 (2009)

[2] M. Ogurreck, H. Lichtenegger, M. Müller. *J. Appl. Cryst.* **43**, 256–263 (2010)

[3] M. Müller, I. Krasnov, M. Ogurreck, M. Blankenburg, T. Pazera, T. Seydel. *Adv. Eng. Mater*. **9**, 767–772 (2011)

[4] I. Krasnov, I. Diddens, N. Hauptmann, G. Helms, M. Ogurreck, T. Seydel, S. S. Funari, M. Müller. *Phys. Rev. Lett.* **100**, 048104 (2008)

[5] T. Seydel, K. Kölln, I. Krasnov, I. Diddens, N. Hauptmann, G. Helms, M. Ogurreck, S.–G. Kang, M. M. Koza, M. Müller. *Macromolecules* **40**, 1035–1042 (2007)

[6] I. Krasnov, T. Seydel, I. Greving, M. Blankenburg, F. Vollrath, M. Müller, J. R. Soc. Interface **13**, 20160506 (2016)

[7] C. F. Schaber, S. Flenner, A. Glisovic, I. Krasnov, H. Stieglitz, E. Di Cola, M. Rosenthal, C. Krywka, M. Burghammer, M. Müller, S. N. Gorb. *Submitted*

0060 - Invited talk

invited talk

Self-assembly of nano-building blocks: towards ceramic nanocomposites with exceptional mechanical properties

*B. Domènech[1], D. Giuntini[1], B. Bor[1], A. Hass[1], G. A. Schneider[1]
[1]Hamburg University of Technology, Institute of Advanced Ceramics, Hamburg, Germany

Natural structural materials such as nacre are able to achieve extraordinary mechanical properties that go beyond the properties of their single constituents thanks to their growth into intricate architectures. In such designs the main structure is build up in a controlled hierarchy at multiple length scales, usually starting with a first hierarchical level formed by nanosized elements glued together by biopolymers. Such hierarchical approach has motivated the fabrication of artificial nacre-inspired materials for a long time, but, so far, the obtaining of large-sized three-dimensional (3D) bulk materials still remains a challenge.

Hereby it is presented the use of self-assembly of nano-building blocks to produce 3D nature-inspired bulk nanocomposite ceramic materials with enhanced mechanical properties [1]. In order to tune the final properties of such materials, it is mandatory to understand the effects of both, the self-assembly process and the nature of the building blocks. Thanks to the combination of Electron Microscopy, Small Angle X-Ray Scattering, Synchrotron Micro-Computed Tomography, and Nanomechanical testing, we are now able to relate the formation, evolution and morphology of the supercrystalline domains to the final mechanical response. For instance, it has emerged that changing the organic functionalization (type and amount) of the ceramic nanoparticles plays a crucial role in the supercrystals" final morphology and properties. Such understanding can be used to establish the key synthetic parameters guiding the obtainment of bio-inspired ceramic-based nanocomposites with improved final properties.

References

[1] Axel Dreyer, Artur Feld, Andreas Kornowski, Ezgi D. Yilmaz, Heshmat Noei, Andreas Meyer, Tobias Krekeler, Chengge Jiao, Andreas Stierle, Volker Abetz, Horst Weller, Gerold A. Schneider, Nature Materials,15, 522–528 (2016)

0061 - Invited talk

invited talk

Synthesis and mechanical properties of organically linked nanoparticle supercrystals

*G. A. Schneider[1]
[1]Hamburg University of Technology, Institute of Advanced Ceramics, Hamburg, Germany

It is commonly accepted that the combination of nanosize and elongated mineral constituents in biological materials is the main reason for their exceptional mechanical properties as compared to their rather weak mineral and organic constituents. Here we show that the self-assembly of spherical iron oxide nanoparticles via solvent evaporation or destabilization can be controlled to produce only supercrystals or nanocomposites with two hierarchical levels. The exceptional elastic modulus, nanohardness and strength of these supercrystals is realized by a thermally induced coupling reaction of oleic acid or oleyl phosphate molecules. It is the covalent backbone of the linked organic molecules, which dominates the mechanical properties. The focus of the presentation is to discuss the self-assembly of the nanoparticles as well as the mechanical properties of the supercrystals.

References

1. Dreyer A. , Feld A., Kornowski A., Yilmaz E.D., Noei, H., Meyer A., Krekeler T. Jiao C., Stierle A. Abetz, V. Weller, H., Schneider G.A. *Nature Materials,* **2016**, 15, 522–528

Acknowledgements: The authors gratefully acknowledge financial support from the German Research

Foundation (DFG) via SFB 986 M3, projects A1, A2, A6 and Z3.

0062 - Invited talk

invited talk

Correlating the 3D structure of nanoporous gold to the mechanical response

*E. Lilleodden[1]
[1]Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Materials Mechanics, Geesthacht, Germany

The mechanical behavior of NPG has been shown to be strongly dependent on its average ligament width, with local stresses approaching the theoretical strength of gold, underscoring the "smaller is stronger" paradigm. Such size-dependent strength can be exploited in NPG through targeted annealing in order to tailor the structural length-scales. Yet strong deviations from classical laws for cellular structures have been found for NPG, pointing to the need for developing new scaling laws for the prediction of mechanical properties as a function of structural length. This in turn is reliant on a more detailed investigation of the 3D network structure and crystallographic domain sizes, and a better understanding of the underlying structure-property relations governing mechanical response. By employing a combination of high-resolution tomographic characterization, micro-Laue diffraction and in situ micromechanical testing to NPG, the structure-property relations, mechanisms of deformation, and associated size effects can be explored and quantified. In this presentation, results obtained on NPG will be discussed with an outlook toward the potential for understanding structure-property relations in other nano-scaled materials.

0063 – Poster presentation

Sponsor

Precession Electron Diffraction Applications in TEM : from crystal structure determination to orientation imaging and strain mapping at nm scale

*T. Galanis[1]
[1]NanoMEGAS, Brussels, Belgium

Based on the early work by Vincent and Midgley in Bristol UK (1994) that developed the Precession Electron Diffraction (PED) technique in transmission electron microscope (TEM), PED is an essential tool for several TEM applications for nanomaterials. Beam precession has been proved to enhance the reflections quality (quasi-kinematical, similar to X-ray intensities). Today, more than 180 articles (that include PED technique) from various laboratories worldwide and dedicated issues of major scientific microscopy journals have been published the last decade.

One of the most important applications for electron crystallography, is the recently developed 3D PED diffraction tomography technique allowed from the collection of several PED patterns complete solution of various structures from complex zeolites and minerals to metals and alloys. Another very interesting application including use of PED is the ASTAR technique where is possible to obtain orientation and phase maps at 1-3 nm resolution (in case of FEG-TEM) for a variety of materials (metals, semiconductors, oxides etc.). The technique is very similar to EBSD-SEM , ASTAR approach is based on collection of several PED patterns on an crystalline area and template matching with theoretically generated templates.

Precession diffraction has been recently successfully applied to obtain Strain mapping analysis of several semiconductor materials at 1-4 nm resolution (in case of FEG-TEM, sensitivity 0.02%), based on comparison of NBD patterns from strained / reference un-strained areas. The technique is very easy to use at any TEM and provides very fast and accurate data (same order of magnitude as dark field holography) without any need to index diffraction patterns. The recent application of e-PDF (electron Pair Distribution Function) techniques allows to analyse at local scale Electron Diffraction (ED) patterns even from amorphous materials. e-PDF technique allows to analyse interatomic distances, bonding and possible short/large scale order of nanocrystalline /amorphous materials at nm scale , enabling to monitor in situ solid state reactions, structure of glassy materials, layered thin films quality and amorphous/ re-crystallization studies in semiconductor devices.

We will herein present various application examples of PED combination with orientation imaging, ADT 3D and e-PDF studies for studies of various materials

0064 – Poster presentation

Sponsor

Phase imaging in STEM from 30 to 300 keV using iDPC-STEM supported by S-Corr and Ulti-Mono

*I. Lazić[1], E. G. T. Bosch[1], E. Yücelen[1], A. Carlsson[1]
[1]Thermo Fisher Scientific, Materials & Structural Analysis, Eindhoven, Netherlands

We demonstrate state of the art direct phase STEM imaging at the limit of resolution, contrast and dose for wide variety of samples. We use the iDPC-STEM [1,2,3], an elegant solution to the phase problem, simultaneously with ADF-STEM for the reference, to resolve the atoms at sub-Å scale and under various extreme conditions, from 30 keV to 300 keV.

We show the ability to image both light and heavy elements together, long range fields (such strain and build in contact potentials), metallization and thickness variations, both for thin as well as thick samples.

We also show that imaging of extremely light elements, such as lithium is possible as well as low dose imaging of beam sensitive materials. We present images of Zeolites (ZSM-5), Hexachloro Phthalocyanines (Cl16CuPc) with angstrom and sub angstrom resolution respectively and Metal Organic Frameworks (MOFs) using dose of only 120 e-/Å2 while demonstrating resolution of 1.6 Å.

References

[1] I. Lazić, E.G.T. Bosch and S. Lazar, *Ultramicroscopy* **160** (2016) 265-280.

[2] I. Lazić, E.G.T. Bosch, *Advances in Imaging and Electron Physics* **199** (2017) 75-184.

[3] E. Yücelen, I. Lazić, E.G.T. Bosch, *Scientific Reports* **8** (2018) pp-pp.

0065 – Invited talk

invited talk

In situ and high precision electron microscopy of strain induced tuning of electrical properties and catalytic activity

*E. Olsson[1]
[1]Chalmers University of Technology, Department of Physics, Gothenburg, Sweden

In situ electron microscopy allows us to directly reveal the correlation between local atomic structure and properties. Strain engineering can be and is used to tune the properties of advanced materials and devices. Catalytic activity of metal nanoparticles and electrical properties of semiconducting nanowires are examples where the strain induced effects have a strong influence on the properties and performances. This talk will address studies of supported Pt nanoparticles and also semiconducting nanowires. We have used high resolution annular dark field (ADF) scanning transmission electron microscopy (STEM) imaging to obtain high resolution (better than 1 Å) and high precision (better than 1 pm) information about the local atomic structure [1]. We have used in situ microscopy to perform electrical conductivity and nanoscale mechanical strain measurements [2, 3]. We have also performed STEM combined with nanobeam electron diffraction to quantitatively evaluate the nanoscale strain distribution [2]. In addition, we have studied electric field induced changes on the atomic scale using in situ microscopy [4]. The experimental studies have been combined with theoretical modelling. New aspects of material properties and mechanisms, not obvious from measurements on the macro scale are revealed using in-situ electron microscopy where interfaces, surfaces, geometries and defects affect the material properties on the macro, micro, nano and atomic scale. The knowledge is crucial for not only the understanding of the mechanisms that are involved but also for the design or materials and devices with tailored properties.

References

[1] T. Nilsson Pingel, M. Jørgensen, A.B. Yankovich, H. Grönbeck and E. Olsson, "Influence of atomic site-specific strain on catalytic activity of supported nanoparticles",Nature Communications 2018, DOI: 10.1038/s41467-018-05055-1.

[2] L. J. Zeng, C. Gammer, B. Ozdol, T. Nordqvist, J. Nygård, P. Krogstrup, A.M. Minor, W. Jäger and E. Olsson, "Correlation between electrical transport and nanoscale strain in InAs/In0.6Ga0.4As core-shell nanowires, Nano Letters 2018, DOI:10.1021/acs.nanolett.8b01782.

[3] J. Holmér, L.J. Zeng, T. Kanne Nordqvist, J. Nygård, P. Krogstrup, L. De Knoop and E. Olsson, "An STM-SEM setup for characterizing photon and electron induced effects in single photovoltaic nanowires", Nano Energy 2018, 10.1016/j.nanoen.2018.08.037

[4] L. de Knoop, M.J. Kuisma, J. Löfgren, K. Lodewijks, M. Thuvander, P. Erhart, A. Dmitriev and E. Olsson, Electric field controlled reversible order-disorder switching of a metal tip surface", Phys. Rev. Mat. 2018, DOI: 10.1103/PhysRevMaterials.00.005000.

0066 – Invited talk

invited talk

Revealing the 3D structure of graphene defects

*C. Hofer[1], C. Kramberger[2], V. Skakalova[3], M. Monzam[3], C. Mangler[3], A. Mittelberger[3], G. Argentero[3], J. Kotakoski[3], T. Susi[3], J. C. Meyer[1]
[1]University of Tübingen, Tübingen, Germany
[2]Vienna University of Technology, Vienna, Austria
[3]University of Vienna, Vienna, Austria

We demonstrate insights into the three-dimensional structure of defects in graphene, in particular grain boundaries [1] and Silicon dopants [2], obtained via a new approach from two atomically resolved transmission electron microscopy images recorded at different angles. The structure is obtained through an optimization process where both the atomic positions as well as the simulated imaging parameters are iteratively changed until the best possible match to the experimental images is found. We first demonstrate that this method works using an embedded defect in graphene that allows direct comparison to the computationally calculated three-dimensional structure. We then applied the method to a set of grain boundary structures with misorientation angles nearly spanning the whole available range (2.6-29.8°). The measured height variations at the boundaries reveal a strong correlation with the misorientation angle with lower angles resulting in stronger corrugation and larger kink angles. We also used our technique to reveal the 3D structure of Silicon substitutes and Silicon tetramers in graphene. Our approach also allows to visualize interesting electron beam induced dynamics, which would not be observable when the sample is not tilted. Our results allow for the first time a direct comparison with theoretical predictions for the corrugation at grain boundaries and Silicon dopants as well as studying out-of-plane dynamics.

References

[1] Hofer et al., 2D materials, Volume 5, Number 4 (2018)

[2] Hofer et al., arXiv:1809.08946

0067 – Invited talk

invited talk

Advanced and In Situ Transmission Electron Microscopy of Functional Nanomaterials

*W. Jaeger[1]

[1] *Christian-Albrechts-University of Kiel, Institute for Materials Science, Kiel, Germany*

Advanced high-resolution imaging and spectroscopic techniques of transmission electron microscopy (TEM) and scanning TEM (STEM) play a crucial role for characterizations of the synthesis and optimization of novel materials and of the structure-property relationships of materials and interfaces. This brief review will illustrate examples related to the synthesis of nanostructured oxide semiconductors, to interface properties of high-efficiency multi-junction solar cells, and to multilayer systems for X-ray optical applications.

Nanostructured oxide semiconductors, such as ZnO or In_2O_3, are of interest for device applications in nanoelectronics, for gas sensing, or in photovoltaic devices. High-resolution and scanning TEM were used to characterize the growth and doping phenomena of ZnO nanorod structures fabricated by a thermal method from powder precursor materials. For ZnO grown with Sn-precursors nanorods with core-shell morphologies form whose core regions contain dislocations, precipitates, or tubular voids partly filled with liquid Sn. Thin surface layers of a spinel phase indicate that interfacial reactions take place during crystal growth. Cathodoluminescence (CL) recorded from ZnO nanorods reflects the inhomogeneous defect distributions by a spatially varying CL emission whereas the CL spectra show a blue-shifted ZnO band gap luminescence which can be attributed to the effects of doping [1]. By applying in-situ (S)TEM experiments Sn-rich core material is identified and found to reversibly melt and expand under varying thermal load exerted by the electron beam [2]. Complex hierarchical phenomena are observed for growth with Al or Ga precursors and are found to be correlated with dopant incorporation. An example is the observation of planar defects enriched in Ga and their spatial connection with a variation of the rod diameter, indicating a possible origin for an oscillatory growth behaviour [3]. Various phenomena are observed for crystal growth of In_2O_3 nanorods, most strikingly the presence of nanotubes or nanopipes with constant diameter extending along the nanorods. Their formation can be understood as evidence for a crystal growth mode which involves a screw dislocation [4].

High-efficiency multi-junction solar cells based on III-V compound semiconductors reach the highest conversion efficiencies and are currently used primarily in terrestrial concentrator photovoltaics and for power generation on satellites and spacecraft. Different semiconductor cell materials are generally combined to absorb solar radiation of different wavelengths and to convert it into electric power. Solar-electric conversion efficiencies of up to 46 % have been obtained with multi-junction cells fabricated by metal-organic vapour phase epitaxy (MOVPE) of III-V semiconductors [5]. To overcome the challenge of integration of III–V compound semiconductors with Ge and Si caused by the large differences in lattice constant and thermal expansion two different process technologies were investigated by using advanced and in-situ (S)TEM techniques: direct epitaxial growth involving buffer layer concepts [6] and layer transfer combined with semiconductor wafer bonding [7]. An example is the wafer bond processing of transparent and electrically conductive interfaces between different III-V semiconductors, such as n-GaSb/n-GaInP bond interfaces. TEM characterizations of the atomic structure and of the elemental distribution at and near these bond interfaces enabled to understand the effects of fast atom beam activation treatments on the formation of amorphous interface layers, their recrystallization during thermal annealing, and the resulting effects on the electrical current-voltage characteristics, thus supporting the optimized engineering of wafer-bond interfaces for solar cells [8].

Periodic and aperiodic multilayer coatings consisting of ultrathin bilayers are essential components of X-ray optics for advanced X-ray analytical equipment and for synchrotron beam lines. Examples are filters of small or large spectral bandwidth, components for shaping high-intensity X-ray beams, or mirrors for light sources. The functionality of these components is based on X-ray scattering from a stack of alternating amorphous or nanocrystalline layers of materials with large differences in atomic number. Modern thin film deposition technologies allow to fabricate such multilayer systems with reproducible control of layer thickness on the nanometer scale and resulting excellent reflectivity properties. TEM characterizations of multilayer cross-sections have proven to be successful for monitoring the layer thickness, the layer periodicity and uniformity, and the interface quality on different length scales [e.g., 9, 10]. An example of aperiodic Mo-B_4C multilayers will be used to illustrate the potential of electron tomography in combination with advanced imaging and spectroscopic techniques of aberration-corrected STEM for extracting quantitative information, especially about the interface roughness of individual ultrathin layers in such multilayer systems [11].

The author acknowledges with pleasure the collaborations with all colleagues and co-authors and their contributions to the various research projects.

References

[1] Y. Ortega, Ch. Dieker, W. Jäger, J. Piqueras, P. Fernández, Nanotechnology 21, 225604 (2010)
[2] Y. Ortega, W. Jäger, J. Piqueras, D. Häussler, P. Fernández, J. Phys. D: Appl. Phys. 46, 395301 (2013)

[3] Y. Ortega, D. Häussler, J. Piqueras, P. Fernández, W. Jäger, Phys. Stat. Sol. A209, 1487 (2012)
[4] D. Maestre, D. Häussler, A. Cremades, W. Jäger, J. Piqueras, Cryst. Growth. Des. 11, 1117 (2011).
[5] F. Dimroth et al. IEEE Journal of Photovoltaics 6, 343 (2016).
[6] J. Schöne, E. Spiecker, F. Dimroth, A. W. Bett, W. Jäger, Journal of Physics: Conference Series 471, 012008 (2013)
[7] D. Häussler, L. Houben, S. Essig, M. Kurttepeli, F. Dimroth, R.E. Dunin-Borkowski, W. Jäger, Ultramicroscopy 134, 55 (2013)
[8] F. Predan, A. Kovács, J. Ohlmann, D. Lackner, F. Dimroth, R. E. Dunin-Borkowski, W. Jäger, Journal of Applied Physics 122, 135307 (2017)
[9] D. Haeussler, E. Spiecker, S. Yang, W. Jäger, M. Stoermer, R. Bormann, G. Zwicker, phys. stat. sol. 202, 2299 (2005)
[10] D. Haeussler, Ch. Morawe, U. Roß, B. Oeguet, E. Spiecker, W. Jäger, F. Hertlein, U. Heidorn, J. Wiesmann, Surface & Coatings Technology 204, 1929 (2010).

[11] G. Haberfehlner, E. Fisslthaler, G. Kothleitner, U. Heidorn, F. Hertlein, J. Wiesmann, W. Jäger, in preparation (2018)

0068 – Invited talk

invited talk

3D reconstruction of FIB/SEM slice data using unsupervised clustering algorithms

*M. Ritter[1]

[1]Hamburg University of Technology, Electron Microscopy Unit, Hamburg, Germany

Focused ion beam (FIB) tomography often is the method of choice to analyse the 3D structure of nano-porous materials. Especially nano-porous gold (npg) is of interest as a functional material but also as a model system for nanomaterials. Because of “shine-through” artefacts [1], nano-porous materials are in most cases infiltrated with epoxy resin before FIB tomography is applied in order to lower the influence of this effect. However, resin infiltration might lead to unwanted impact on the material, such as deformation due to cure shrinkage.

Here, we examine the effect of such imaging artefacts on several segmentation algorithms that have to be used for the 3D reconstruction of FIB tomography data. To allow for comparison of infiltrated versus non-infiltrated materials, we simulated FIB slices by creating backscatter electron images of npg with MC X-ray software [2]. MC X-Ray allows having dozens of regions with various shapes and all these regions can have a different composition. In our case, we created a npg network using randomly distributed gold cubes, and voids or epoxy cubes, respectively in a 40 nm x 40 nm x 40 nm voxel mesh volume. Virtual FIB slices with a thickness of 7 nm were virtually cut and backscatter electron images (BSE, 2 kV, 25 pA, 3.98 nm pixel resolution) of the a) npg-epoxy and b) npg-void volumes were calculated.

For comparison, several segmentation algorithms were used prior to 3D reconstruction, some already implemented in commercial software (Avizo, ThermoFisher) or in open source software (ImageJ). In addition, k-means [3], a cluster analysis algorithm related to machine learning was applied with for segmentation but also for clustering. Three clusters (k=3) were defined with the intention, that information in the images is either nano-porous material, resin or void, or artefact, respectively.

As expected, segmentation and volume reconstruction results yield a large error in the simulated data of non-infiltrated npg. Presumably, this is mostly due to the “shine-through” effect, which is larger in non-infiltrated nano-porous samples than in resin filled npg. Our cluster analysis approach, however, proves to be more robust against the effect as the volume comparison of infiltrated vs. non-infiltrated npg shows a 6% increase in deviation.

References:

[1] T. Prill et al., Scanning 35, 189-195, (2013).
[2] G. Gauvin et al., Micros. Microanal. 15(Suppl 2), 488-489 (2009).
[3] S. P. Lloyd, IEEE Trans. Inf. Theory 28(2), 129-137, (1982).

The authors gratefully acknowledge support by Deutsche Forschungsgemeinschaft (DFG) through the collaborative research centre SFB 986 "Tailor-Made Multi-Scale Material Systems".

0069 – Poster presentation

Sponsor talk

Development of custom electronics for HAADF STEM upgrade

U. Grauel[1], W. Joachimi[1], S Selve[2], D. Berger[2] and *G. Moldovan[1]

[1] point electronic GmbH, Halle (Saale), Germany
[2]Technische Universität Berlin, ZELMI, Germany

Requirements for equipment in TEM and STEM regularly divert from complete microscopes or standard options, and instead calls for development of custom parts to match a particular technique or system. Such developments are possible and practical, and this work presents an example of a customisation and upgrade process of a 200 kV LaB6 TECNAI from TEM to STEM using new non-factory electronics. The TEM column was already equipped with scanning coils, but required a complete scanning unit and STEM detectors, including software for hardware control and data acquisition.

A custom scanning unit was configured to include a scan generator, a scan amplifier and power supplies for the lenses, alongside a standard external microscope interface for integration with EDS. The scan generator is able to produce up to 16k x 16k pixels resolution, with a pixel dwell time down to 220 ns, including line start delay time, run-in pixels and synchronisation, as well as pixel, line and frame averages. All signals are digitized at 12-bits, transported over USB2 to PC where may be tiled or mixed in grayscale or colour, and saved to standard 16-bit multi-page TIFF. All available microscope information is saved as standard XMP tags into the TIFF metadata.

A custom STEM detector units was developed for mount under the CCD camera. A detector-grade Si sensors with one Bright-Field (BF1) and three Annular Dark Field sensors (ADF1, ADF2 and HAADF) segments was integrated with 4x independent preamplifiers. Key detector specifications include simultaneous operation of all four segments, independent input offsets (brightness) and second stage amplification (contrast) for each signal, as well as fast operation down to 220 ns/pixel.

Results of an initial comparative study with standard STEM electronics [1] has found easy alignment and image acquisition, similar to that of standard STEM workflows. Imaging results has shown no significant difference in imaging performance and resolution, with a measured probe diameter of 3 nm, which compares well with the 1 nm STEM manufacture specification. Planned further customisation include electronics for independent readout of all segmented ADF sensors (3x4 quadrants), upgrade of image acquisition to increase number of simultaneous signals (13x).

Acknowledgements
The German Ministry for Economic Affairs and Energy (BMWi) via the project "innoKA" (number 03ET6096B) and the German Research Foundation (DFG) via the Cluster of excellence "UNICAT" for financial support of the TEM.

References
[1] S Selve et al. A comparative study of customized and standard STEM electronics, International Microscopy Congress, Sydney 2018.

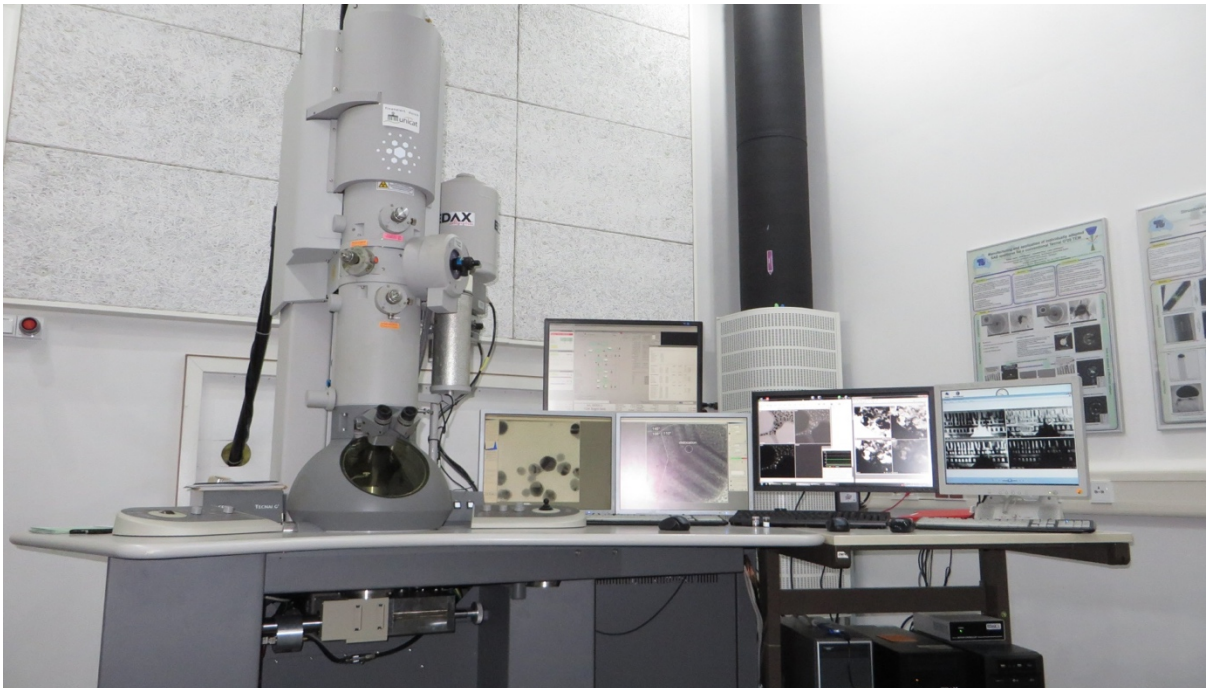


Figure 1: LaB_6 TECNAI G²20 S-TWIN STEM upgraded with custom HAADF and scanning electronics.

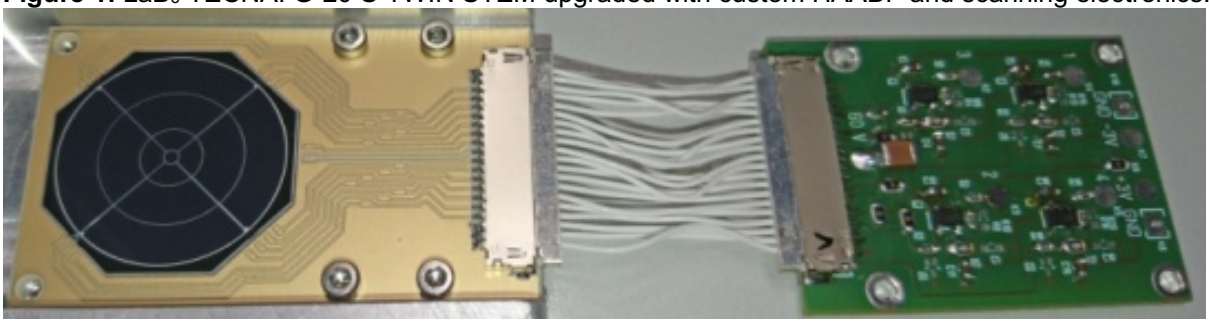


Figure 2: custom BF/HAADF detector electronics, including segmented Si sensor and preamplifiers.

Figure 3: custom scanning electronics, including scan generator, amplifiers and power supply units.