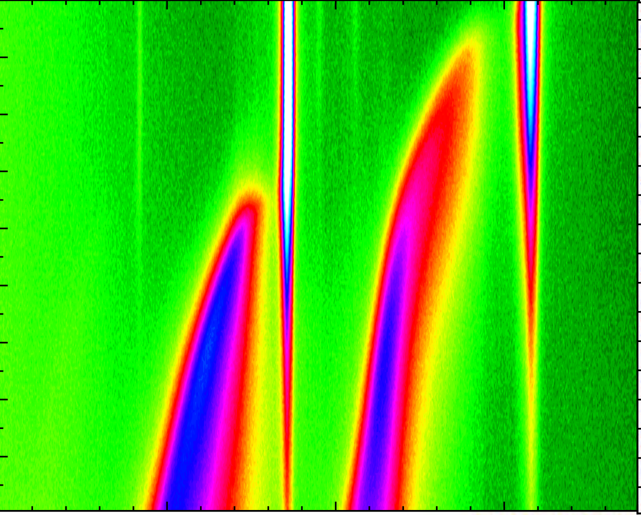
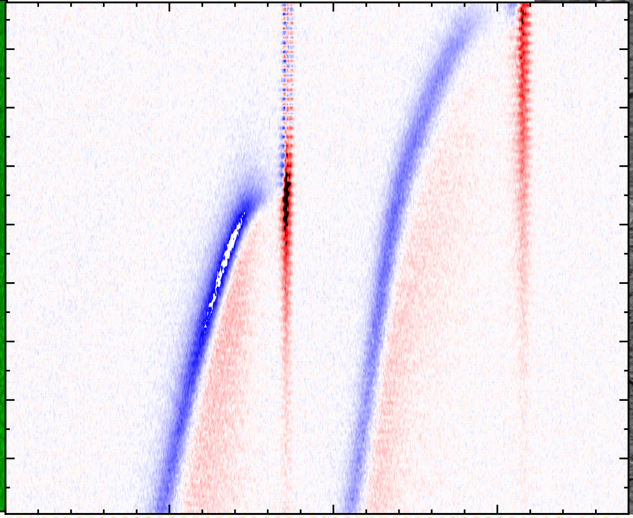

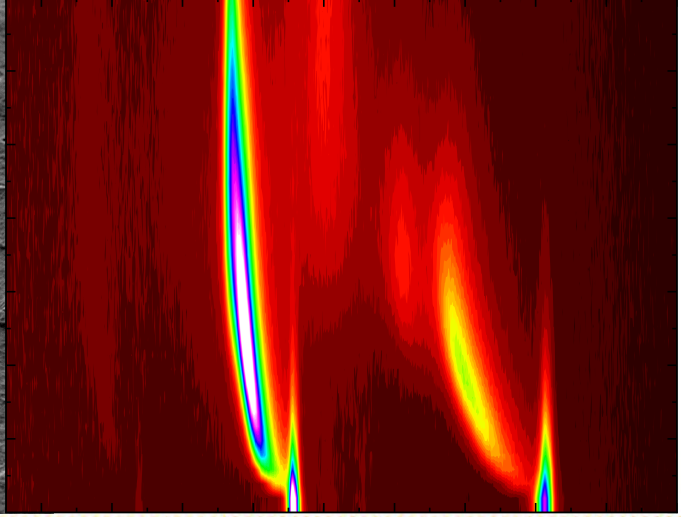

DEPTH RESOLVED MEASUREMENTS USING IN-SITU XRD DURING ION BEAM SPUTTERING

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IOM Leipzig

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Mühlleithen, 13. – 16. März 2023

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Content

- Motivation — why *in-situ* XRD during ion etching
- Experiment — *in-situ* XRD during etching of expanded austenite
- Results — depth resolved data
  - investigation of gradient layers
  - "broadening" of (200) peak
  - initial formation of expanded austenite
- Discussion & Conclusions

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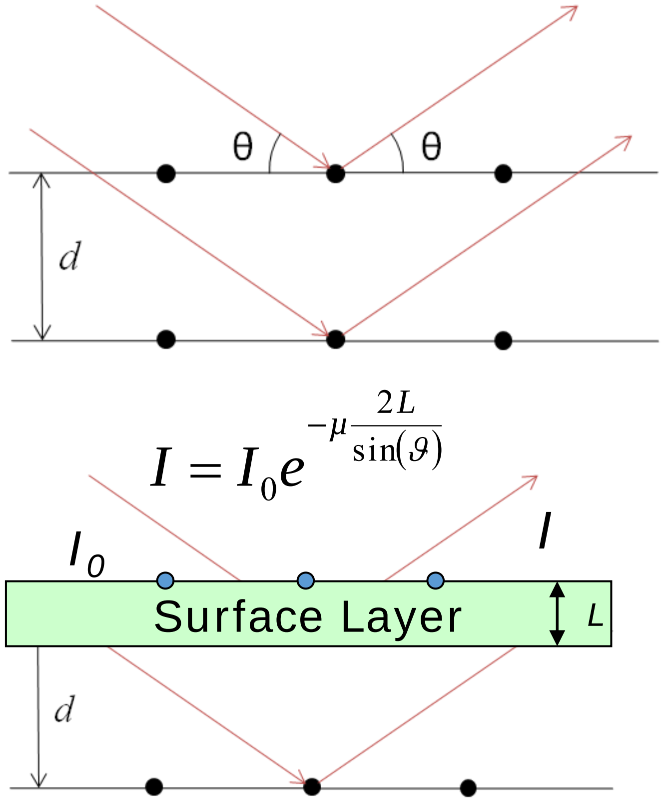
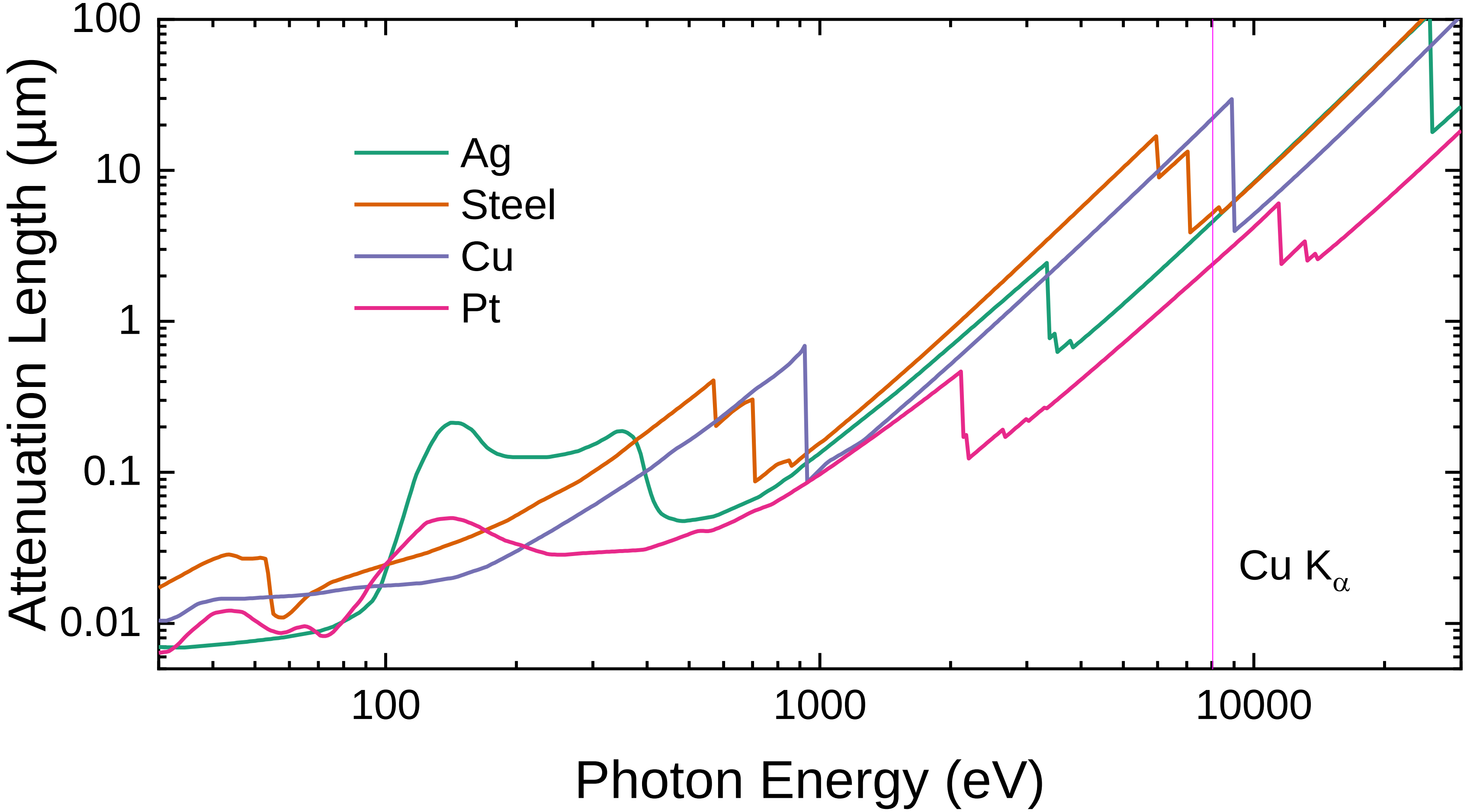
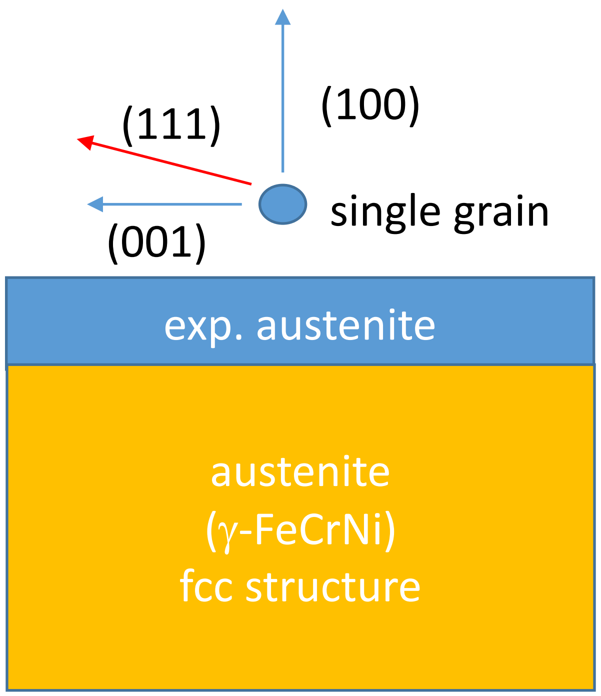
Motivation

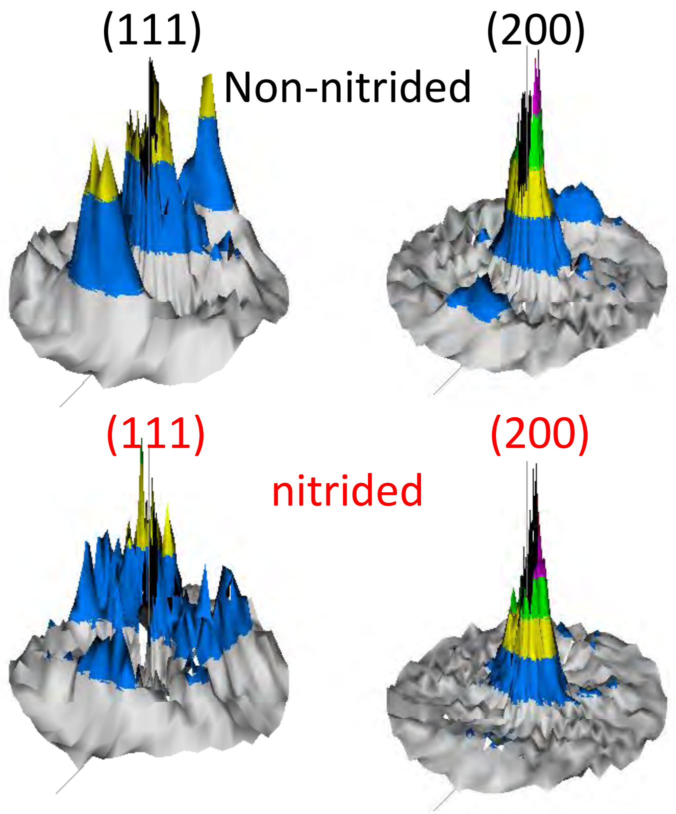


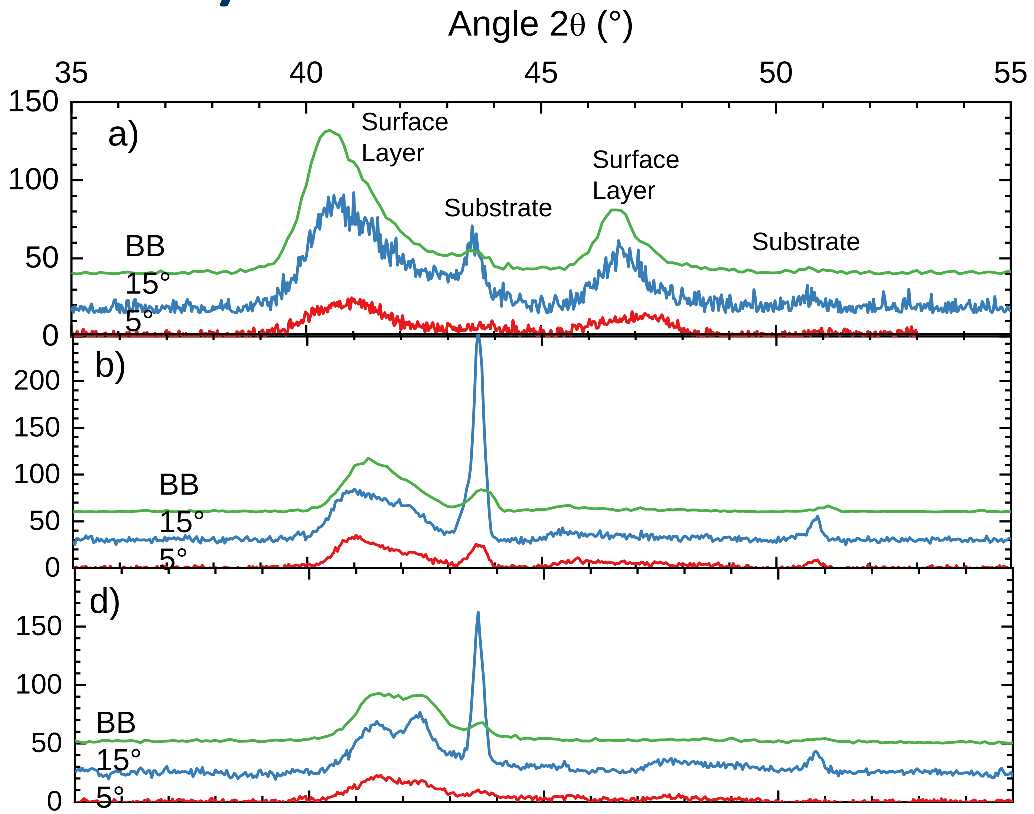


- Information depth correlated with attenuation length
- Parameters: angle and wavelength
- Depth resolution ~ 1 µm – limited to the surface

Glancing Angle XRD (GAXRD)







S. Mändl, B. Rauschenbach, J. Appl. Phys. 88 (2000) 3323 J. Lutz et al., IEEE Trans. Plasma Sci. 39 (2011) 3056

- Using fixed angle for incident beam can lead to artefacts for layered systems
- Example shows three layers where the substrate intensity is highest for $\theta = 15°$
- Highly textured materials ≠ GAXRD

Variable Wavelength XRD

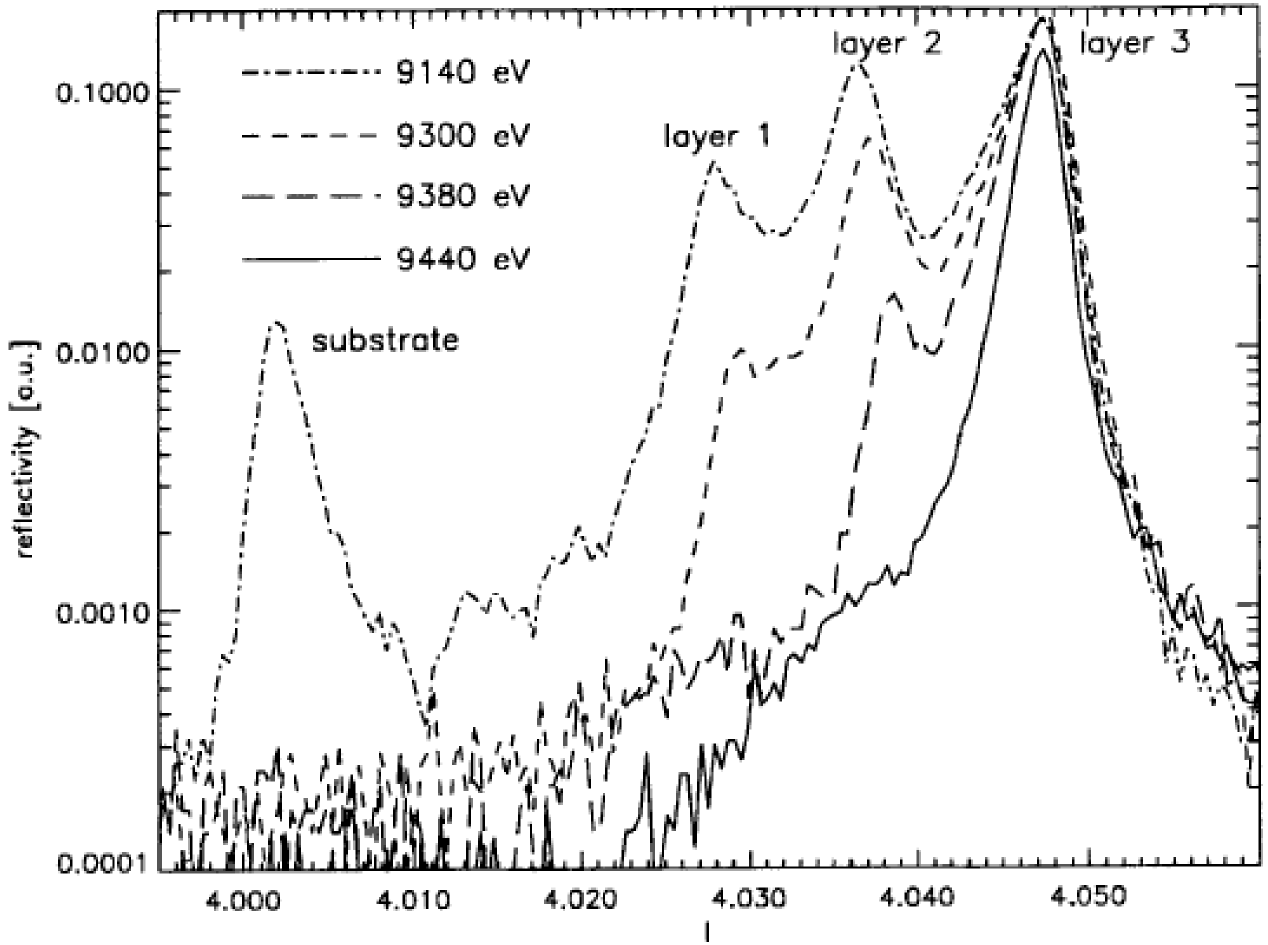


Fig. 3. – *l*-scans at 9140 eV, 9300 eV, 9380 eV, and 9440 eV, in wavelengths: 1.357 Å, 1.333 Å, 1.322 Å, and 1.313 Å.

Table I. – *Structure of the investigated sample, γ is the strain parameter as defined in* [8] *and a_{rel} the lattice constant, if the layer would be relaxed.*

	Material	Thickness (nm)	γ	a_{rel} (Å)
layer 3	$(Mg_{0.26}Zn_{0.61}Be_{0.13})$ Se	400	0.96	5.6247
layer 2	$(Mg_{0.24}Zn_{0.64}Be_{0.12})$ Se	400	0.97	5.6325
layer 1	$(Mg_{0.22}Zn_{0.67}Be_{0.11})$ Se	400	0.98	5.6375
buffer	BeTe	3	1	5.622
substrate	GaAs	∞		5.65325

- Technique necessitates synchrotron radiation
- Coordinated control of monochromator and diffraction angles
- Depth resolution still $\gg$ 100 nm

M.O. Möller, T. Gerhard, H.R. Reß, G. Landwehr, Il Nuovo Cimento 19D (1997) 321

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Motivation

- Variations of incident angle and wavelength in XRD only allows a limited increase in the depth resolution compared to conventional XRD measurements
- Mechanical polishing between measurements similarly gives only a restrained depth resolution of ~ 2 − 5 µm

- Alternative: *In-situ* XRD during ion beam sputtering with inert ions
- Mathematical analysis allows us to deduce depth dependent information on phase composition from a time series – as long as diffusion and phase transformations are not present during sputtering
- $\Rightarrow$ Depth resolution better than 50 nm

- Depth resolved XRD complementary to GDOES & SIMS

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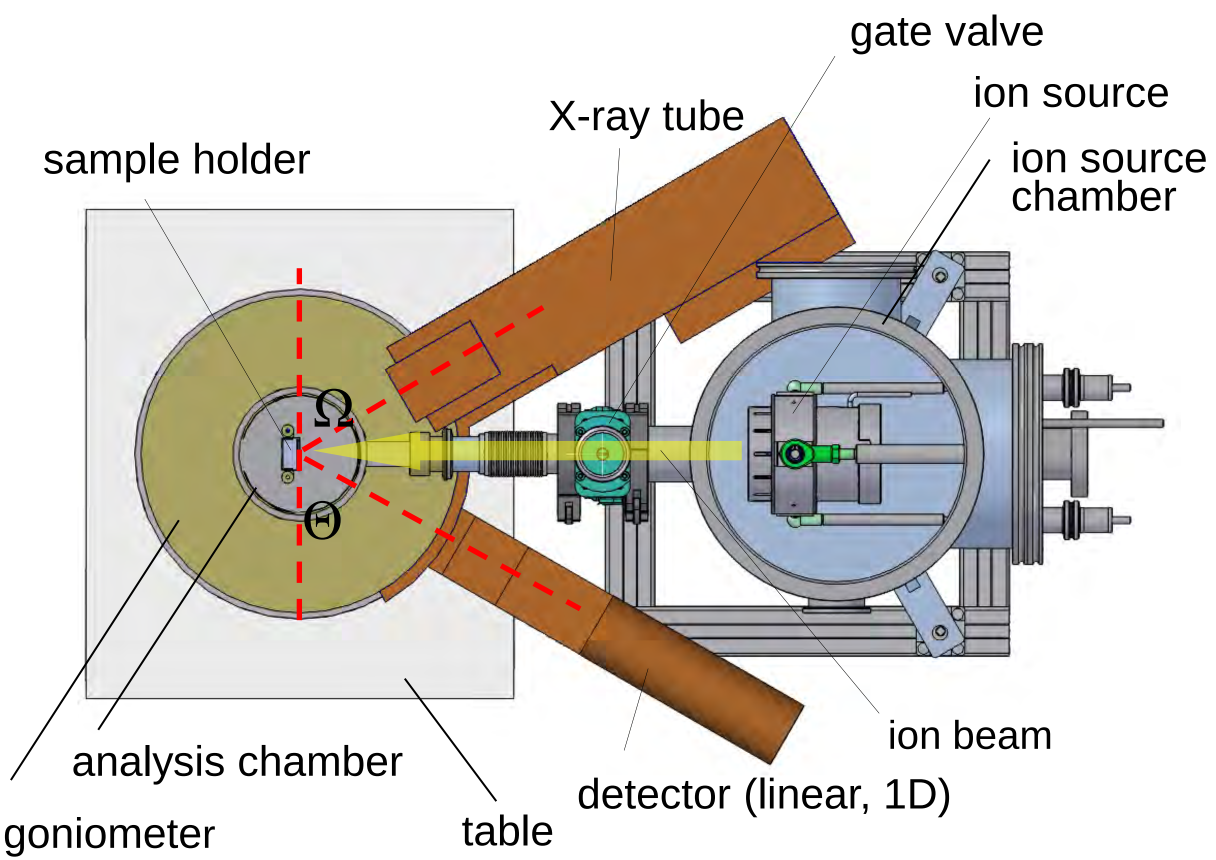
Experiment



- Concept: two separate, differentially pumped vacuum chambers
- Diffractometer in Bragg-Brentano geometry
- Fast position sensitive linear detector
- External heating system with fast control loop
- Ion source ISQ 40 (Kaufman-type): ion energy up to 2 keV
- *In-situ* movable ion source: independent beam alignment
- Stability of ion beam: ion beam current density measured at sample position before and after every experiment

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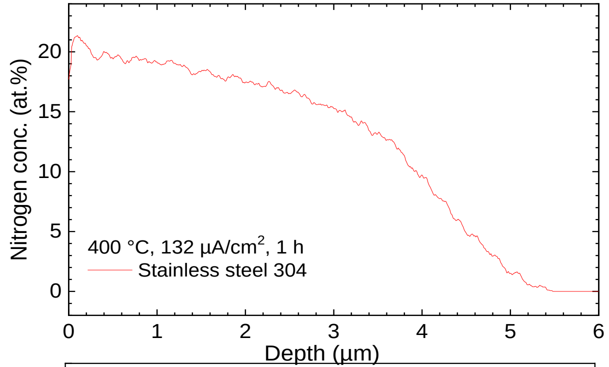
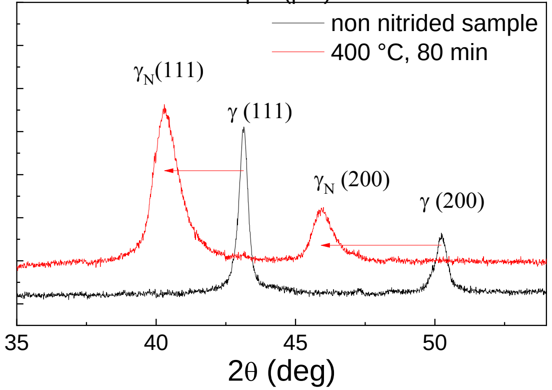
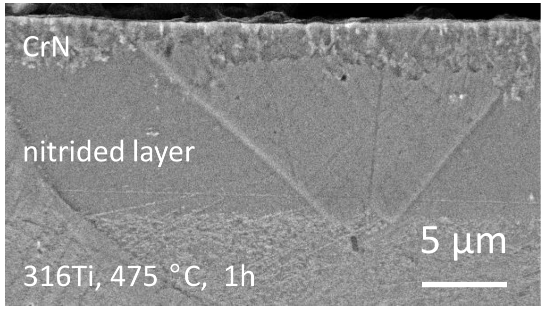
Experiment

- Nitrided austenitic stainless steel ≡ *expanded austenite*
- Solid solution of nitrogen up to 25 – 30 at.%
- Strongly reduced wear rate, hardness up to 15 – 20 GPa
- Corrosion resistance identical or improved

- Grain size ~ 10 – 30 µm
- Coherent phase formation on surface: identical texture
- Metastable, decay into CrN + FeNi: small grains with random orientation

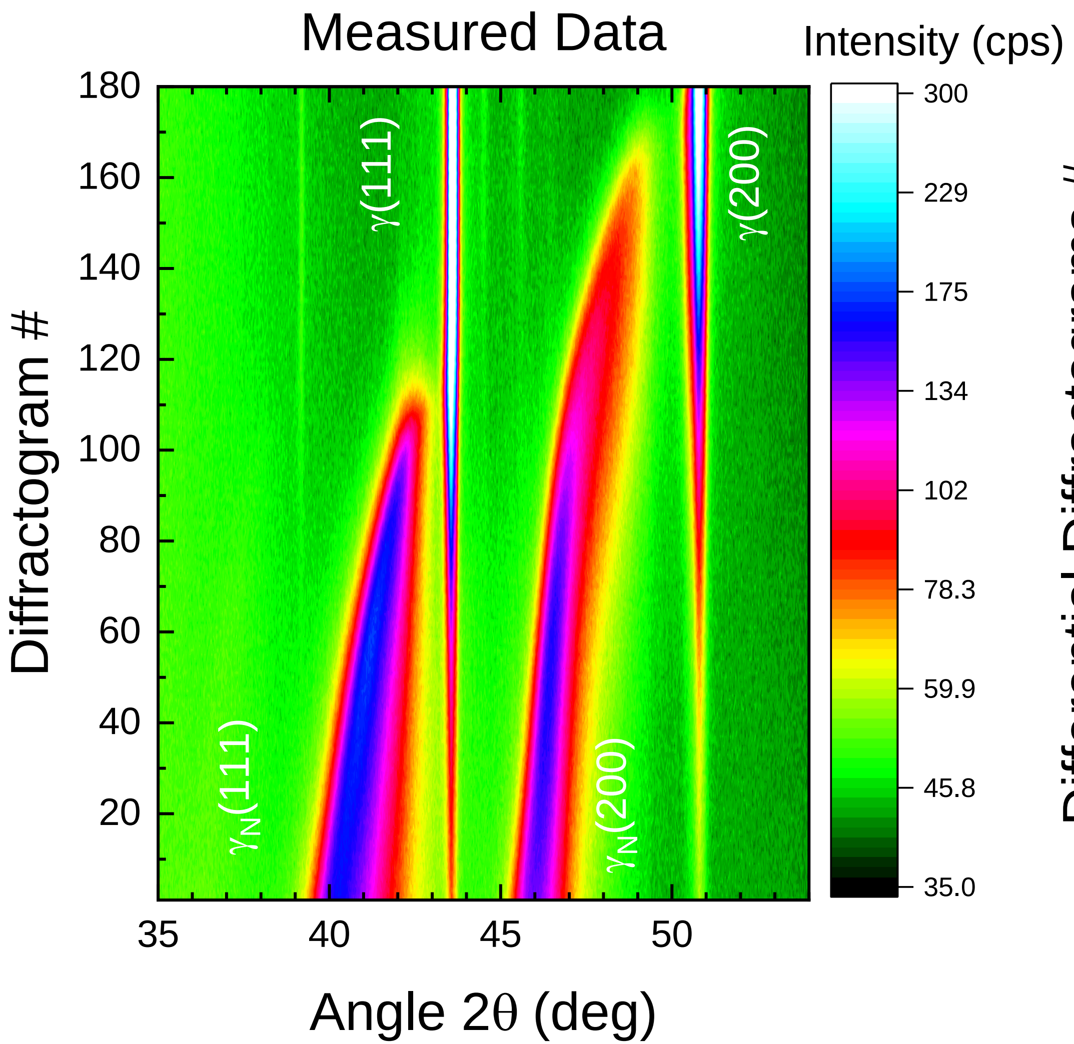


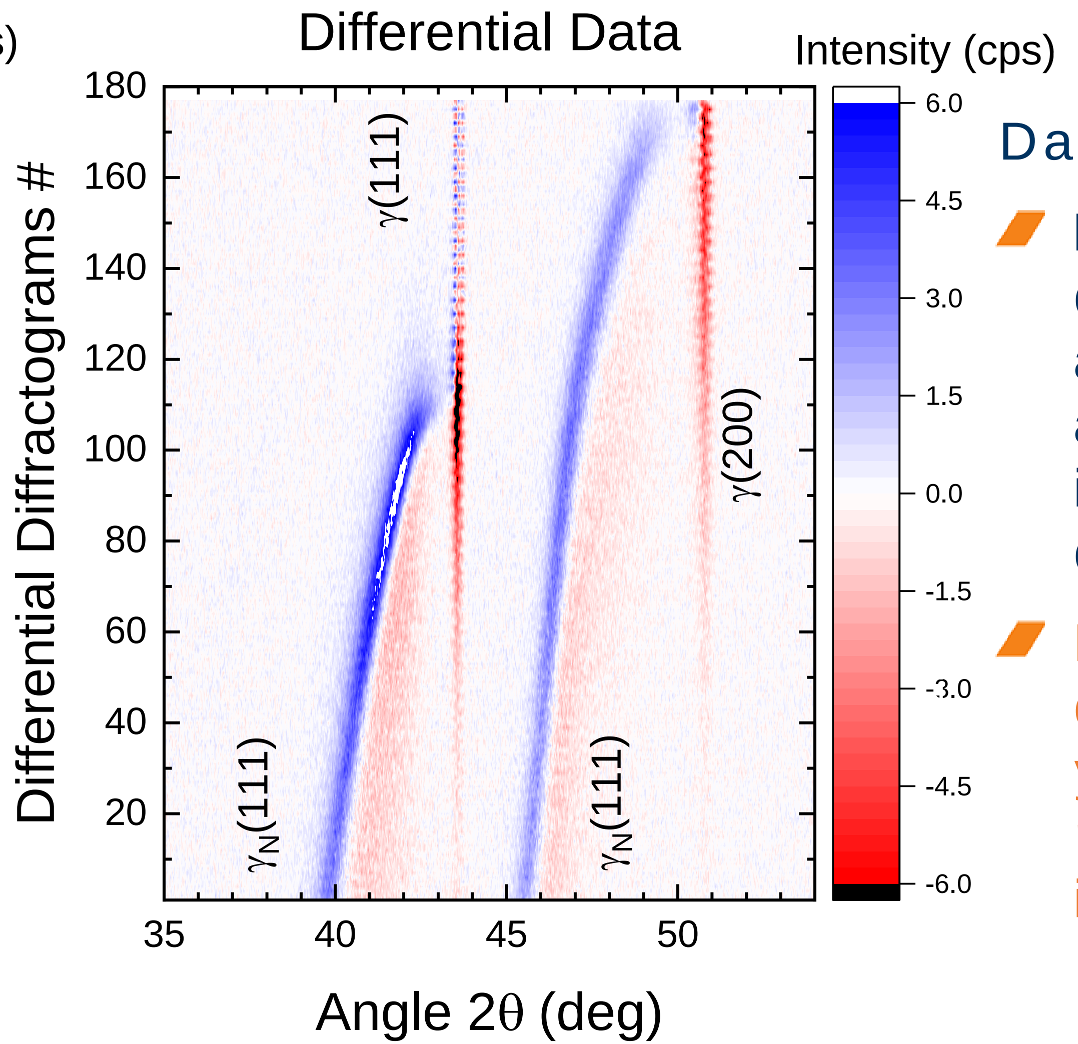




S. Mändl, R. Dunkel, D. Hirsch, D. Manova, Surf. Coat. Technol. 258 (2014) 722

Results





Data Analysis

- Measured data still averaged across information depth
- Differential diffractograms yield depth resolved information

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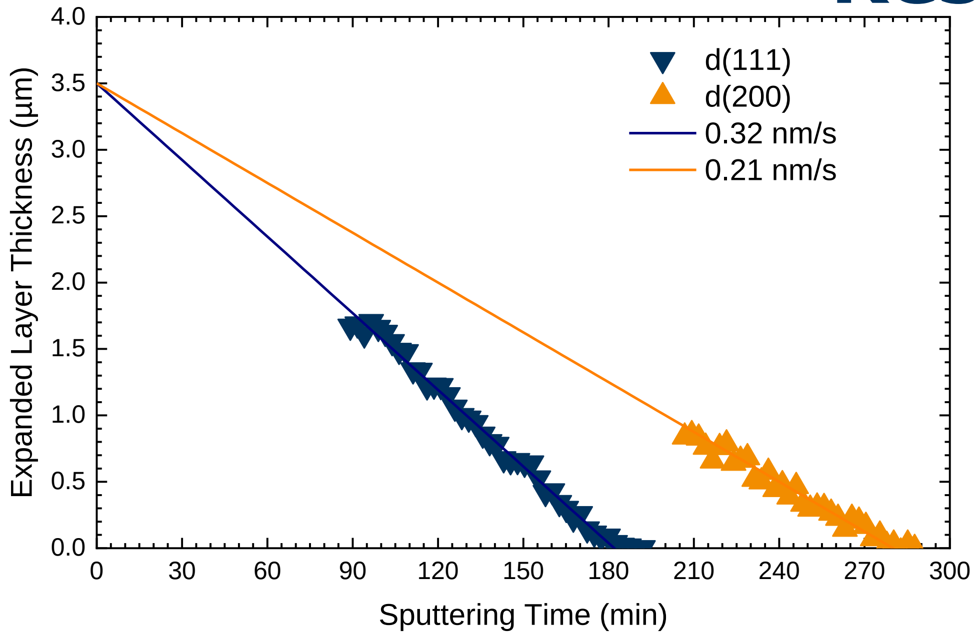
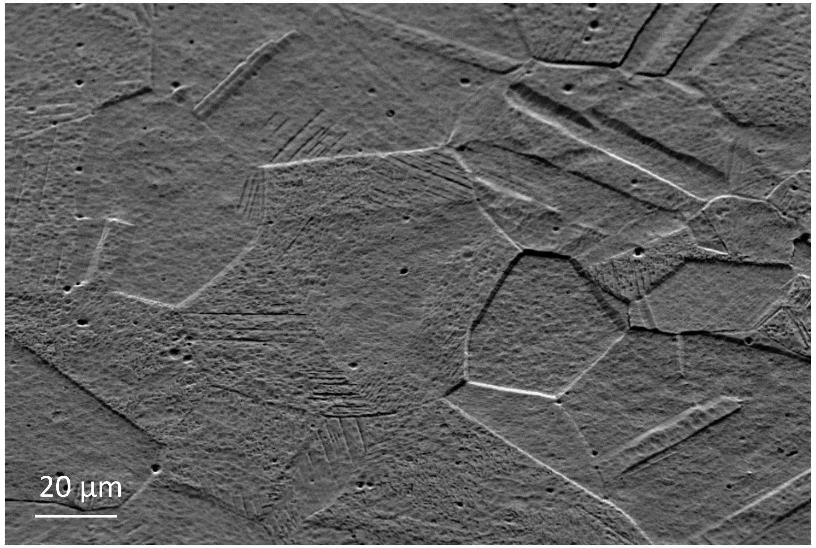
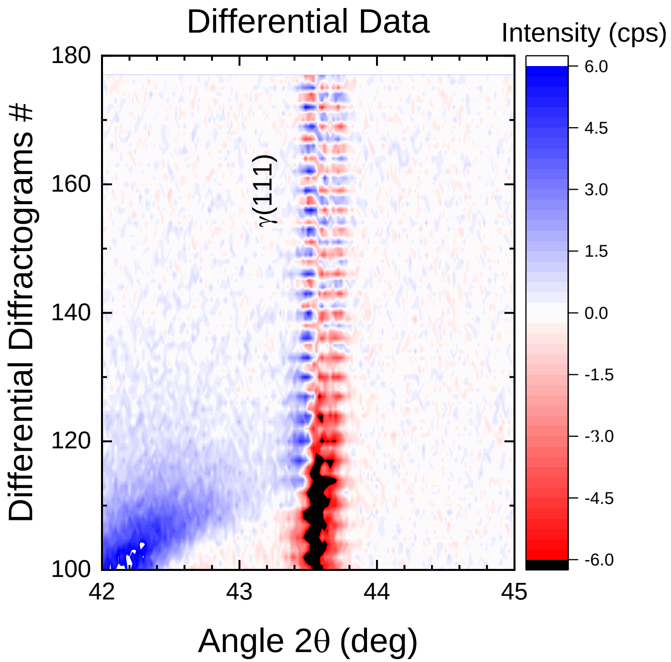
Results: "Artefacts"







- Known orientation-dependent sputter yield leads to degradation of depth resolution in SIMS & GDOES
- *In-situ etching:* probing of grains with special orientation keeps excellent depth resolution (with different time-depth conversion for each orientation)
- Limitation: only a fraction of all grains are measured
- Thermal expansion: direct temperature display (including control loop fluctuations)
- High ion current: measurement time for one diffractogram ~ 2 min. ≈ 35 nm

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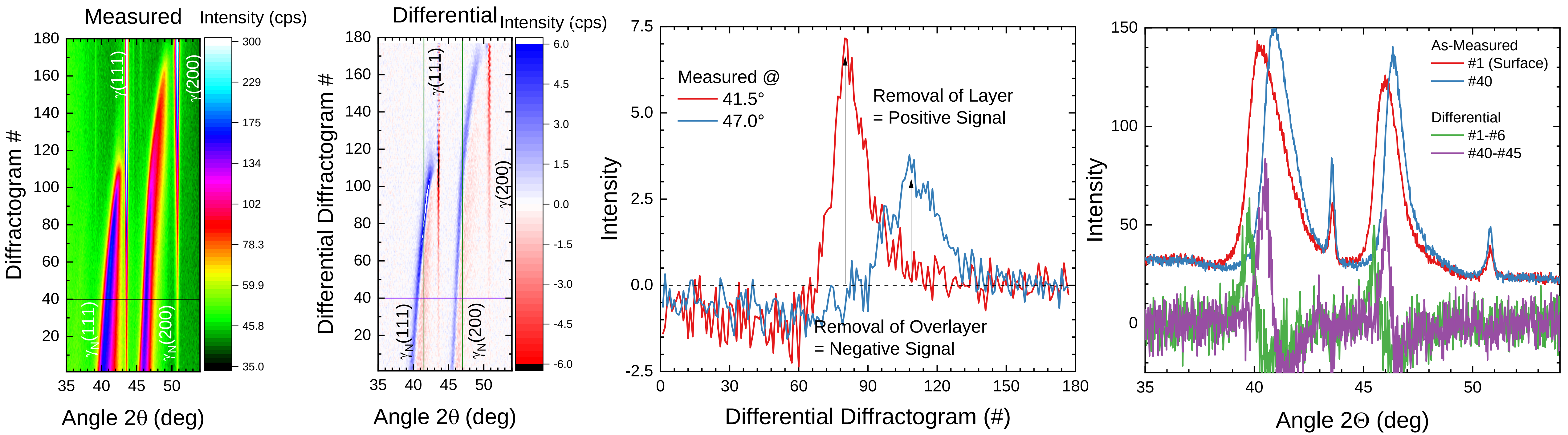
Results: Reconstruction of Layers



- Small continuous change in intensity due to thinner overlayer (negative)
- Sudden change when this sublayer is on the surface, thus etched away (positive)
- Differential diffractograms show actual lattice expansion at each depth
- Peak width of measured diffractogram at surface is a convolution of sublayers

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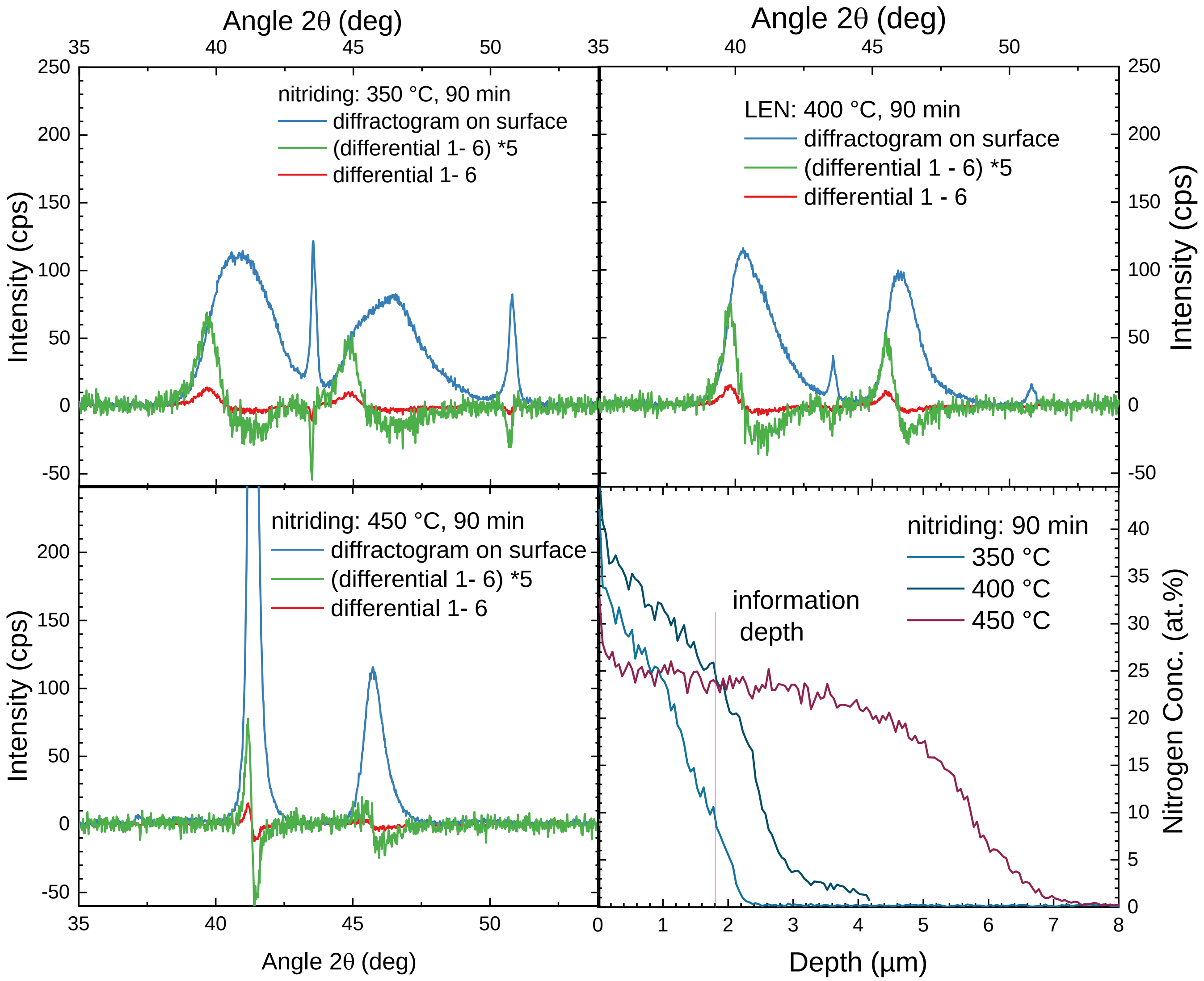
Results: Deconvolution



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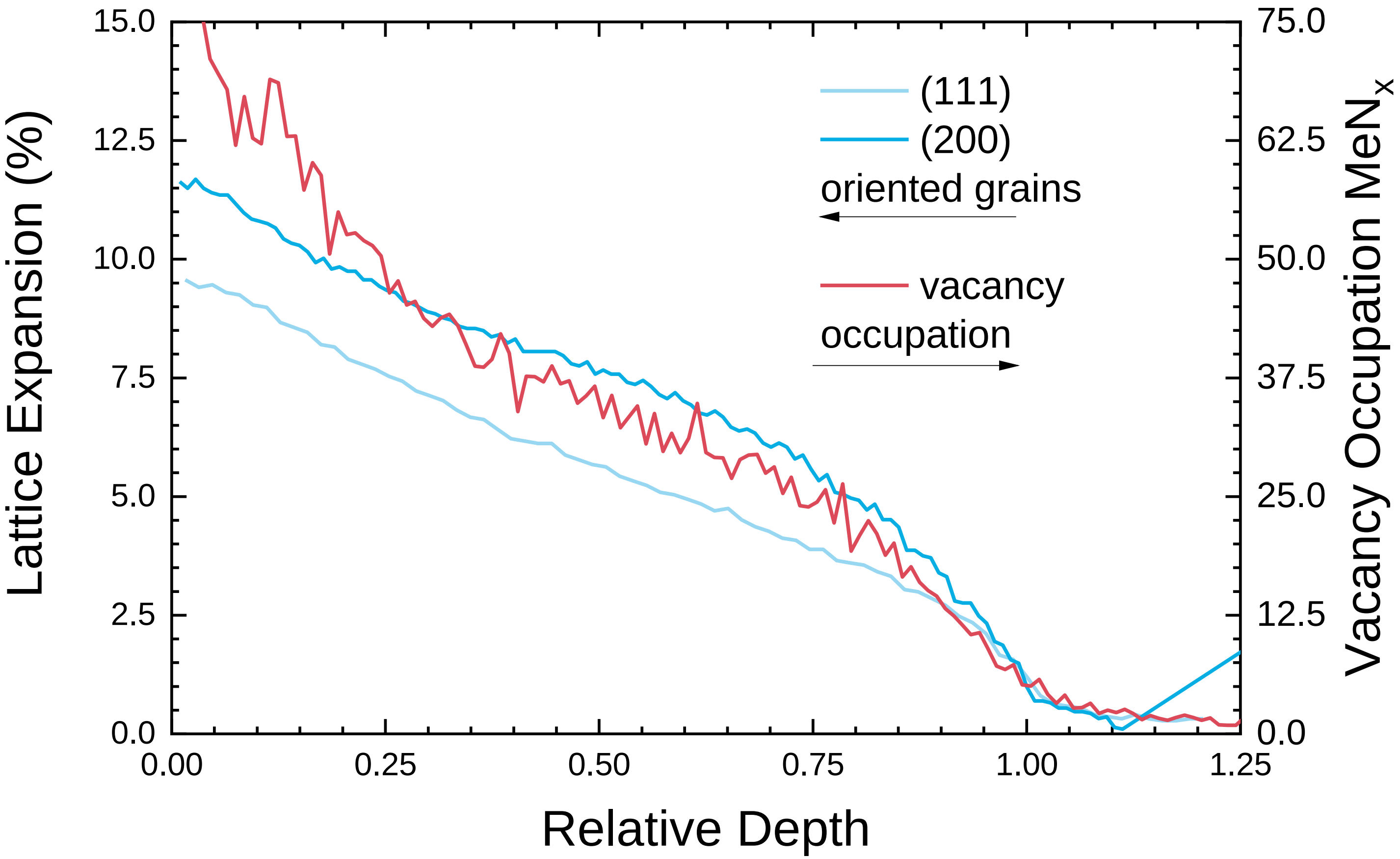
- Thicker layers (higher nitriding temperature) = narrower peaks in surface diffractograms
- Deconvolution of the peak shape using differential diffractograms
- Thus, strongly reduced peak width in differential diffractograms
- Determination of reduced peak width integrated over only 50 – 100 nm
- Nevertheless, still variations with T: inhomogeneous broadening
- This information is not accessible using conventional methods

Results: Nitrogen vs. Expansion



- Vegard's law as empirical finding: correlating lattice expansion and surface concentration of a solid solution
- Composition as function of depth for compositional gradient easily determined (SIMS, GDOES, ..)
- Now: comparison of depth resolved lattice expansion with nitrogen depth profile possible after correcting for orientation dependent sputtering
- Problem: similar orientation dependent sputter yield in SIMS resulting in "averaging across whole surface"

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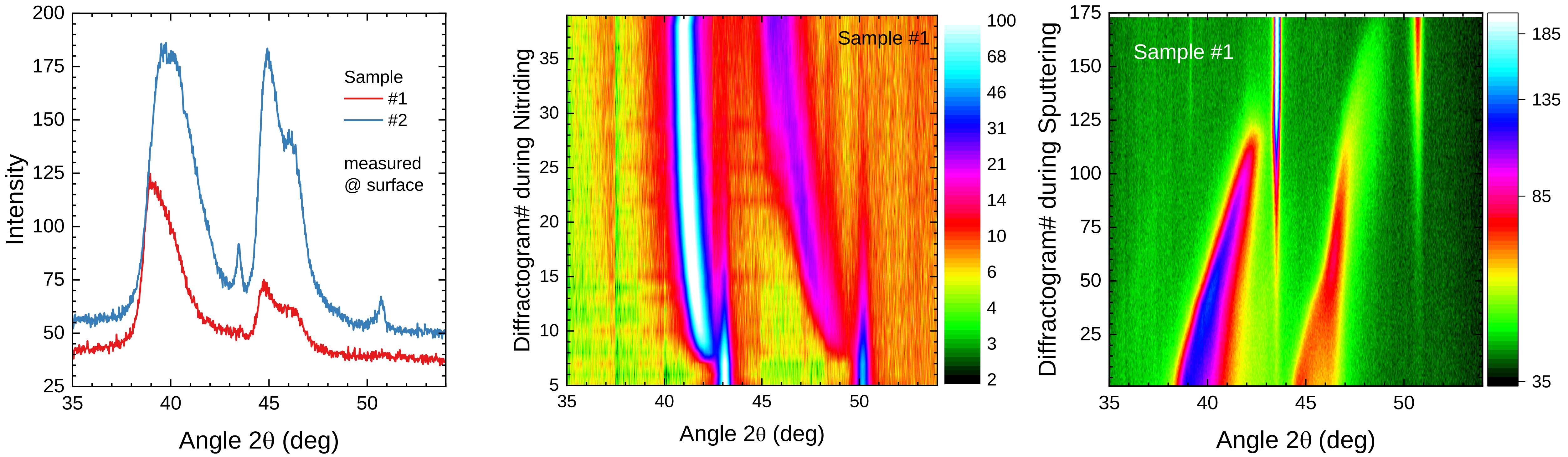
Results: Broadening of (200)



- Selected samples show a distinct broadening of the (200) expanded peak
- Effect most pronounced in conventional θ-2θ in Bragg-Brentano geometry
- Measurements during nitriding indecisive as diffusion is dominating
- *In-situ* measurements during sputtering point towards layered structure

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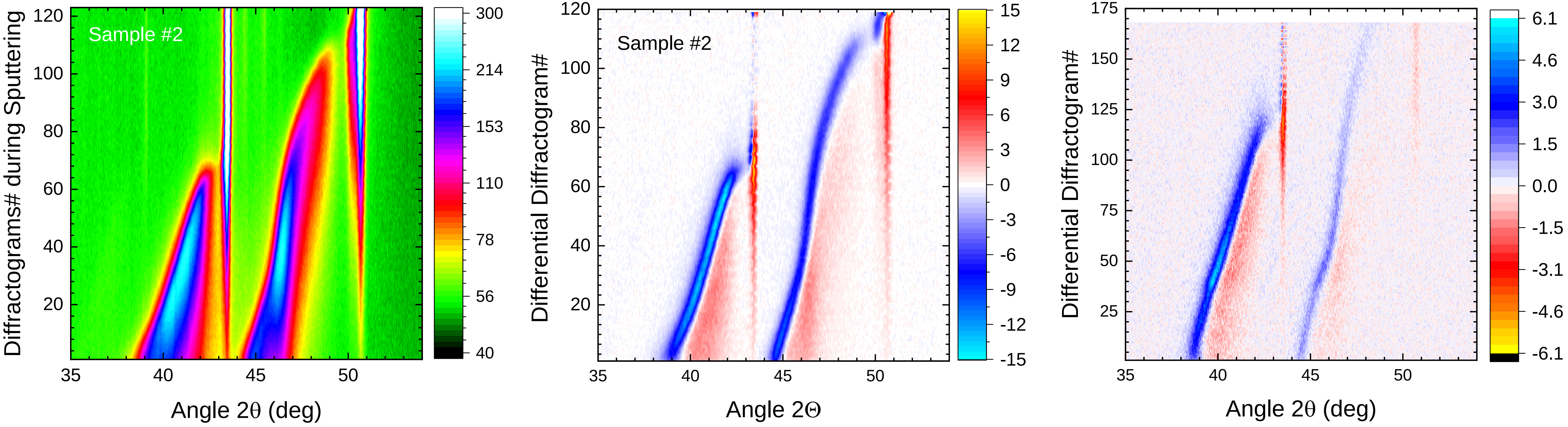
Results: Broadening of (200)



- Differential diffractograms allow clarification
- Presence of two different $\gamma_N(200)$ expanded phases – at different depths
- $\gamma_N(111)$ never affected!!
- fct symmetry with changing orientation (200) → (002) near surface??

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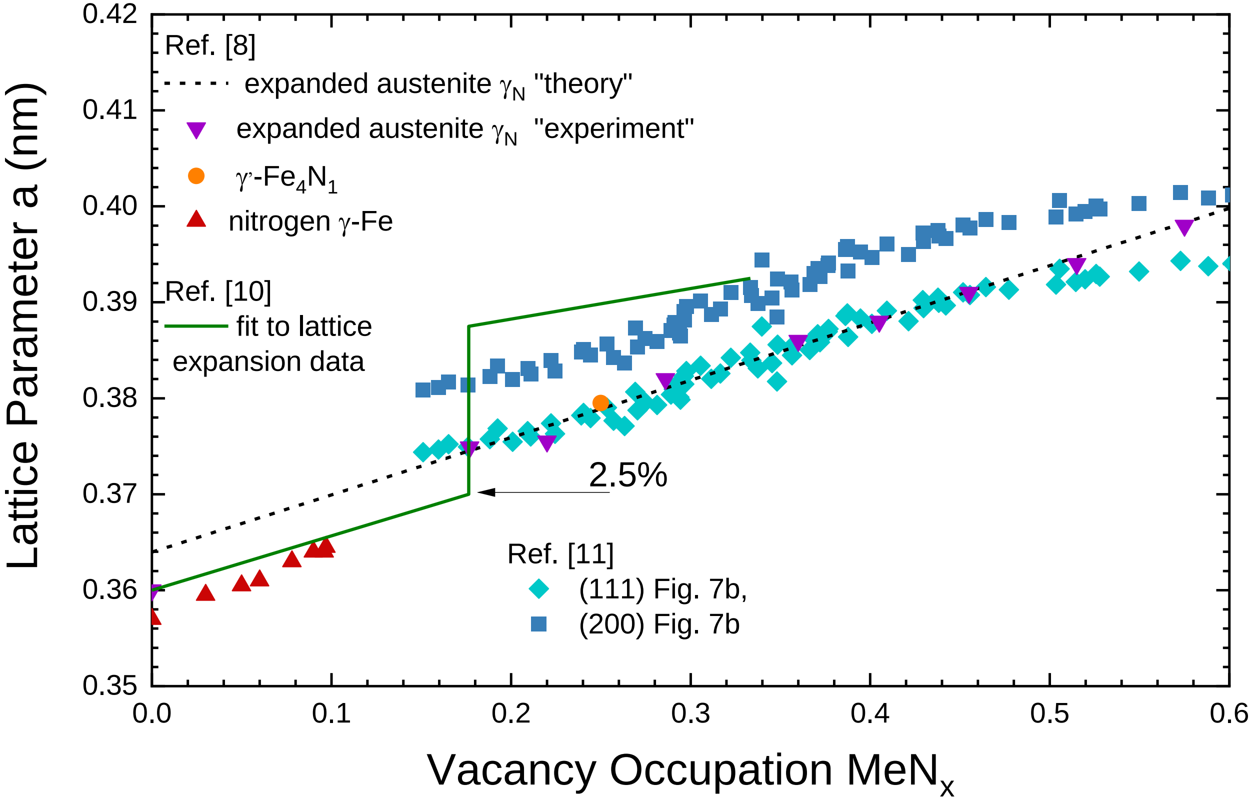
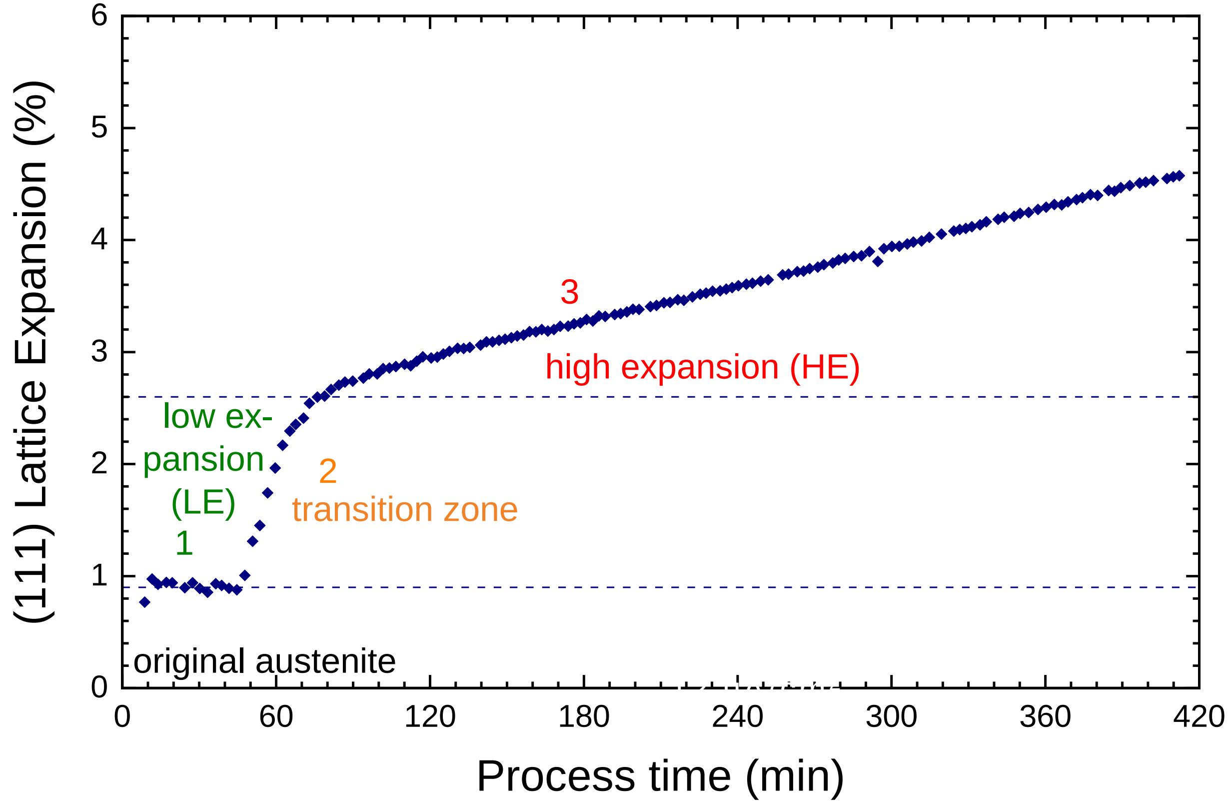
Results: Initial Phase





- Restricted stability of expanded austenite between 15 and 40 at.% nitrogen
- Time resolved measurements during nitriding show fast transition between low and high expansion phase
- Dynamics of "phase transition"?

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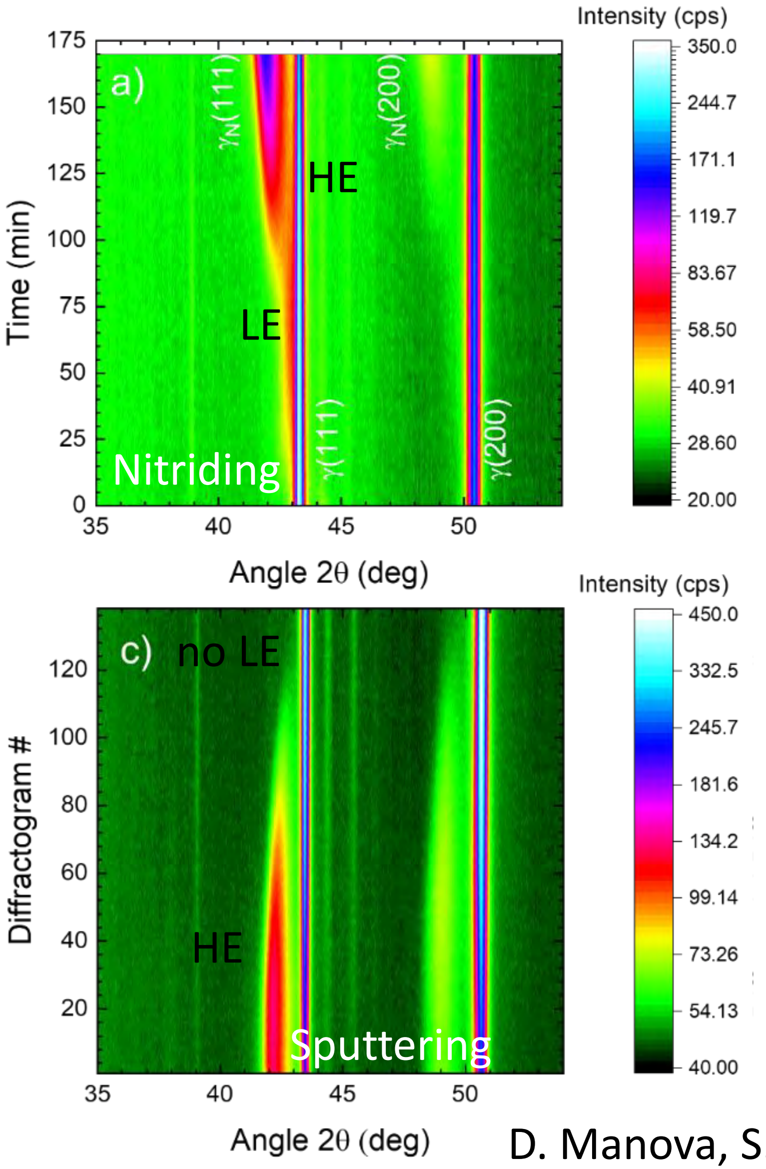
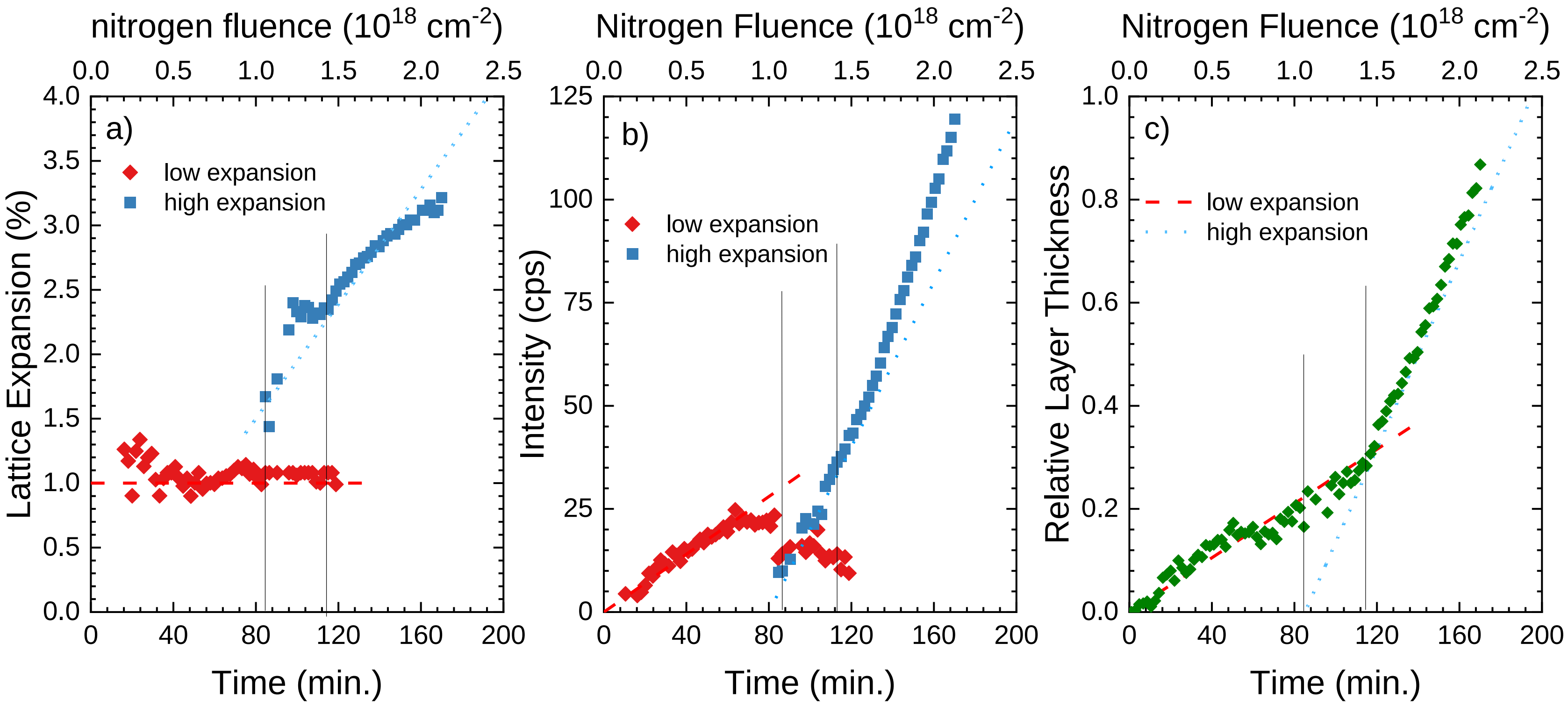
Results: Initial Phase





- Analysis shows competition of two phases: LE vs. HE
- LE - constant expansion, slow growth, HE - increasing expansion, fast growth
- Delayed nucleation of HE and complete loss of LE phase even at interface

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Conclusions

- *In-situ* XRD measurements during sputter etching as powerful, laboratory-based method for elucidating phase information on layered structures
- Deconvolution of x-ray diffractograms measured at the surface is impossible for complex, layered structures or gradient layers
- Investigation of nitrogen in austenitic stainless steel:
  - peak broadening dominated by compositional nitrogen gradient
  - determination of orientation and depth-resolved lattice expansion
  - depth-resolved stress should be accessible
- Orientation dependent sputter yield does not cause degradation of depth resolution as grain orientations are probed independently

- Drawback: investigation of dynamic process requires sophisticated experiments

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