Session V

Tuesday, September 6 - afternoon

I5

OPERANDO HIGH ENERGY SURFACE SENSITIVE X-RAY DIFFRACTION

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The atomic structure determination of surfaces and nano-objects under operando conditions is an important step towards tailoring their properties for applications in the field of heterogeneous catalysis or corrosion science. Recently significant progress towards faster surface sensitive x-ray characterization has been made by the use of higher energy x-rays in the 70 keV - 90 keV range [1,2].

I will discuss in my presentation the principles of surface sensitive high energy x-ray diffraction and I will elucidate in several examples why it is beneficial for operando studies: during ambient pressure CO oxidation over a Pd(100) single crystal the full 3D surface structure of the catalytically active phase could be determined in data recording times below 10 minutes [2,4]. The shape dependent sintering of Pt-Rh nanoparticles during CO oxidation can be monitored by instantaneous reciprocal space mapping [1]. A combinatorial sample design in combination with grazing incidence high energy x-ray diffraction allowed to identify a composition dependent oxidation mechanism for Pd-Rh nanoparticles on $MgAl_2O_4(100)$. With the advent of diffraction limited synchrotron light sources in the near future, improved nanofocussing of high energy x-ray beams will enable single nano object studies under operational conditions.

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C14

IN OPERANDO X-RAY CHARACTERIZATION OF NANOWIRE DEVICES

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To characterize strain in nanodevices it is important to measure complete devices, since the strain is affected by deposited metal and oxide films. In addition to these static effects, semiconductor devices in operation are exposed to high electric fields and temperatures. We demonstrate how in operando hard X-ray diffraction using a nanofocused beam can quantitatively measure both strain and bending in a nanowire device under electric bias, and how nanowires can be used as X-ray detectors.

Nanowire transistors were mounted in a special sample holder which allows simultaneous X-ray and electrical measurements, and characterized with nanofocused X-rays at the ESRF and PETRA-III synchrotrons. Scanning X-ray Bragg diffraction was performed with 100 nm real-space resolution along the nanowire axis, also behind the metal contacts. The 3D shape of the nanowire was reconstructed from the XRD data.

In the as-processed device, the strain was small but the nanowire was bent in an arch between the contacts. The device was then exposed to increasing bias voltages until breakdown, while simultaneously measuring the electrical current and performing scanning X-ray Bragg diffraction at each bias. We observed small and non-reversible bending at 2V bias. At higher bias voltages the arch gradually disappeared while the lattice constant changed in the contact regions. The structural changes were correlated with a reduction in electrical conductance [1].

Measurements with another nanowire device show that carriers generated by X-ray absorption increased the electrical conductance by five orders of magnitude. By 2D scanning the device, and measuring the current at constant electrical bias for each point, we created an image of the X-ray nanofocus with submicron resolution [2].

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bending in single nanowire device" *Adv. Mater.* **28** (9), 1788 (2016) http://dx.doi.org/10.1002/adma.201504188

2. J. Wallentin, M. Osterhoff, R. N. Wilke, K.-M. Persson, L.-E. Wernersson, M. Sprung, and T. Salditt, "Hard X-ray detection using a single 100 nm-diameter nanowire" *Nano Lett.* **14** (12), 7071 (2014) http://dx.doi.org/10.1021/nl5040545.

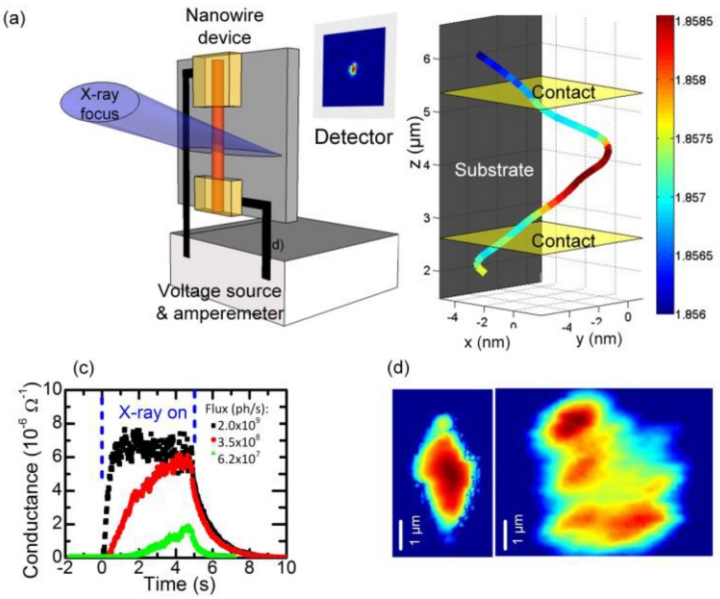

Figure 1. (a) Experimental setup, (b) 3D model of nanowire in the device [1], (c) Conductance of a nanowire device as function of time, for three different X-ray fluxes [2], (d) Imaging of a focused X-ray beam using the nanowire device, at (left) and 24 mm (right) after the nanofocus.

C15

GROWING SELF-CATALYSED GaAs NANOWIRES PROBED BY TIME-RESOLVED IN-SITU HIGH-RESOLUTION X-RAY DIFFRACTION

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Time-resolved X-ray measurements can provide valuable insight in the dynamics of the growth of semiconductor nanostructures as e.g. GaAs nanowires, in particular in the evolution of their crystallographic properties and their shape. Here, we report on the growth of self-catalysed GaAs nanowires onto Silicon (111) substrates using the portable molecular beam epitaxy setup of LAS/IPS [1] at KIT. These nanowires are grown by the vapor-liquid-solid mode using a liquid Ga-droplet as catalyst. We probe the crystallographic properties and the shape of the growing nanowires *in-situ* by means of time-resolved high-resolution X-ray diffraction.

The X-ray experiments have been performed at the P09 beamline of PETRA III at DESY, where the (311) and (220) zinc-blende and (10.3) wurtzite Bragg reflections have been monitored during growth.

We gain insight in the evolution of polytypism in self-catalyzed GaAs nanowires during growth. Further, we obtain information on radial growth processes of wurtzite and zinc-blende segments in the growing GaAs nanowires. In particular, we separate radial facet growth processes from tapering caused by an inflation of the liquid Ga droplet and compare the findings with ex-situ SEM and theoretical growth models.

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C16

SYNCHROTRON X-RAY BRAGG DIFFRACTION IMAGING TECHNIQUES TO CHARACTERISE ICE DISTORTION UNDER LOADING

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The way ice distorts under an external force is an important topic for both mechanics (because ice is an example of very anisotropic solids [1]), and environmental science. Indeed strain and orientation heterogeneities occur in each of the crystallites of polycrystalline ice when submitted to applied stresses. These intra-granular inhomogeneities, as well as the interactions of dislocations with grain boundaries [2], play an important role in processes like yielding, creep, recrystallisation or fracture. We investigated, at the ESRF beamline BM05, a high crystalline quality tricrystal of ice (initial dislocation density less than 100 cm/cm^3), which constitutes the simplest model for a polycrystal. This tricrystal was submitted, within a specially designed cold cell, to several steps of compression.

A first, qualitative, approach, was carried out by using white beam diffraction topography, which allows following the movement and multiplication of the dislocations at the inception of the deformation. Their velocity was found to be in the 0.5 - 1 ms^{-1} range at -10 °C under a compression stress of 0.3 MPa, in agreement with the order of magnitude of the mobility of dislocations in ice found in the literature [3]. The dislocation density increases during loading, and stress concentrations occur at the level of grainb boundaries: they appear as areas of increased diffracted intensity ('black', with the usual convention) on the

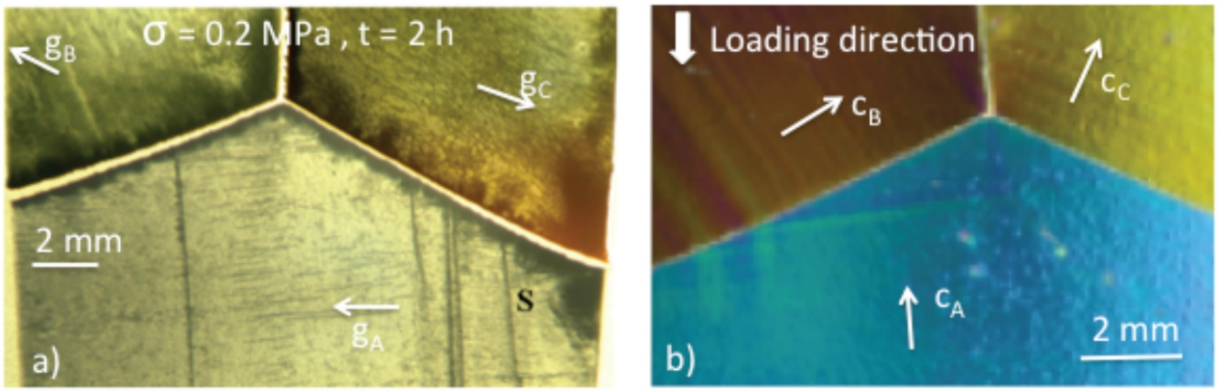

Figure 1. a) Bragg diffraction composite image (the reflection used is different for the different grains, but the images are simultaneous) of the deformation of an ice tri-crystal under a compression of 0.2 MPa. b) Photo taken with polarised light. The projection of the c-axis of each grain on the plane is indicated by the arrows. The c-axes are perpendicular to the basal slip lines.

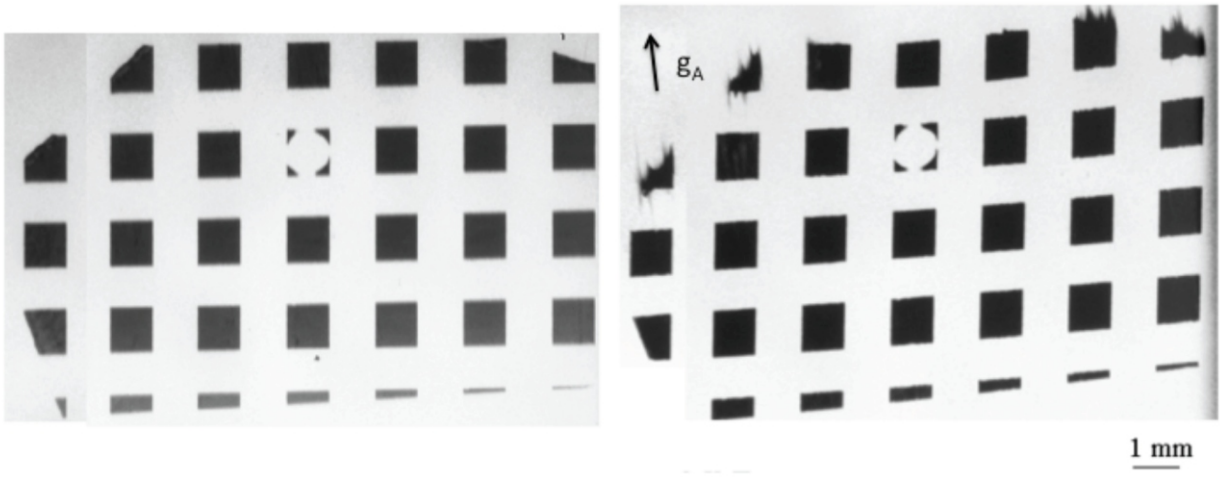

Figure 2. Example of the measurement of the curvature field map (which is directly related to the geometrically necessary dislocation density map) through the use of "reticulography": a tungsten grid located in front of the crystal lead to a number of spatially independent Bragg spots (in this case corresponding to the (1-100) reflecting planes), allowing measuring the variation of position/orientation of the areas imaged on these spots in the deformed state with respect to the position in the initial (non-deformed) one.

composite topograph shown on Fig. 1a. At the beginning of loading, the black regions appear to be related to the internal elastic strain since they disappear when the external load is removed. However, after the specimen has been loaded for some time then unloaded, the topographs still exhibit black areas at the grain boundaries, suggesting that this distortion is related to the dislocations piling up at the level of the grains, as already observed in the Fe-Si bicrystal case [4]. The orientation of the grains (fig1b) determines their degree of strain compatibility: if the two grains have a-axes in the same direction, they behave as "strain-compatible", because the Burgers vectors of the basal dislocations in both grains are parallel to each other. We observe distortions associated with the energy stored by the dislocation piling up, which are stronger for grains where the dislocation Burgers vectors are not compatible than for those where they are.

More quantitative results were obtained by using 3D-RCI [5], which combines rocking curve imaging with section and pinhole topography, in order to measure lattice distortions in all three spatial dimensions. This 3D-RCI method allowed quantifying the lattice orientations with a spatial voxel of about 50 × 50 × 50 m^3, and an angular resolution is in the few radians range. 3D-RCI is a sophisticated and powerful technique, but, as it rests on the assumption that an elementary volume in the crystal always diffract on a given pixel of the detector (size p), it can only be applied when the local mosaic spread of this elementary volume is such that < p / (2D sin), where D is the sample-to-detector distance. This leads, with our usual experimental conditions, to a limit 1 mrad) which remains low with respect to the distortions that are important to investigate.

Another technique, "reticulography" [6], allows characterising distortions induced under higher or longer compressions. It implies locating an absorbing grid in front of the sample, to split the beam into a series of sub-beams. Each diffraction spot is thus split into sub-regions. By pointing the grid nodes on the topographic image obtained by using various reflecting lattice planes (at least two), it is possible to obtain the components of the diffraction vectors, and consequently the crystallographic orientation at each node. An example of application of reticulography is presented on Figure 2.

These two techniques (3D-RCI for the lower statesof distortion, and reticulography) were used to measure the crystalline orientation in a whole grain volume. From these experimental results we have calculated the gradient of lattice rotation, and estimated the curvature tensor field in the grain. This later tensor allows reaching the density of "geometrically necessary dislocations"[7], which is directly related to the viscoplastic deformation of the crystalline material. To our knowledge no experimental results as these ones have been published up to now. These results are very promising, but have to be improved both for RCI (where an enhanced stability is required) and reticulography (where the grid size must be reduced), if we wish acquiring measurements of the strong strain gradients that occur in ice, which are actually useful for the mechanical simulations that are developing nowadays.

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C17

HIGH-ENERGY LOW-DOSE MAMMOGRAPHY USING EDGE ILLUMINATION X-RAY PHASE-CONTRAST IMAGING

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Edge illumination (EI) is an X-ray phase-contrast imaging (XPCI) technique that has been under intensive development at University College London (UK) in recent years. Besides being applicable at synchrotron radiation facilities [1], EI was also demonstrated to be compatible with table-top setups based on non-microfocal X-ray tubes [2]. In fact, EI is insensitive to both beam polychromaticity and relatively large source sizes (up to at least 100 μm). This directly follows from the incoherent nature of the method, which in fact can be described accurately through simple geometrical optics.

The goal of this study was to demonstrate that EI, when used at X-ray energies much larger than those employed in clinical practice, enables the achievement of very low

doses in mammography. Since the first days of XPCI, mammography has been considered as one of the most important candidates for a clinical application [3]. In fact, the imaging of breast can greatly benefit from soft tissue contrast improvements and/or from radiation dose reductions provided by XPCI.

In order to achieve this aim, a proof-of-principle experiment was performed at the European Synchrotron Radiation Facility (ESRF, France), on excised human breast specimens. A photon-counting detector achieving almost 100% efficiency at high X-ray energies was used in order to minimize the image noise. Moreover, a new retrieval algorithm capable of extracting the phase shift from a single EI image was exploited to process the acquired images [4]. This method presents the twofold advantage of being stable with respect to noise (thus allowing further dose reductions) [5] and of needing only one input image, thus significantly simplifying and speeding up the acquisition. Importantly, although this proof-of-principle study was carried out with synchrotron radiation, the method has potential for an application in table-top setups, which represents an essential requirement for any future clinical implementation.

In this talk, we will first introduce the EI technique and its main features. We will then present the recently developed single-image retrieval algorithm and the pilot experiment carried out at the ESRF, and suggest ways to exploit these results for potential future clinical applications.

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Session VI

Tuesday, September 6 - afternoon

I6

SYNCHROTRON-BASED X-RAY STRUCTURAL ANALYSIS OF FUNCTIONAL MATERIALS TOWARDS CATALYTIC STRUCTURE-ACTIVITY RELATIONSHIPS

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Heterogeneous catalysis plays a significant role in chemical industry. To arrive at a knowledge-based catalyst design, fundamental insight into relations between structure and catalytic properties, such as activity, selectivity and stability, is needed. During this lecture, examples from recent work at ESRF beamlines ID01 and ID03 will be discussed. Three showcase applications from the field of heterogeneous model catalysis will be highlighted.

1) Zeolites are commonly used as solid acid catalysts in many large scale industrial processes, such as the Methanol-to-Hydrocarbons process. Zeolite H-ZSM-5 is a well-known candidate and has been studied extensively because of its intriguing 3D intergrowth structure. We have applied micro-focused X-ray diffraction imaging at higher order Bragg reflections to unravel the intergrowth pattern of individual large H-ZSM-5 crystals [1]. Additionally, information about aluminium zoning, which sensitively impacts on catalytic properties, could be obtained based on subtle changes of the lattice constants. Recently, we extended the μXRD approach by coupling optical detection of X-ray excited optical fluorescence (XEOF) of labelled H-ZSM-5 crystals [2]. Recording XEOF of styrene oligomers as a Brřnsted acid site specific label together with μXRD response led to the simultaneous characterization of local crystallinity and the presence and nature of catalytically active sites.

2) *Operando* surface X-ray scattering experiments under electrochemical conditions have been carried out to arrive at catalytic structure-activity relationships for single crystal (here Pt(111)) model electrodes [3]. In this experiment, SXRD, XRR and GISAXS have been applied together with On-Line-Electrochemical Mass Spectrometry (OLEMS) to study the influence of surface structural changes on activity of the model electrode in hydrogen and oxygen evolution reactions. OLEMS adds chemical specificity to electrochemically measured currents and plays to its strength when reactions with a selectivity dimension are studied.

3) Most recently, nanocrystal model catalysts have been introduced for *in-situ* studies of individual nanoparticle catalysis. Real space structure and strain distribution is studied by Coherent X-ray Diffraction Imaging (CXDI). *In-situ* cells for both heterogeneous gas phase catalysis and electrocatalysis have been constructed and successfully applied; showcases from both field will be highlighted.