Session I

Monday, September 4 - afternoon

I1

MICROSTRUCTURE AND FUNCTIONALITY OF MATERIALS INTERFACES

J. Keckes

Department of Materials Physics, Montanuniversität Leoben and Erich Schmid Institute for Materials Science, Austrian Academy of Sciences, A-8700 Leoben, Austria
jozef.keckes@gmail.com

Although interfaces represent only a small volume fraction of biological and man-made materials, their influence on functional properties like fracture toughness, hardness and overall mechanical integrity is decisive. In this contribution, the relationship between microstructure and mechanical properties of interface-based materials like wood, multilayered thin films and ceramic nanocomposites is discussed on the bases of experimental data, obtained using synchrotron X-ray diffraction and transmission electron microscopy techniques. The results demonstrate that using clever microstructural and interface design it is possible to enhance mechanical properties of materials significantly.

First, the microstructure of a macroscopic branch-stem interface of Norway spruce is analysed using wide-angle X-ray diffraction and evaluated magnitudes of the microfibril angle are correlated with various protective mechanisms operating at different length scales . It is demonstrated that wood adjusts the cellulose fibre texture in order to protect both the stem and the branch from structural damage.

In order to understand the functionality of micro- and nano-scopic interfaces, cross-sectional synchrotron X-ray nanodiffraction experiments on thin films are performed at ID13 and P03 beamlines of ESRF and Petra III, respectively. By comparing cross-sectional distributions of phases, texture, crystallite size and strains, it is possible to understand the influence of distinct thin film regions on the overall and local mechanical response of the films. In-situ diffraction experiments combined with indentation are used to determine microstructural changes and stress concentrations accompanying various fracture modes .
Finally, a combinatorial refinement of microstructure, property and process conditions at graded TiAlN thin film cross-sections is performed using X-ray nanodiffraction in order to identify interface microstructures with the highest hardness. The micromechanical and X-ray diffraction experiments are performed iteratively in three steps and are applied as a basis to design novel types of coating materials.

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2. J. Keckes, M. Bartosik, R. Daniel, C. Mitterer, G. Maier, W. Ecker, J. Vila-Comamala, C. David, S. Schoeder, M. Burghammer, *Scr. Mater.* **67** (2012) 748–751.
3. A. Zeilinger, J. Todt, C. Krywka, M. Müller, W. Ecker, B. Sartory, M. Meindlhumer, M. Stefenelli, R. Daniel, C. Mitterer, J. Keckes, *Sci. Rep.* **6** (2016) 22670.

C1

XRD VS. PHOTOLUMINESCENCE A NEW CLASS OF DEVICES TO CALIBRATE DEFORMATION POTENTIALS

D. Ziss[1], J. Martín-Sánchez[1], T. Lettner[1], R. Trotta[1], J. Stangl[1], A. Rastelli[1], G. Piredda[2], J. Edlinger[2], G. Trevisi[3]

[1]Institute of Semiconductor Physics, JKU, Altenbergerstr. 69, 4040 Linz, Austria
[2]Research Center for Microtechnology, FH Vorarlberg, 6850 Dornbirn, Austria
[3]IMEM - CNR Institute, Parco Area delle Scienze 37/a, 43124 Parma, Italy
dorian.ziss@jku.at

In the last several years many methods have been established to manipulate the optical properties of III-V semiconductors which are a very promising material class for non-classic quantum light sources [1]. One highly effective possibility to change their band structure (e.g. order of LH/HH bands), which defines the optical properties, is to get full control of the strain/stress tensor. The deformation potentials describe the changes in the band structure upon variation of the applied strain.

A versatile way to control the strain state is to bond a semiconductor membrane onto a piezoelectric carrier material. By applying an electrical field to the carrier and therefore, making use of the inverse piezoelectric effect, strain acts on the membrane. This approach has already

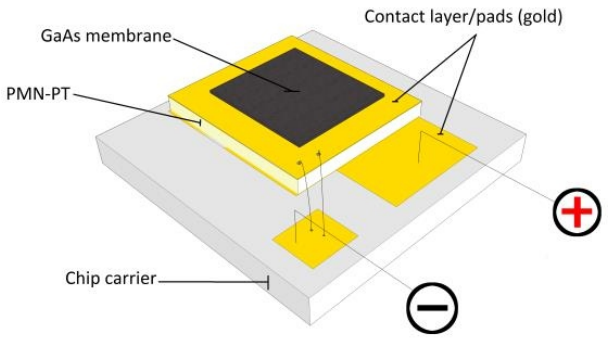

Figure 1. Schematic representation of the device for straining the GaAs membrane. The gold layers on the top and the bottom side of the piezoelectric carrier (PMN-PT) were used to apply a homogenous electric field.

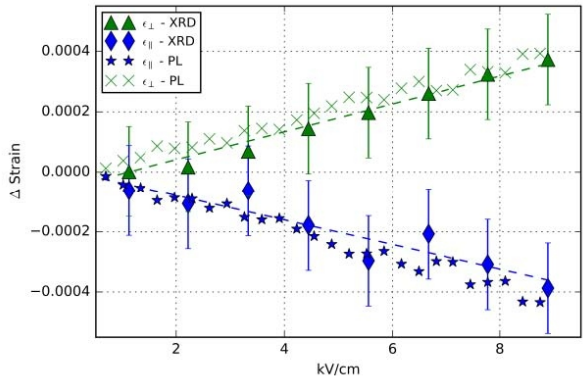

Figure 2. In-plane (♦,★) and out-of-plane (^,×) strain components of GaAs measured with XRD and calculated from PL line shifts (using a=-8.75eV). The pre-strain is set to 0. Thus the strain value at 0 kV/cm defines the offset for all following values.

been used to change the optical properties of GaAs and the embedded quantum dots on top of the carrier. Such devices (schematically shown in Fig. 1) have been fully characterized by the change in the photoluminescence (PL) spectra for a varying electrical field applied to the piezoelectric carrier [2]. Looking carefully at these PL changes, one is able to recalculate the strain tensor, yet these calculations sensitively depend on the accurate knowledge of the deformation potentials (*a* is the hydrostatic and *b, d* are called the shear potentials). The literature values for these deformation potentials vary in a rather wide range, depending on the applied calibration method (experimentally or theoretical calculation) [3]. To overcome the problem of uncertainties in the deformation potentials, we now investigated the strained GaAs in-situ by X-ray diffraction (XRD), while sweeping the electrical field. Information about the strain in the GaAs membrane, and the piezo carrier was acquired simultaneously. This allows a direct comparison of the strain tensor calculated from the PL shift and the physical strain induced in the material, see Fig. 2. Thus, by combining the results from both techniques we can finally re-define the deformation potentials.

The big advantage in using piezoelectric straining devices is the possibility to continuously tune the strain from a minimum value given by the pre-strain induced during processing of the device up to a strain of 1-2% with advanced geometries of the carrier material. Furthermore, this technique is not limited to GaAs, in principal strain can be applied in this way to every material.

We present first results on the relation of PL line-shifts with measured strain values from XRD comparing different device geometries and re-calculating the deformation potentials by comparing the results acquired by both methods.

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2. J. D. Plumhof, R. Trotta, V. Křápek, E. Zallo, P. Atkinson, S. Kumar, A. Rastelli, and O. G. Schmidt, *PHYSICAL REVIEW B 87*, 075311 (2013) .
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C2

X-RAY NANOBEAMS FOR NITRIDE WIRES

J. Eymery[1,2], A. Messanvi[1,2,3], C. Durand[1,2], M. Tchernycheva[3], F. Julien[3], M. Elzo Aizarna[1,2], G. Martinez-Criado[4], D. Salomon[4], M.-I. Richard[5,4], S. Labat[5], O. Thomas[5], T. Cornélius[5], O. Mandula[6], V. Favre-Nicolin[1,2,4]

[1]University Grenoble Alpes, CEA, INAC-SP2M, F-38000 Grenoble, France
[2]CEA-INAC, 17 rue des Martyrs, 38054 Grenoble Cedex, France
[3]IEF, UMR 8622 CNRS, Université Paris Sud, Orsay, France
[4]European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France
[5]Aix Marseille University, CNRS, IM2NP UMR 7334, 13397 Marseille, France
[6]Fondation Nanoscience, 23 Rue des Martyrs, 38000 Grenoble, France
[7]Institut Universitaire de France, Paris, France
joel.eymery@cea.fr

One-dimensional nitride heterostructures demonstrated novel optical and electronic properties making use of quantum confinement effects and strain engineering. The emergence of disruptive functionalities is now related to the growth and technology controls [1], but also to the development of advanced characterization techniques having high spatial resolution. To complement the information provided by grazing incidence diffraction techniques, the use of focused micro/nano X-ray beams provides innovative solutions to analyse quantitatively the morphology, defects, strain and composition of these materials. This will be illustrated in this paper by recent breakthroughs obtained at the European synchrotron radiation facility (ESRF) with the study of nitride wires and their core-shell heterostructures grown by Metal Organic Vapour Phase Epitaxy.

First, it will be shown how the structure of single defects such as Inversion Domain Boundaries (IDB) inside n-doped GaN wires can be extracted from the *X-ray coherent diffraction imaging* with a monochromatic beam [2] with an unprecedented accuracy. The complex 3D IDB configuration inside a single wire can be measured without any slicing in contrast to electron microscopy and the lattice displacements along/across the wire length deduced from the analysis of the intensity of several Bragg peaks by *phase retrieval* methods (with pm resolution) will be shown to be in full agreement with electronic structure *ab initio* calculations [3].

Then, GaN/InGaN Multiple Quantum Well (MQW) core-shell heterostructure grown on the m-plane sidewalls of c-axis GaN wires [2,3] will be analysed by multimodal hard X-ray nanoprobe to perform *X-ray excited optical luminescence* (XEOL) and *X-ray Fluorescence* (XRF) [4]. The localized blue light emission can be measured in the spatiotemporal domain with 50 ps resolution to get the photoluminescence time decay (100 ps) that can be related the electron confinement/local composition in the wire [4]. These techniques will be also applied on connected wire-LED devices to evidence fluctuations of XEOL and X-ray Beam Induced Current (XBIC).

More generally, the interest of these statistical/fluctuation mappings in nitride optoelectronic devices with a nanometre beam will be presented, as well as new XANES spectroscopy results. This work will be extended to other heterostructures such as GaN/AlInN MQW tubes (*i.e.* etched wires) dedicated to UV emission.

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2. S. Labat et al., *ACS Nano,* **9**, (2015), 9210.
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4. G. Martinez-Criado *et al., Adv. Mater.* **26** (2014), 7873-7879.

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C3

X-RAY DIFFRACTION STUDY OF STRAIN RELAXATION IN COALESCED GaN NANOWIRES

V. Kaganer, B. Jenichen, O. Brandt

Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany
kaganer@pdi-berlin.de

GaN nanowires form spontaneously on various substrates without requiring a metal droplet to induce growth. A decisive advantage of this spontaneous formation is the possibility to synthesize abrupt axial heterojunctions. However, the spontaneous formation inevitably results in dense arrays, and thus in subsequent nanowire coalescence during growth [see Fig. 1(a)]. We have found that the process of coalescence is governed by nanowire bundling, which reduces the surface energy of the side facets at the expense of elastic bending energy [1]. In the present work, we study the strain state of GaN nanowire ensembles by laboratory X-ray diffractometry in conjunction with an analysis of the energetics of nanowire bundling. Our results demonstrate that the elastic bending of nanowires caused by their bundling gives rise to a large elastic strain, which is reduced plastically via the creation of dislocation walls at the joints.

The shape of the bundled nanowires in Fig. 1(b) and the elastic energy of bending are deduced in the framework of the elasticity of thin rods. Alternatively, dislocations at the joints form small angle boundaries, as shown in Fig. 1(c). This introduction of dislocations is found to significantly reduce the total energy of the bundle. The relative misorientation of the nanowires at the joint due to the small-angle boundary reduces the nanowire curvature by an order of magnitude and hence gives rise to narrower diffraction lines.

The X-ray diffraction intensity is produced by the whole volume of a nanowire ensemble, while the volume of the joints containing dislocations is only a small fraction of this volume. As a result, x-ray diffraction reveals mainly the residual bending of the nanowires due to their bundling, but is insensitive to details of plastic relaxation at the joints. Figure 2(a) compares the experimental X-ray diffraction profiles from a spontaneously formed GaN nanowire ensemble on Si(111) in successive reflection orders [2] with the calculated profiles. The calculation is performed with a Monte Carlo average over random lengths, diameters, and distances between nanowires, as well as random orientations of the bundled pairs. We also take into account the vertical divergence of the X-ray beam in a laboratory diffraction experiment, which gives rise to the asymmetry of the profiles [2] observed in Fig. 2(a). The shapes of the tails of the calculated diffraction profiles well agree with the observed ones, which confirms the inhomogeneous bending of the bundled nanowires as a main source of the x-ray scattering.

An agreement between calculated and observed diffraction profiles is obtained with a broad and asymmetric distribution of the lengths of bundled segments, as shown in Fig. 2(b). We describe this asymmetry by log-normal distributions with comparable mean value and standard deviation, which makes shorter segments more probable. Symmetric distributions, such as Gaussians, do not provide an agreement with the experiment. The effective distances between bundled nanowires in Fig. 2(d) are notably smaller than the real distances. Hence, a partial relaxation of the bending energy by dislocations at the joints takes place, which may be limited by the difficulty to introduce dislocations when atomically flat facets of the two nanowires merge. Our X-ray diffraction experiments show that a major part of the elastic bending energy of the nanowires is released by creation of dislocations at the coalescence joints.

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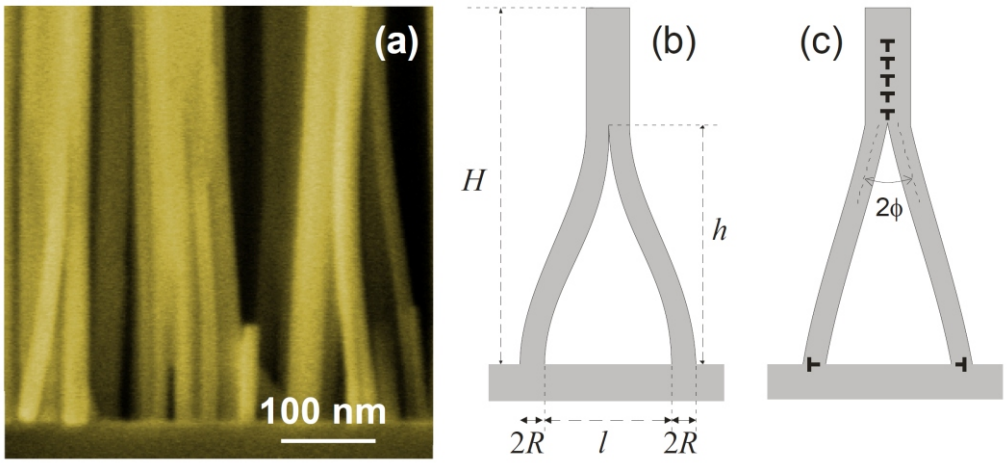

Figure 1. (a) Bottom part of coalesced nanowires, (b) coalescence by bending, (c) coalescence with creation of dislocations at the joints.

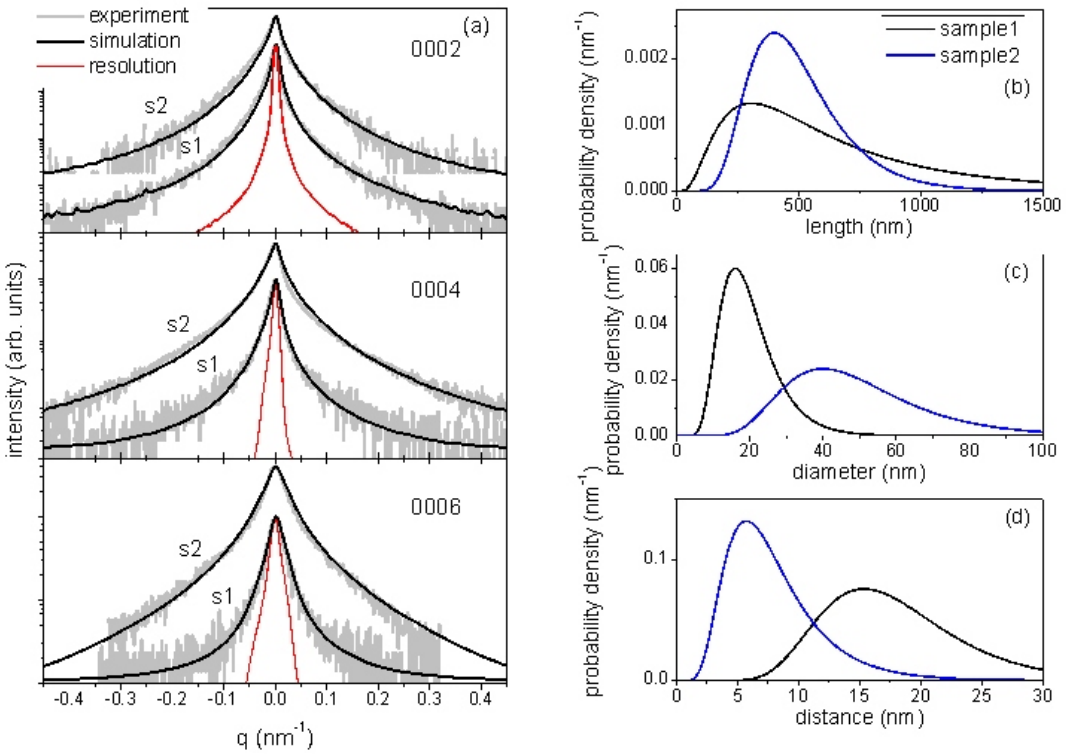

Figure 2. Measured and calculated X-ray diffraction profiles in successive reflection orders (a) and probability density distributions of the lengths of the bundled segments (b), nanowire diameters (c), and distances at the base of bundled segments (d) used in the Monte Carlo calculations.

2. V. M. Kaganer, B. Jenichen, O. Brandt, S. Fernández-Garrido, P. Dogan, L. Geelhaar, H. Riechert, *Phys. Rev. B* **86**, (2012), 115325.

C4

SCATTERING FROM FERROELECTRIC DOMAINS IN STRAINED (K, Na)NbO_3 EPITAXIAL FILMS ON (110) $TbScO_3$ SUBSTRATE

M. Schmidbauer[1], D. Braun[1], A. Kwasniewski[1], M. Hanke[2], L. von Helden[1], J. Schwarzkopf[1]

[1]Leibniz-Institute for Crystal Growth, Max-Born-Str. 2, D-12489 Berlin, Germany
[2]Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, D-10117 Berlin, Germany
martin.schmidbauer@ikz-berlin.de

Oxides with perovskite-like structure represent a fascinating class of advanced materials which have been extensively studied in the past decades since they exhibit a variety of functionalities, e.g., ferromagnetism, ferroelectricity or ferroelasticity. In ferroelectric materials phase symmetry and structural distortions are strongly coupled to piezoelectric properties. Periodic domain structures are of particular interest from both fundamental and technological point of view. Such periodic polarization modulations on a nanometre scale can be engineered by the use of substrates with suitable (anisotropic) misfit strains. However, understanding and controlling of ferroelectric phases and dimensions of the domain pattern is still hallenging.

We focus on $K_{0.75}Na_{0.25}NbO_3$ thin films grown on (110) $TbScO_3$ orthorhombic substrates using metal-organic chemical vapour deposition. A highly regular one dimensional ferroelectric domains pattern is formed which extends over several micrometres with a lateral periodicity of 50 nm (Fig.1a). The monoclinic symmetry of the domains is controlled by the anisotropic epitaxial lattice strain, which is highly compressive in one in-plane direction and weakly tensile in the corresponding orthogonal direction. Using piezoresponse force microscopy (PFM) and X-ray diffraction (Fig.1c,d) the monoclinic M_A phase is identified, which is associated with both a strong vertical and lateral electrical polarization component. The lateral

component of the polarization vector is collinear with the ± $[-110]_{pc}$ shear direction of the pseudocubic (pc) unit cell of the film and periodically changes by 180° in adjacent domains.

A structural variant of a 90° rotated M_A domain pattern, where the monoclinic distortion of the pseudocubic unit cells occurs along ± $[110]_{pc}$ is also observed (Fig.1b). However, this variant appears with significantly lower probability in agreement with energy considerations based on linear elasticity theory and cannot be independently resolved in a conventional X-ray diffraction experiment as shown in Fig.1c. Nevertheless, a 100 nm-focus experiment recently carried out at ID01 beamline (ESRF) could be used to individually investigate the two domain variants. Distinct differences between the 0° variant and the 90° variant were observed and will be discussed.

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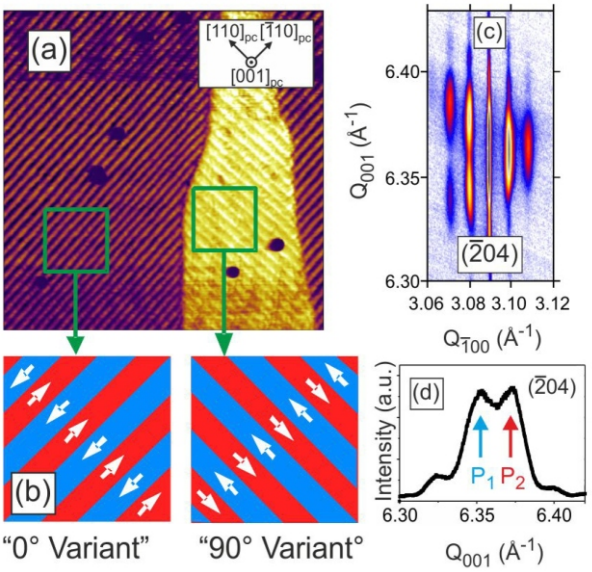

Figure 1. (a) Lateral PFM image (2 m x 2 m) of a 30 nm $K_{0.75}Na_{0.25}NbO_3$ film grown on (110) $TbScO_3$, (b) models of 0° and 90° variants (white arrows indicate the in-plane component of the polarization vector), (c) out-of-plane x-ray diffraction and, (d) section along the CTR at Q_{-100} = 3.09 $Å^{-1}$ (adapted from [1]).

Session II

Monday, September 4 - afternoon

I2

X-RAY PHASE-CONTRAST IN VIVO TOMOGRAPHY

Julian Moosmann

Helmholtz-Zentrum Geesthacht, Institute of Materials Research Metallic Biomaterials, Max-Planck-Str. 1, Geesthacht, 21502 Germany

Four-dimensional imaging techniques are essential tools in biology to understand the behaviour of cells during embryonic development. Here, we apply X-ray phase-contrast microtomography to capture the early development of the African clawed frog (Xenopus laevis), an important vertebrate model organism, over the course of time and in 3D. Early developmental stages of the Xenopus frog are optically opaque and lack conventional X-ray absorption contrast. For hard X-rays such embryos essentially are pure-phase objects. The probing wave front is thus characterised by a 2D phase map representing the projection of the object along the X-ray beam. Employing quasi-monochromatic and spatially coherent X-rays, we thus use propagation-based phase-contrast.

In Fresnel theory, the formation of 2D intensity contrast upon free-space propagation from a given phase map is studied and how linear approximations to the inverse problem of phase retrieval from a single-distance intensity measurement break down for large propagation distances and strong phase variations. Important properties of linear contrast transfer, which are conserved for a wide range of phase variations and propagation distances, are exploited in order to devise a phase-retrieval method which exhibits a high spatial resolution and contrast at low photon statistics.

Constraints imposed by in vivo imaging are discussed and results from experiments on living Xenopus embryos are presented.