Session IX

Wednesday, September 7 - afternoon

I9

FROM GLOBAL AND LOCAL Ge INTEGRATION APPROACHES ON Si(001): NOVEL INSIGHTS BY ADVANCED SYNCHROTRON-BASED SCANNING XRD

M. H. Zoellner[1,*], G. Chahine[2], M.-I. Richard[2,3], P. Zaumseil[1], C. Reich[1], M. Häberlen[4], G. Capellini[1], F. Montalenti[5], A. Marzegalli[5], P. Storck[4], T. U. Schülli[2], and T. Schroeder[1,6]

[1]IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany
[2]European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France
[3]Aix-Marseille Université, CNRS, IM2NP UMR 7334, 13397 Marseille, France
[4]Siltronic AG, Hans-Seidel-Platz 4, 81737 München, Germany
[5]Dipartimento di Scienza dei Materiali, Universita B degli Studi di Milano-Bicocca, Italy
[6]Brandenburgische Technische Universität Cottbus, Konrad -Zuse-Strasse 1, 03046 Cottbus, Germany
**zoellner@ihp-microelectronics.com*

Global and local integration schemes of Germanium (Ge) based heteroepitaxial systems on a Silicon (Si) platform are of crucial importance for advanced complementary metal-oxide-semiconductor (CMOS) technology and electronic photonic integrated circuits (EPICs). To improve the performance of such heterostructures for Ge-based devices, fundamental insights into the local crystal structure are required. This information can be a valuable input to engineers for theoretical simulations to correlate the structural properties with materials electronic and photonic properties.

A recently developed synchrotron-based scanning X-ray diffraction microscopy technique, called quic*K-map*ping (K-map), from the beam line ID01 of the European Synchrotron radiation facility (ESRF) is ideally suited to non-destructively image with sub-micron resolution local tilt and lattice constant variations (a/a) with a sensitivity down to 10^{-3} degree and 10^{-5}, respectively. Local lattice orientations and constants are extracted by the X-ray Strain Orientation Calculation Software (XSOCS) [1]. In the presentation, K-map results from SiGe buffer layers and Ge micro-stripes are demonstrated as examples for global and local Ge heterostructures.

SiGe „virtual substrates“ are a promising approach for the very large scale integration (VLSI) of Ge as closed films on Si(001). Although, growth and relaxation processes of SiGe buffer layers on Si(001) are well investigated and major achievements were made, control over the structural homogeneity of SiGe buffers below micro-meter scale is still a challenge for global integration on 300 mm Si(001) wafers. The capability of the K-map technique to determine lattice parameters in a quantitative way demonstrates the achieved quality given by the influence of plastic relaxation to the tilt, strain and composition of Ge/SiGe/Si(001) systems.[2,3]

Ge micro-structures on Si(001) achieved by top-down or bottom-up approaches suffer as well from inhomogeneities due to growth and relaxation processes. Additionally, process steps as capping layers and local etching or doping may further influence the crystal structure. However, these approaches enable to engineer local structural properties as the strain distribution.[4]

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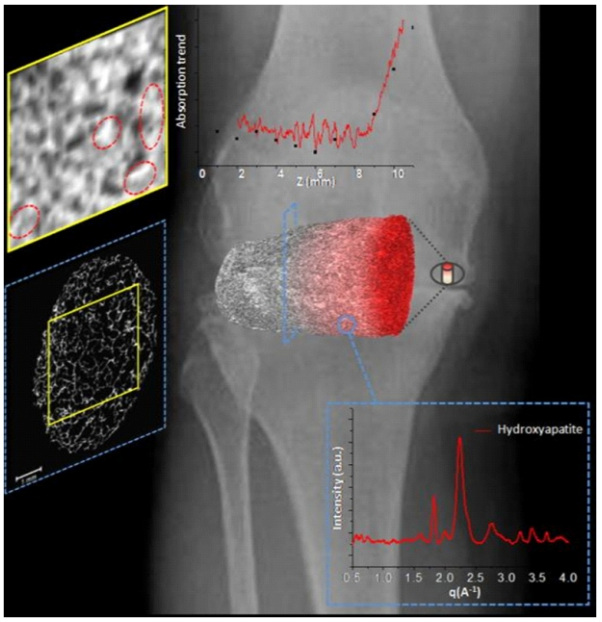
C27

TABLE-TOP SAXS/WAXS (SCANNING) MICROSCOPY PROBES HYDROXYAPATITE CONCENTRATION GRADIENTS IN ENGINEERED BIO-SCAFFOLDS

Davide Altamura[1], Stella G. Pastore[1], Maria G. Raucci[2], Dritan Siliqi[1], Rocco Lassandro[1], Fabio De Pascalis[3], Michele Nacucchi[3], Luigi Ambrosio[2,4] and Cinzia Giannini[1]

[1]Institute of Crystallography (IC), National Research Council, Bari 70125, Italy
[2]Institute of Polymers, Composites, and Biomaterials (IPCB), National Research Council, Naples, Italy
[3]Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Brindisi 72100, Italy
[4]Department of Chemical Sciences and Materials Technology (DSCTM), National Research Council, Rome 000133, Italy

A structural study of a scaffold made of bovine gelatin and hydroxyapatite (HA) is carried out, for bone tissue engineering purposes [1]. The great relevance of such a material relies on its potential application in the healing process of osteochondral defects, which are responsible for the damage of cartilage and adjacent subchondral bone, compromising the quality of life of millions of patients. Two techniques exploiting X-ray radiation, with table-top setups, are used: micro-CT and microdiffraction. The former allowes 3D imaging at the micrometer scale spatial resolution, the latter provides combined 2D structural/morphological information at the atomic and nano-scale, with a hundred microns spatial resolution. The combination of these two techniques allowed the study of the scaffold density gradient, related to the HA concentration gradient, engineered on purpose to mimic the natural bone structure model. Micro-CT defines the directionality of the gradient; WAXS probes the crystalline phases in the sample; SAXS microscopy selectively probes HA distribution through mapping of the SAXS intensity in specific q-ranges. Scanning SAXS micrographs and WAXS patterns were collected by using a high brilliance Rigaku Fr-E+ SuperBright microsource, coupled to a SMAX3000 three pinhole camera through a focusing multilayer optics (CMF 15-105) [2].



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EXTENDED RANGE ULTRA SMALL-ANGLE X-RAY, SMALL-ANGLE, AND WIDE-ANGLE SCATTERING FOR ADVANCED ALLOY DEVELOPMENT

J. Ilavský[1], F. Zhang[2], L.E. Levine[2], A.J. Allen[2]

[1]Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA
[2]National Institute of Standard and Technology, Gaithersburg, MD, USA
ilavsky@aps.anl.gov

Development of new high-performance materials, e.g., new aluminum or steel alloys, is critical for advances in energy production and utilization (and many other areas). These materials often exhibit complex microstructures spanning multiple length scales that control their performance. In this context, it is important to simultaneously characterize, ideally *in situ* or *in operando*, various facets of the microstructure – for example precipitate shape and size, together with their phase and chemical composition. Over many years, the Advanced Photon Source (APS) with NIST has developed and optimized a combined Ultra-Small, Small, & Wide Angle X-ray Scattering

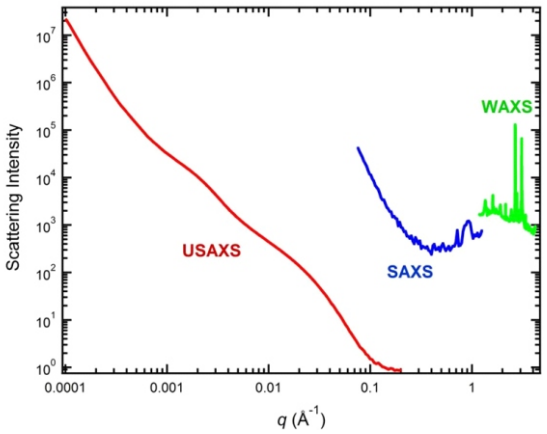

Figure 1 Example of combined USAXS, SAXS, and WAXS for AA202024 alloy.

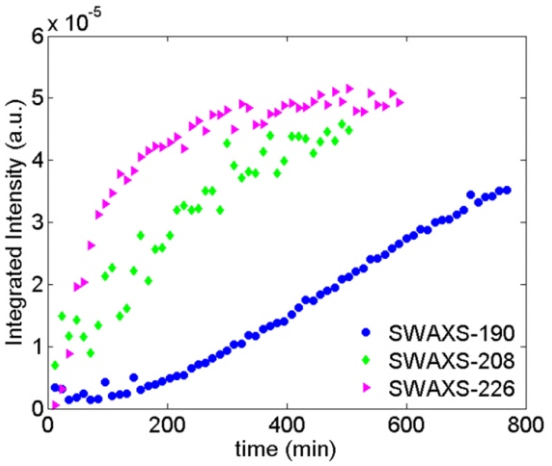

Figure 2. Evolution of the integrated 112 reflection of the S phase precipitate peak intensity at d = 2.570 Å (or q = 2.445 Å^{-1}) at 190 °C, 208 °C, and 226 °C,...

(USAXS/SAXS/WAXS) facility [1]. Data spanning over 5 decades in microstructural size can be collected sequentially in 4 to 6 minutes, from the same volume during one *in-situ* experiment. In the case presented, we have studied the Al-Cu-Mg alloys, e.g., AA2024, at different aging conditions.

The precipitate structure and precipitation kinetics in the Al-Cu-Mg alloy, AA2024, aged at 190 °C, 208 °C, and 226 °C have been studied using *ex situ* TEM and *in situ* combined USAXS/SAXS/WAXS at the APS across a length scale from sub-Angstrom to several micrometers, Fig.1. TEM provided information concerning the nature, morphology, and size of the precipitates, while USAXS/SAXS/WAXS provided qualitative and quantitative information concerning the time-dependent size and volume fraction evolution of the precipitates at different stages of the precipitation sequence.

Using a three-parameter scattering model constructed on the basis of the TEM results, we established the temperature-dependent kinetics for the cluster-dissolution and S-phase formation processes. These two processes, while occurring simultaneously, have different kinetic rates, with the cluster-dissolution rate approximately double the S-phase formation rate. We also identified a dissolution activation energy at (149.5 ± 14.6) kJ mol^{-1}, which translates to (1.55 ± 0.15) eV/atom, as well as an activation energy for the formation of S precipitates at (129.2 ± 5.4) kJ mol^{-1}, i.e. (1.33 ± 0.06) eV/atom. The SAXS/WAXS results show the absence of an intermediate GPB2/S" phase in the samples under the experimental ageing conditions. These results are further validated by precipitation simulations that are based on Langer-Schwartz theory and a Kampmann-Wagner numerical method. This study [2] clearly shows how the extended-range USAXS/SAXS/WAXS facility simplifies and speeds up new advanced materials characterization and development.

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C29

NANODIFFRACTION OF HIGHLY MISMATCHED COMPOSITIONALLY GRADED SiGe/Si MICROCRYSTALS

M. Meduňa[1,2], F. Isa[3,4], A. Jung[3,4], A. Marzegalli[5], Y. Arroyo Rojas Dasilva[4], G. Isella[6], R. Erni[4], P. Niedermann[7], K. Zweiacker[8], A. Neels[8], A. Dommann[8], P. Gröning[5], and H. von Känel[3,4]

[1]Department of Condensed Matter Physics, Masaryk University, Kotlářská 2, Brno, CZ-61137, Czech Republic
[2]CEITEC, Masaryk University, Kamenice 5, Brno, CZ-60177, Czech Republic
[3]Laboratory for Solid State Physics, ETH Zürich, Otto-Stern-Weg 1, Zürich, CH-8093, Switzerland
[4]Electron Microscopy Center, Empa, Überlandstrasse 129, Dübendorf, CH-8600, Switzerland
[5]L-NESS and Department of Materials Science, Universita di Milano-Bicocca, Via Cozzi 55, Milano, I-20125, Italy
[6]L-NESS and Department of Physics, Politecnico di Milano, Via Anzani 42, Como, I-22100, Italy
[7]CSEM, Rue Jaquet-Droz 1, Neuchâtel, CH-2002, Switzerland
[8]Center for X-Ray Analytics, Empa, Überlandstrasse 129, Dübendorf, CH-8600, Switzerland
mjme@physics.muni.cz

The heteroepitaxial growth of materials with different lattice and thermal expansion coefficients, particularly in the form of various semiconductor layers on silicon, is one of the cornerstones of functional scaling for integrating high-speed electronic and optoelectronic devices. Unfortunately, the mismatched materials suffer from misfit (MDs) and threading (TDs) dislocations formed at the material interface and from wafer bowing. Both MDs and TDs negatively impact the electrical and optical properties of the potential device. Wafer bowing can lead even to cracking of whole chips.

Recently Falub et al. achieved a breakthrough in the attempt to eliminate threading dislocations from heteroepitaxial SiGe/Si layers. This was realized by using a novel kind of epitaxial growth in which densely packed 3D SiGe crystals are formed on patterned Si substrates instead of continuous films [1]. Thanks to a fully faceted morphology and limited lateral crystal size, all threading dislocations stemming from the heavily defected heterointerface are forced to leave the crystals through their sidewalls, leaving the upper crystal region defect-free [2].

Although this method is highly effective in eliminating threading dislocations, it does not prevent the formation of misfit dislocations at the SiGe/Si heterointerface, as presented in our previous experiments using scanning X-ray nanodiffraction [3]. However M. Salvalaglio et al. have recently proposed [4] an innovative approach to eliminate misfit dislocations in highly mismatched, compositionally graded SiGe/Si heterostructures. The misfit stress may be relaxed entirely elastically by choosing the appropriate crystal width and Ge grading rate. Such heterostructures have been recently realised [5] and form the basis for this paper.

In this work we present X-ray nanodiffraction experiments performed at the ID01 beamline of the ESRF in Grenoble on isolated 3D $Si_{1-x}Ge_x$ microcrystals (see Fig. 1), in which the Ge content x is linearly increased from 0 to

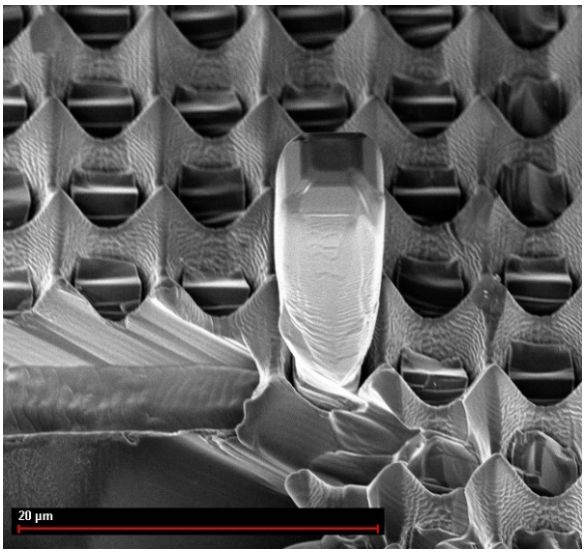

Figure 1. Perspective scanning electron microscope (SEM) image of an individual graded SiGe crystal probed by an X-ray nanobeam.

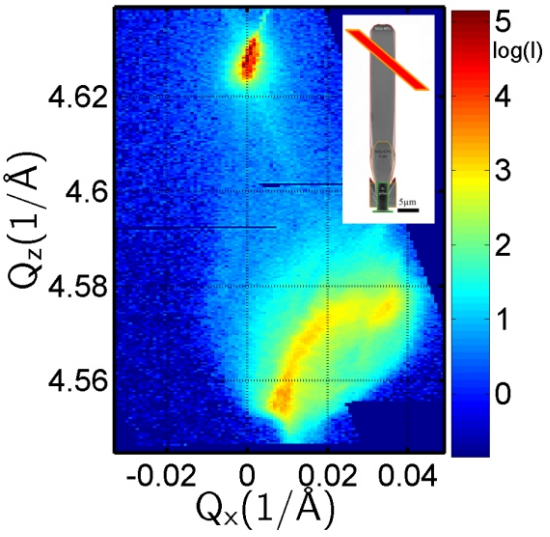

Figure 2. RSM around the (004) Bragg reflection of a SiGe crystal probed by a skewed nanobeam through the top part of the crystal.

40% at the rate of 1.5% μm^{-1}. Depending on the crystal width, the 3D SiGe crystals are expected to be completely free from misfit and threading dislocations. During the experiment we have performed series of scanning X-ray diffraction microscopy (SXDM) images for different incidence angles from which 3D reciprocal space maps (RSMs) have been built (see Fig. 2). RSMs around the (004) and (115) Bragg reflections have been collected on 2D meshes for microcrystals with different Ge grading rates and different widths, and on an unpatterned area. By combining series of RSMs we obtain an evolution of the crystal lattice tilt and strain depending on the Ge grading rate and crystal width at various positions inside the crystal. The X-ray data are compared with finite element calculations.

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TITLE X-RAY DIFFRACTION STUDY OF THE (MAGNETO-)STRUCTURAL TRANSITION IN FeRh THIN LAYERS

L. Horák

Faculty of Mathematics and Physics, Charles University in Prague, Ke Karlovu 5, 121 16 Praha 2
horak@karlov.mff.cuni.cz

The $Fe_{50}Rh_{50}$ material exhibits a reversible magneto-structural transition between a room-temperature antiferromagnetic (AFM) and a high-temperature ferromagnetic (FM) phase approximately at 350 K [1]. After the transition to the FM state, the lattice is discretely expanded and this transition shows the temperature/field hysteresis in the lattice parameter and in the magnetic net moment [2]. Most probably, the initial growth of the ferromagnetic phase is stimulated by the defects located at the surface and/or the interface with the substrate [2]. Further, in the thin FeRh layers, the presence of the stable residual FM volume located at the layer/substrate or layer/capping interfaceis is being observed [3].

Using High-Resolution X-ray diffractometry (HR-XRD), we have measured several samples of FeRh thin layers with various thicknesses benefiting from the different lattice parameter of the AFM and the FM phase. We performed the temperature dependent measurements (during the heating and the cooling) of the distribution of diffracted intensity in the reciprocal space. For the simulation we assumed the mosaic-like model of FM and AFM domains that allowed to interpret the experimental data. From the fitting we determined the vertical and lateral size of domains together the relative volume of both phases.

We confirmed the presence of the FM volume at the room tempereature. However, in contrary to the common interpretation based on thin FM interlayer, the diffraction

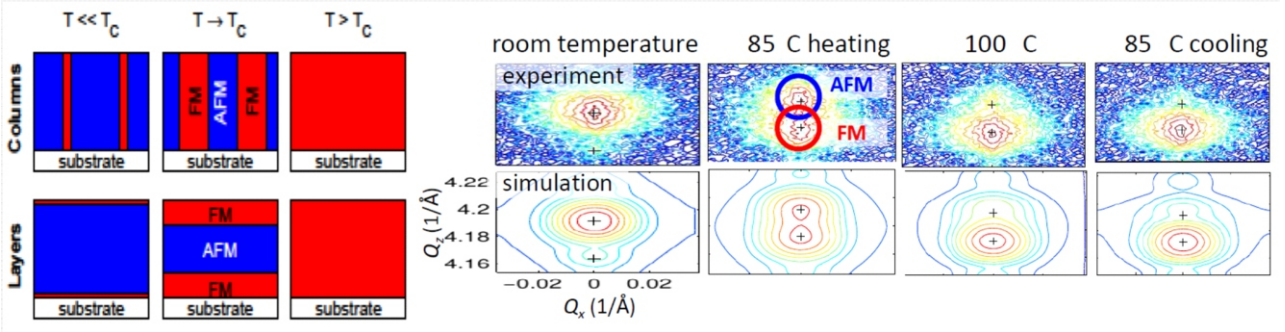

Figure 1. The sketch of two competitive model of FM/AFM domains arrangement (left panel). The comparison of the measured and simulated reciprocal space maps at various temperatures (right panel).

data indicated that both the FM and the AFM domains have constant vertical size being equal to the layer thickness obtained from the X-ray reflectivity. At room temperature, the FM volume (although very small) is spread from the very bottom to the top of the thin layer, probably in the form of thin columns laterally distributed in the layer. Just these columns could be the seeds for the emerging FM phase during the heating.

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Session X

Wednesday, September 7 - afternoon

I10

HIGH RESOLUTION X-RAY SPECTROSCOPY OF ELECTRONIC AND ATOMIC STRUCTURE OF TIO2 NANOSTRUCTURES AND CHARGE TRANSFER PROCESSES

Federico Boscherini[1]*, Lucia Amidani[2], Luca Pasquini[1], Giacomo Rossi[1], Marco Malvestuto[3] and Alberto Naldoni[4]

[1]Department of Physics and Astronomy, University of Bologna, Italy
[2]ESRF, The European Synchrotron, Grenoble, France
[3]Elettra, Sincrotrone Trieste, Trieste, Italy
[4]CNR-ISTM, Milano, Italy
federico.boscherini@unibo.it

Refined X-ray spectroscopy can play a key role in understanding the fundamental mechanisms responsible for the physical and chemical properties of advanced functional materials and devices. In this contribution, we will focus on TiO_2 – based nanostructures, which are actively studied for many applications, including photocatalysis. Despite many potential advantages, one limitation of TiO_2 is the wide band gap, which limits solar light absorption. By using high resolution X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) we have recently studied the atomic and electronic structure of two materials systems designed to overcome this limitation: nanostructures formed by close assembly of Au and TiO_2 nanoparticles [1] and V-doped TiO_2 [2].

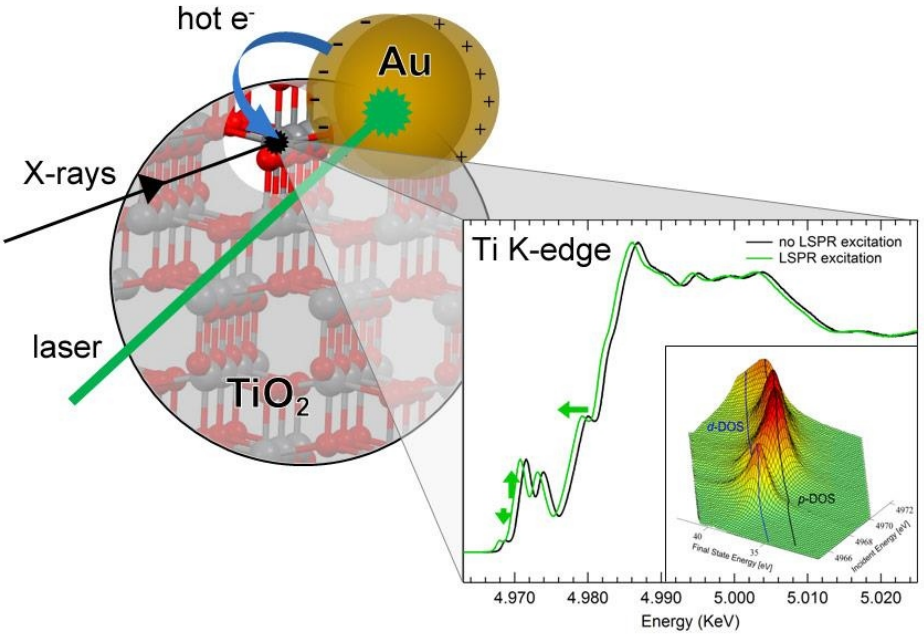

Figure 1: Graphical description of the experiment on Au:TiO_2 and of hot electron charge transfer. The inset reports the effect of laser illumination on high resolution XAS spectra and a typical RIXS plane.