KR 2: Crystallography in nanoscience

Time: Tuesday 9:30–13:00 Location: H9

Invited Talk KR 2.1 Tue 9:30 H9

Coherent X-ray Diffraction for mapping strains in ZnO Nanocrystals — •Ian Robinson — London Centre for Nanotechnology — Diamond Light Source

In condensed matter physics, we consider nanometre-sized crystals to be a new frontier of opportunity to tailor physical properties using "size" as a control variable. However, when we think about nanostructures, we must reconsider the standard bulk concepts of lattices and crystal defects. Changes here provide nanomaterials with new and exciting properties. This talk will illustrate how coherent X-ray diffraction at a 3rd generation synchrotron source can be used to obtain quantitative three-dimensional maps of the deformation of a crystal from its equilibrium lattice spacing. To invert the diffraction, we have solved the crystallographic "phase problem" by oversampling using a support-constrained HIO algorithm. The ZnO crystals we have been investigating were attached by bonding to a SiO_2 substrate and show internal strain arising from accidental damage during manipulation. Use of more than one Bragg peak from the same crystal has allowed components of the full strain tensor to be mapped inside the crystal.

"Coherent Diffraction Imaging of Strains on the Nanoscale", Ian Robinson and Ross Harder, Nature Materials 8 291-298 (2009)

"Three-dimensional imaging of strain in a single ZnO nanorod", M. C. Newton, S. J. Leake, R. Harder and I. K. Robinson, Nature Materials (2010)

KR 2.2 Tue 10:15 H9

X-ray characterisation of single GaAs nanorods grown on Si — •Andreas Biermanns[1], Anton Davydok[1], Steffen Breuer[2], Lutz Geelhaar[2], and Ullrich Pietsch[1] — [1]Universität Siegen, Festkörperphysik, Germany — [2]Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany

Semiconductor nanorods are of particular interest for new semiconductor devices. The nanorod approach can be used to form radial or axial heterostructures of materials with a large lattice mismatch. For the inspection of average structural parameters of the nanorods, typically x-ray or electron diffraction techniques are used. Alternatively, transmission electron microscopy can be used to inspect few individual nanorods after respective sample preparation. Complementary, recent developments in x-ray optics allow to focus a synchrotron beam down to the nanometer scale and to perform nondestructive diffraction studies at several individual nano-objects grown the same substrate. In this contribution we report on x-ray diffraction studies at individual GaAs nanorods grown Au seed-free on a Si[111] substrate. Due to the nanometer-sized x-ray beam, size and lattice parameters of individual nanorods could be measured and compared to the value obtained from the whole ensemble. Using the coherence properties of the focused beam we could observe speckle-like interference fringes in the surrounding of particular sensitive Bragg reflections which are a measure for the appearance of stacking faults within the nanorods. The separation of the speckles could be used to estimate the number of stacking faults and the size of the coherently scattering nanorod-segments.

KR 2.3 Tue 10:30 H9

Mechanical properties of single nanostructures investigated by in-situ AFM and micro-XRD — •Thomas Cornelius, Thomas Scheler, Rogerio Magalhães-Paniago, and Till Hartmut Metzger — ESRF, 38043 Grenoble Cedex, France

In recent years, nanostructures attracted enormous attention due to size-effects influencing the structural, optical, electrical, and mechanical properties of materials with low dimensions. Concerning the mechanical properties mainly the plastic regime was explored showing a trend that "smaller is stronger". In contrast, studies of the elastic behaviour of nanowires revealed contradictory results concerning the influence of size-effects on the elasticity. To investigate single nanoobjects in the elastic regime, we combined an in-situ AFM with XRD in a microfocused beam. The AFM is used to image the sample surface, to select an individual nanostructure, and to apply pressure on a chosen object. Due to the interaction between the AFM-tip and the compressed object the resonance frequency of the AFM force sensor shifts to larger values enabling us to derive the stiffness of the contact area. Simultaneous to the pressure application, XRD images around a pre-defined Bragg peak are recorded. These images allow for the determination of the elastic lattice parameter change in-situ. From the contact stiffness and the lattice parameter change, the Young modulus of an individual nanoobject is derived. Here, we will present results both for SiGe islands grown by liquid-phase epitaxy on Si wafers and GaAs nanorods created by selective-area metal organic vapor phase epitaxy on GaAs substrates.

KR 2.4 Tue 10:45 H9

Correlation of structure and conductance in nanowires and nanotubes — •Sibylle Gemming — Institute of Ion Beam Physics and Materials Research, FZ Dresden-Rossendorf, P.O. Box 51 01 19, D-01314 Dresden, Germany.

In nanostructured materials spatial confinement effects lead to structure-dependent deviations from the bulk transport properties. Such modifications may in part be accounted for by classical transport simulations, but a microscopically more detailed and mostly parameter-free picture is obtained from quantum-mechanical density-functional theory (DFT). DFT calculations yield the atom arrangement and electronic structure of nanotubes and nanowires in the electronic ground state. Additionally, an extension by a Green's function formalism leads to the determination and analysis of electronic transport through contacted nanostructures. A combination of both approaches allows to correlate structural and transport properties of nanostructures. The applicability of this approach will be demonstrated for a mechanically triggered metal-insulator transition in nanowires.

[1] Kibsgaard et al. *Nano Lett* **8** (2008) 3928; [2] Popov et al. *Nano Lett* **8** (2008) 4093.

KR 2.5 Tue 11:00 H9

The X-ray investigation of GaAs nanorods grown onto Si[111] substrate — •Antron Davydok[1], Andreas Biermanns[1], Ullrich Pietsch[1], Steffen Breuer[2], and Lutz Geelhaar[2] — [1]University of Siegen, Siege, Germany — [2]Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany

Nanorods (NR) are of particular interest due to the ability to synthesize single-crystalline 1D epitaxial structures and heterostructures in the nanometer range. It was found that nearly any AIIIBV semiconductor material can be grown as NRs onto another AIIIBV or group IV [111] substrate independent from lattice mismatch. We presented an X-ray characterization of GaAs NRs on Si [111] grown by gold-seed assist MBE method. We concentrated our research on 4 samples with different growth time: a) at 5s growth time several island but no NWs are found on the surface; b) at 60s first NWs appeared; c) at 150s the size of rods is increased; d) at 1800s many NWs occupy the whole surface. Using synchrotron radiation we have performed experiments in symmetrical and asymmetrical out-of plane scattering geometry and depth resolved grazing-incidence diffraction. Combining the results we were able to determine the strain gradient between wurzite like NR and zincblende substrate. Using particularly asymmetric wurzite-like reflections under coherent beam illumination we could quantify the number of stacking faults In the talk we present details of the analysis and first simulation results.

15 min. break

KR 2.6 Tue 11:30 H9

Inspection of single CdSe nanowires by use of microfocused x-ray diffraction — •Özgül Kurtuluş[1], Zhen Li[2], Bahia Arezki[3], Andreas Biermanns[3], and Ullrich Pietsch[3] — [1]Doguş University, Istanbul,Turkey — [2]University of Queensland, Brisbane, Australia — [3]University of Siegen, Siegen, Germany

The morphology of CdSe nanowires (NW) can easily be controlled by various growth methods. In this study, CdSe NWs are prepared by solution-liquid-solid (SLS) approach providing needle-shaped wires of about 60nm in diameter and several microns in length. To make x-ray single NW inspection possible, the NWs were dispersed in toluen and hexadecylamine, homogenized by centrifugation and finally spin-coated on silicon substrate. SEM images revealed that the NWs are randomly oriented with length axis parallel to the substrate. However, at selected areas, the distance between neighboured NWs is in the order of one micron. These samples were investigated by x-ray diffraction

using a 300nm x 600nm micro-focus at beamline ID1 of ESRF. Diffraction from 110W/2-20ZB basal plane was selected for single nanowire inspection. In order to measure various single objects subsequently, the sample was laterally scanned through the beam keeping the diffraction angle fixed. It was observed that the individual NWs differ slightly in peak position and peak width. From powder diffraction, it is known that NWs consist of an admixture of a wurtzite (W) and zinc-blende (ZB) structure units and the coherent illumination of sample by the micro-focus enables to visualize these zinc-blende and wurzite units seperated by stacking faults.

KR 2.7 Tue 11:45 H9

Nanolaminate's thermal conductivity at low temperatures — •Erik Mehner[1], Stefan Braun[2], Mathias Dörr[3], and Dirk C. Meyer[1] — [1]Institut für Strukturphysik, Technische Universität Dresden,D-01062 Dresden,Germany — [2]Fraunhofer IWS, Abteilung Röntgen-EUV-Optik Dresden — [3]Insitut für Festkörperphysik, Technische Universität Dresden,D-01062 Dresden,Germany

Due to their importance for application in solar cells and gas turbines thermal barrier coatings were investigated.

Current understanding of the heat conductivity between nanoscale interfaces is still incomplete and subject of ongoing scientific work. The 3-omega-method is a well established method for thin-film thermal conductivity measurements. [1]

First results of the implementation of a low temperature 3-omega-measurement which was devised to seperate phononic and electronic heat conduction with respect to the conception of an thermal barrier coating are presented. Likewise the morphological and structural aspects of the multilayer coatings, were included in design considerations. After the setup's qualification with glass-substrates W/Al2O3-multilayer samples were examined. Their thermal conductivity of 0,6 Watts per meter Kelvin at room temperature is confirmed. [2] Alternatively the system ZrO2/Al2O3 was investigated showing good suitability for thermal barrier coating up to at least temperature of 800°C.

[1] R. M. Costescu, David G. Cahill, F. H. Fabreguette, Z. A. Sechrist, and S. M. George. Science, 303(5660), 989-990, (2004)

[2] David G. Cahill. Rev. Sci. Instrum., 61(2), 802-808, (1989)

KR 2.8 Tue 12:00 H9

Polarization dependent Diffraction Anomalous Fine Structure of rutile TiO_2 001 and 111 reflections — •Matthias Zschornak[1,2], Carsten Richter[1], Hartmut Stöcker[1], Tilmann Leisegang[1], Sibylle Gemming[2], and Dirk C. Meyer[1,3] — [1]Nachwuchsgruppe Nanostrukturphysik, Institute of Structural Physics, TU Dresden, Germany — [2]Institute of Ion Beam Physics and Materials Research, FZ Dresden-Rossendorf, Germany — [3]Institute of Experimental Physics, TU Bergakademie Freiberg, Germany

Energy and polarization dependent *Diffraction Anomalous Fine Structure* (DAFS) also known as *Anisotropic Anomalous Scattering* (AAS) can be employed in addition to *X-ray Absorption Fine Structure* (XAFS) to study electronic transitions from core states to unoccupied states. Here, we present results from resonant X-ray diffraction experiments on TiO_2 rutile, space group (136) $P4_2/mnm$. For this model structure, site symmetry information was extracted from determination of the structure factor tensor by refining elements of Ti atomic scattering factor tensors. Influences of oxygen vacancies on the anomalous scattering contributions have been studied on a series of rutile wafers of different oxygen concentration. Samples investigated were $10 \times 10 \times 1$ mm^3 single crystal wafers and experiments were carried out at DESY/HASYLAB beamlines C and E2 using a Si (111) double crystal monochromator in the vicinity of the Ti-K absorption edge. Considered reflections include the 'forbidden' 001 and allowed 111 reflection.

KR 2.9 Tue 12:15 H9

Electric Field Induced Structural Modifications in Metal/$SrTiO_3$ Junctions and their Resistive Properties — •Hartmut Stöcker[1,2], Juliane Seibt[2], Florian Hanzig[2], Susi Wintz[2], Matthias Zschornak[1], and Dirk C. Meyer[2] — [1]TU Dresden, Institut für Strukturphysik, Zellescher Weg 16, 01062 Dresden — [2]TU Bergakademie Freiberg, Institut für Experimentelle Physik, Leipziger Straße 23, 09599 Freiberg

In oxides with perovskite-type of structure, mobile oxygen can cause the formation of non-stoichiometric regions when an electric field of sufficient strength (∼1000 V/mm) is applied. Our *in-situ* investigations of metal/$SrTiO_3$ junctions revealed reversible structural changes at room temperature caused by a systematic field-induced redistribution of oxygen. The investigations were carried out using wide-angle X-ray scattering, X-ray absorption spectroscopy, photoluminescence, nanoindentation and time-dependent electric I-U measurements.

Motivated by the successful use of $SrTiO_3$ with different doping metals for memory cells on the basis of resistive switching combined with the findings on the major importance of oxygen vacancy redistribution, we want to show the possibility of realizing a resistance change memory based on vacancy-doped $SrTiO_3$. The formation of corresponding metal/$SrTiO_3$ junctions in an electric field will be discussed as well as the switching between ohmic and Schottky-type resistive properties. A notable hysteresis in the I-U characteristics can be used to carry out Write, Read and Erase operations to test the memory cell properties of such junctions.

KR 2.10 Tue 12:30 H9

Microstructure study of gold-zirconia yolk-shell nanostructures using XRD line profile analysis — •Arti Dangwal Pandey[1], Robert Güttel[1], Matteo Leoni[2], Ferdi Schüth[1], and Claudia Weidenthaler[1] — [1]Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany — [2]University of Trento, Italy

The detailed microstructure study of gold nanoparticles encapsulated inside crystalline zirconia hollow-spheres is presented. This system is a potential nano-catalyst for CO-oxidation such as in automotive exhaust gas treatment.[1] The crystalline zirconia shell of 200 nm diameter separates the 15 nm gold nanoparticles from each other and provides high temperature stability to this system. To retrieve the microstructure details like size distribution, dislocation density, dislocation character, and defect content from the powder diffraction data of this two phase nanostructure system, we used whole powder pattern modeling (WPPM) for line profile analysis [2]. A series of diffraction and microscopic measurements were performed to investigate how the microstructure of these nanostructures evolves after some chemical and heat treatments. The observed variation in the crystallite size and defect contents after gold-leaching or quenching of the as prepared material from 900°C will be discussed in detail and the influence on the catalytic activity of gold nanoparticles will be presented.

1. P.M. Arnal, M. Comotti and F. Schüth, Angew. Chem. Int. Ed., 2006, 45, 8224.

2. Scardi P. and Leoni M., Acta Cryst. A, 2002, 58, 190-200.

KR 2.11 Tue 12:45 H9

Confocal Raman investigation of the zoning in synthetic $Ca(CO_3,CrO_4)$ crystals — •Alexander M. Gigler[1,2], Nuria Sanchez-Pastor[1], Guntram Jordan[1], and Wolfgang W. Schmahl[1,2] — [1]Section Crystallography, LMU-München, D-80333 München — [2]CeNS, LMU-München, D-80799 München

Due to its high mobility and toxic effects even in very low concentrations, hexavalent chromium (Cr^{6+}) is known as one of the most common environmental contaminants resulting from its widespread use in industrial applications.[1] Here, we present data on the crystallization of $CaCO_3$ in a silica hydrogel medium in the presence of different concentrations of Cr^{6+}.[2,3] Morphological changes in calcite correlate with chromium incorporation in its structure. This incorporation is evidenced by the appearance of new vibrational bands in the Raman spectrum, which are consistent with the substitution of carbonate groups by chromate groups. Therefore, chromium incorporation into calcite could be described as an anionic solid solution with a very limited maximum chromate concentration. By means of Raman microscopy, we observed a zoning of the crystals. The central region was chromium-rich, while pure calcite was present in the outer region due to a depletion of chromium in the gel. Incorporation of chromium into calcite may solve a major environmental problem, since toxic chromium can be rendered harmless.

[1] Katz, Salem: The Biological and Environmental Chemistry of Chromium, VCH, 1994. [2] Henisch: Crystal growth in gels, Dover Publ., 1996. [3] Cruz et al. Geochim. Cosmochim. Acta 73, A252, 2009.