MS23-O4 X-ray nano-diffraction of semiconductor nano-structures for photonic and electronic applications

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The last 20 years have seen a massive development of crystalline structures with sub-micrometer sizes, either with a simple miniaturization goal, or in order to exploit quantum confinement effects. The study of these objects is a challenge for crystallographers, as their size implies a weak, dif- fuse scattering rather than sharp Bragg peaks. Moreover, nano-structures, either due to the synthesis method or by design, are often heterogeneous and therefore present inhomogeneous strain and com- position 3D fields.

Thanks to the development of focused X-ray optics, it is now possible to measure the scattering from single nano-objects using X-ray Coherent Diffraction Imaging (XCDI) [1,2] and Ptychography. When used in the Bragg geometry, it allows not only to recover the shape (electronic density), but also the deformation field relatively to a perfect lattice, in the case of an inhomogeneous strain. We will illustrate the use of X-ray nanobeams on single homogeneous and heterogeneous nano- structures [3,4,5] used for photonic (single photon emission) and electronic (strained silicon-on- insulator) applications, and discuss the current performance, limits and prospects of the method.

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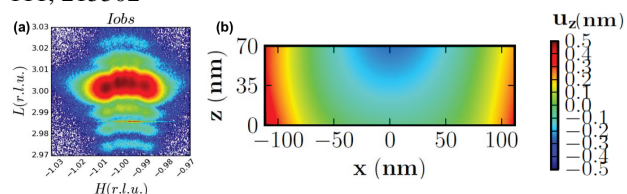**Figure 1.** (a) Coherent diffraction pattern from a single strained Silicon-On-Insulator (sSOI) line, with a 225×70 nm2 cross-section. The curved shape is due to the bending of the strained line. (b) the displacement field refined for this line using the diffraction pattern.[5]

Keywords: Nanostructures, coherent diffraction, semiconductor

MS23-O5 Solvent-nanoparticle interfaces – source of solvent restructuring in solvation shells and disorder in nanoparticles

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Pair distribution function (PDF) measurements have originally been used to study the structure of liquids and glasses. [1] Almost forgotten since, the method experienced a revival with increasing interest in nanoparticles and in situ studies of chemical reactions, where common x-ray diffraction fails. [2] To our knowledge, all previous in-situ PDF studies were undertaken in either aqueous or supercritical solvents [3], although manifold nanoparticle syntheses use organic solvents. The drawback to study nucleation in organic solvents are the direct implications of using them. Not only do they scatter x-rays stronger than water, but more importantly organic molecules possess several internal interatomic distances as well as feature pronounced intermolecular ordering within the bulk solvent. [1] In highly diluted systems as often found in nanoparticle nucleation, these intra- and intermolecular distances of the solvent molecules contribute to more than 99% of the overall signal in the experimental PDFs. The extraction of the nanoparticle signal hence requires understanding of the organic solvent. It has been theoretically predicted, that solvent molecules restructure at nanoparticle surfaces inside a nanoscopic solvation shell. [4] Within a well-chosen matrix of dispersed nanoparticles (ZnO, TiO_2, ZrO_2, Ag) in the primary alcohols methanol to 1-propanol as well as in nonpolar hexane, we could for the first time experimentally proof this restructuring effect at solvent-nanoparticle interfaces. The rearrangement of molecules reaches out as far as 2 nm into the bulk liquid and decays exponentially, see Fig. 1. [5] The interaction of the solvent molecules with the nanoparticle surface does, however, also influence the internal nanoparticle structure during nucleation. In reactions with high supersaturation, surface-bond ligand molecules trap the disorder within the particles before crystalline order is established. We show how different organic ligand molecules influence the crystallization process and that obviously gradual dynamic exchange processes of ligand and solvent molecules at the nanoparticle surface enable relaxation into a crystalline particle.

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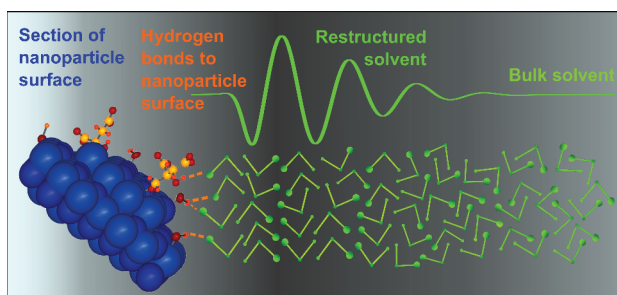[5] Zobel, M., et al, *Science* **347** (2015), 292

Figure 1. Solvent restructuring of ethanol at a ZnO nanoparticle interface (hydrogen atoms omitted for clarity) and resulting density oscillation observable by PDF. [5]

Keywords: nanoscopic solvation shell; nanoparticle; organic solvents;

MS24. Short range order and diffuse scattering

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MS24-O1 Short-range order in cubic $RbNbWO_6$ and phase transition to tetragonal phase. Interpretation of X-ray diffuse scattering using group theory approach

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A complex scheme of atomic displacements (modes; cf. Perez-Mato et al. [1]) that break the *Fd*-3*m* symmetry of the high-temperature (T_c > 395 K) cubic phase of $RbNbWO_6$ and ultimately lead to a phase transition to the tetragonal phase was determined using the group theory approach (program MODY [2]). The resulting set of modes was used to construct a model of the disordered crystal that provides diffuse scattering (calculated with DISCUS program from DIFFUSE package [3]) that is consistent with the experimental results. Particularly characteristic extinctions are well reproduced (cf. Withers et al. [4]).

The resulting solution reveals a disordered structure of cubic $RbNbWO_6$, which is a system of intersecting {111}-type planes in which Nb/W atoms (statistically occupying centers of oxygen octahedra) are shifted along three symmetry-equivalent ⟨110⟩ directions parallel to these planes. Oxygen atoms also move in a characteristic manner, but their shifts are considerably smaller and do not substantially affect the diffuse scattering pattern. The movements of Rb atoms are large but uncorrelated.

The obtained picture of the local structure of cubic $RbNbWO_6$ makes it necessary to change the interpretation of existing physical measurements, particularly dielectric measurement. Furthermore, the determined structure of the low-temperature tetragonal phase that exists below 395 K was found to be non-polar (*I*-42*d* space group).

Group theory analysis provides a coherent picture of the phase transition from the disordered cubic phase to the ordered tetragonal phase. At T_c, in a multimodal crystal of the high-temperature phase, mode symmetry breaking occurs, and each of the four displacive modes is decomposed: only 1/4 of the atoms of every mode of k =