Physikalisch-Technische Bundesanstalt
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Characterization of artificial and aerosol nanoparticles with reference-free grazing incidence X-ray fluorescence analysis

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Introduction

In most cases, bulk-type or micro-scaled reference-materials do not provide optimal calibration schemes for analyzing nanomaterials as e.g. surface and interface contributions may differ from bulk, spatial inhomogeneities may exist at the nanoscale or the response of the analytical method may not be linear over the large dynamic range when going from bulk to the nanoscale. Thus, we have a situation where the availability of suited nanoscale reference materials is drastically lower than the current demand.

Reference-free XRF

Reference-free X-ray fluorescence (XRF), being based on radiometrically calibrated instrumentation, enables an SI traceable quantitative characterization of nanomaterials without the need for any reference material or calibration specimen. This opens a route for the XRF based qualification of calibration samples.

Sherman equation for K fluorescence

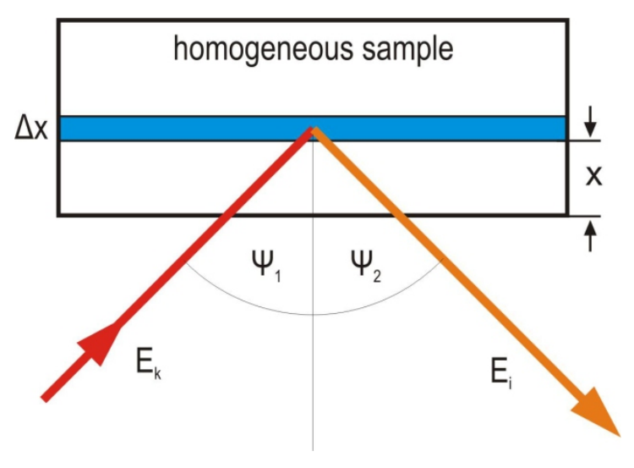
$$I_{i,j} = I_0(E_k)\varepsilon_{eff}(E_{i,j})\frac{d\Omega}{4\pi}\, e^{-\mu_s(E_k)\rho x/\cos(\Psi_1)}\; W_i \tau_i(E_k)\omega_i T_{i,j}\frac{1}{\cos(\Psi_1)}\Delta x\; e^{-\mu_s(E_{i,j})\rho x/\cos(\Psi_2)}$$

absorption

fluorescence production

absorption

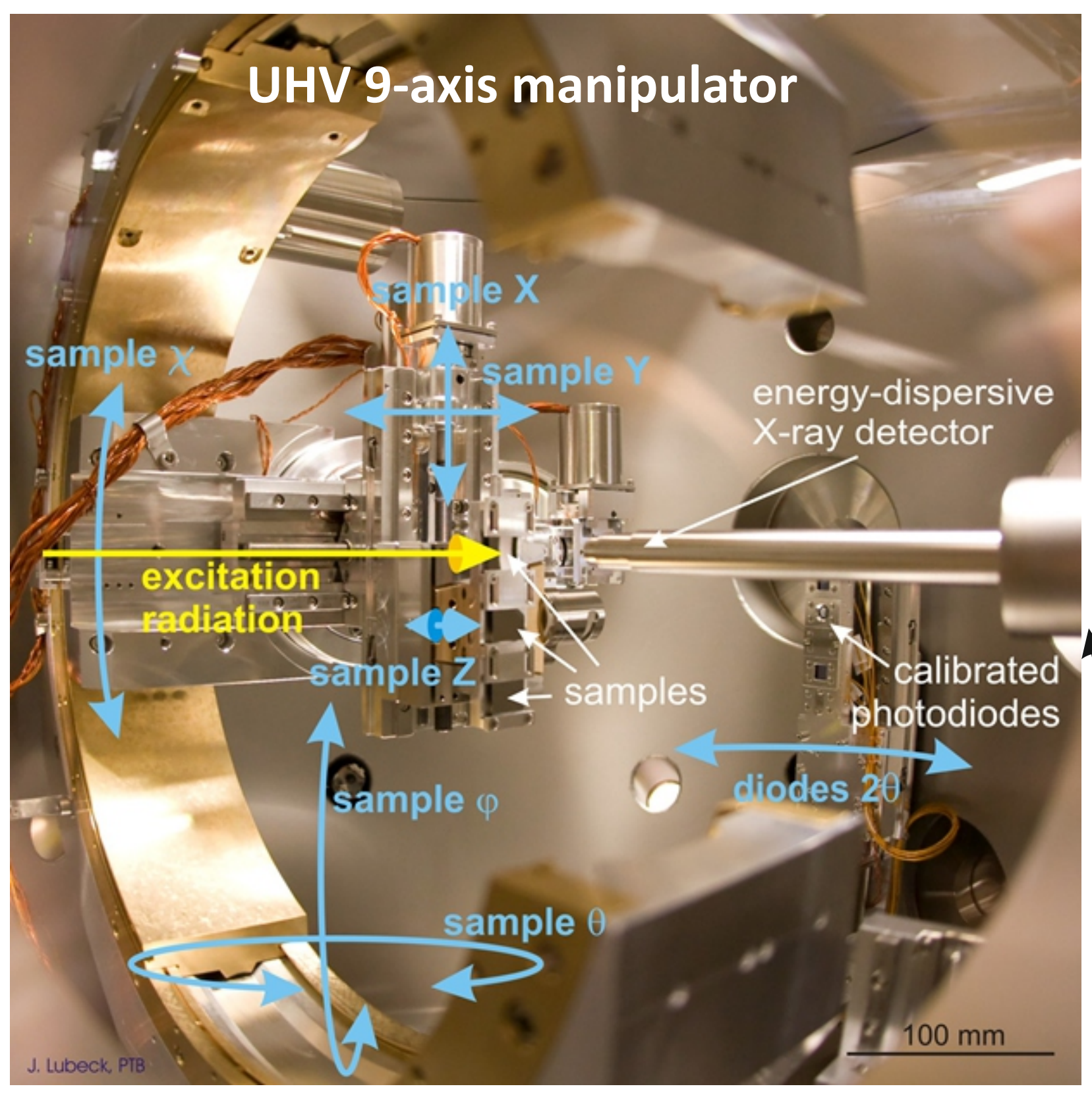
instrumental parameters:
$\varepsilon_{eff}(E_{i,j})$, $d\Omega/4\pi$
atomic fundamental parameters:
μ_S, τ, ω_i, T_i, ρ
specimen composition
W_i weight fraction of element *i*



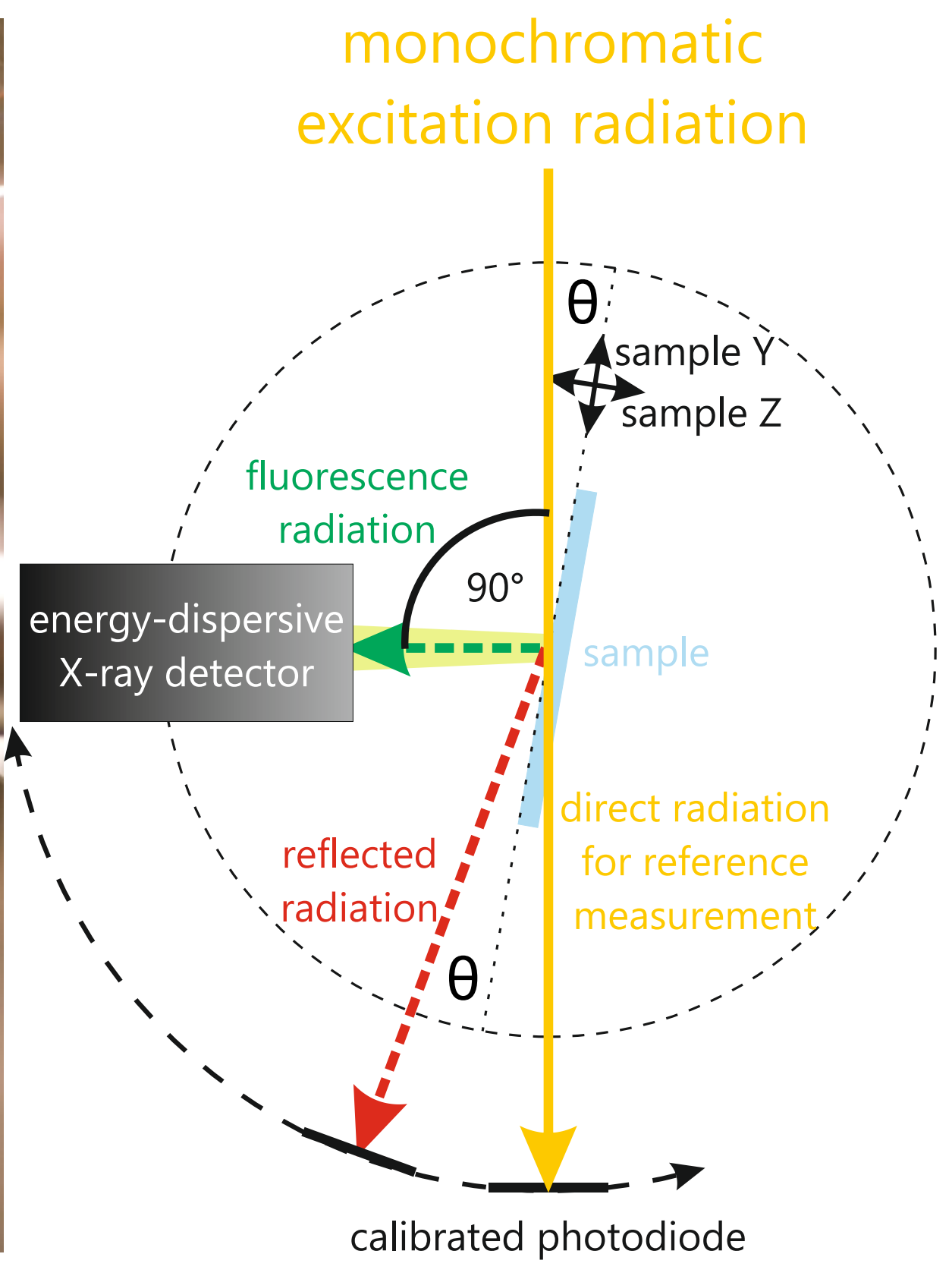
J. Anal. At. Spectrom. (2008) 23, 845 - 853

Experimental capabilities

• TXRF, GIXRF and XRF	Accessible photon energy range:
• NEXAFS / XANES	80 eV – 1875 eV @ PGM beamline
• EXAFS	1.740 keV – 10.5 keV @ FCM beamline
• XRR	6.5 keV – 80 keV @ BAMline



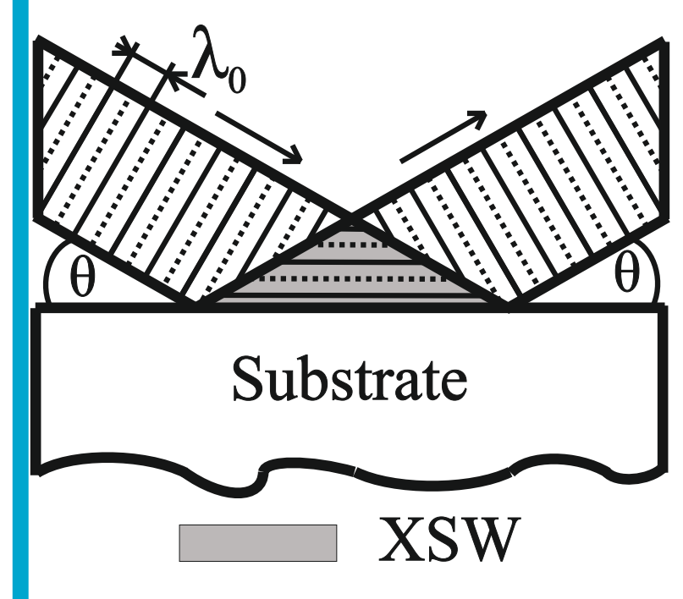
View into the experimental chamber



Sketch of the experimental setup

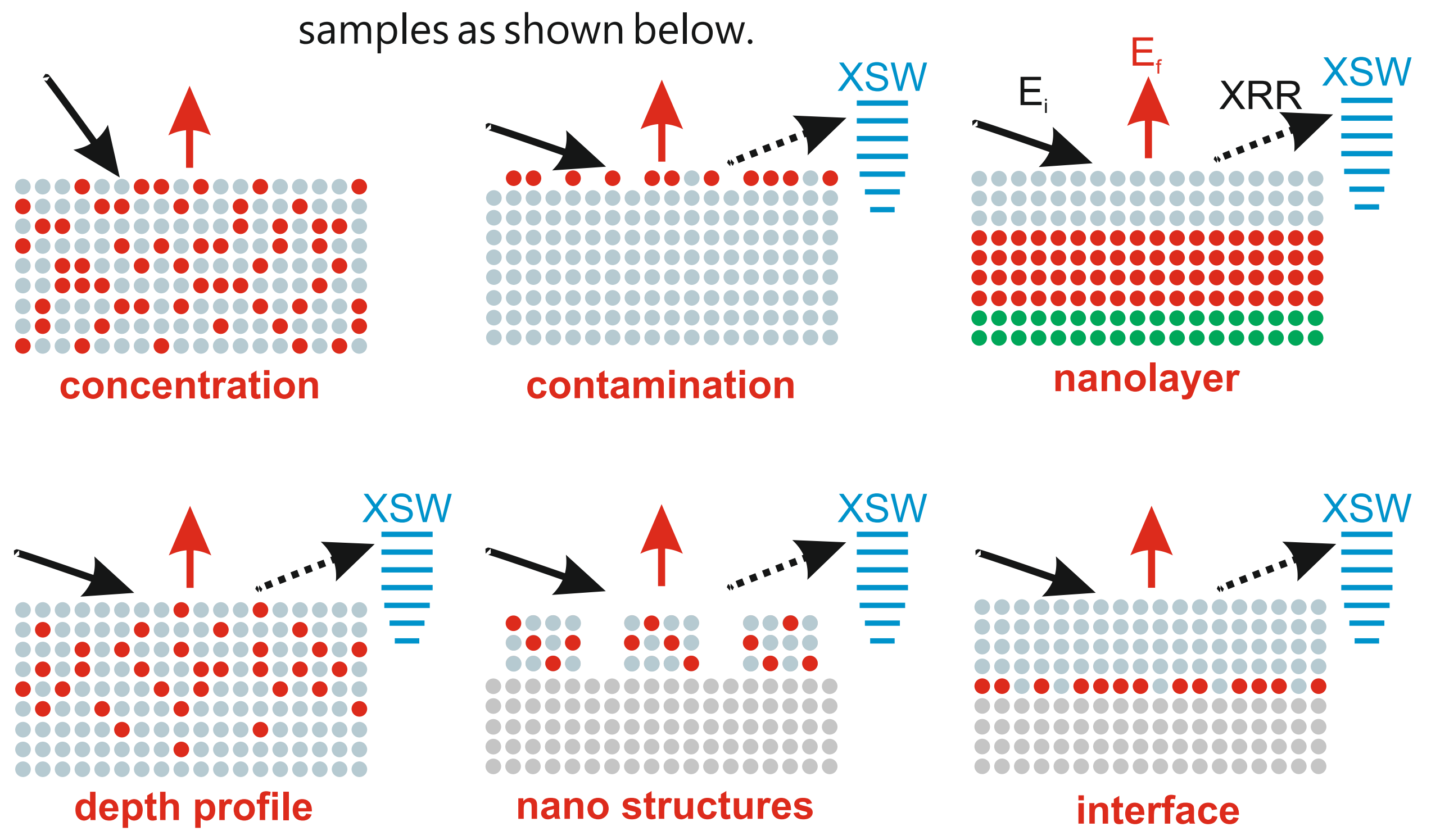
Rev. Sci. Instrum. (2013) 84, 045106

Reference-free XRF in grazing incidence geometry



Principle of GIXRF

Grazing incidence XRF is based on a variation of the incident angle of the exciting radiation. Due to the interference between incident and reflected beam an X-ray standing wave field (XSW) arises and strongly modifies the local intensity. By scanning the angle, the depth dependent changes of the XSW can be used as a nanoscaled depth sensor in order to gain dimensional information about the sample. In conjunction with the reference-free setup, this can be used to reveal quantitative information about different types of samples as shown below.



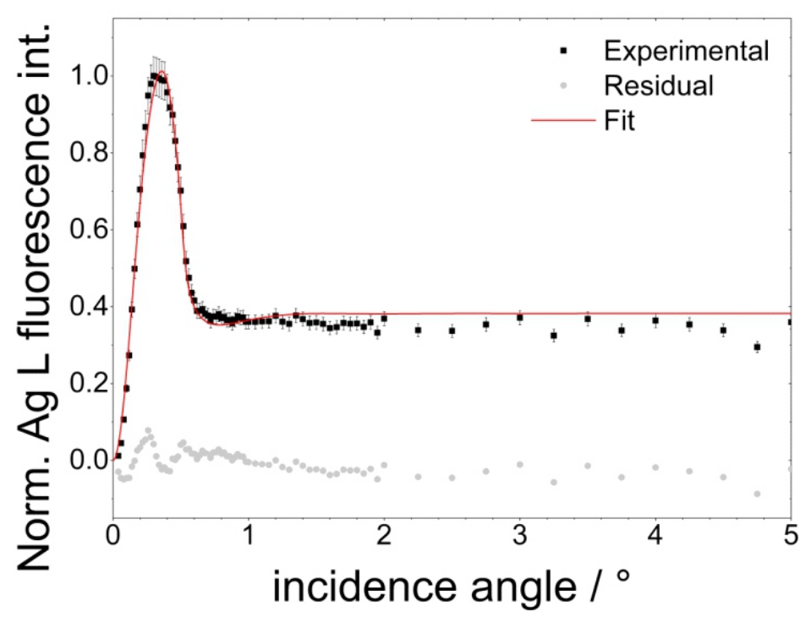
Sketch of the different accessible sample types for characterization with reference-free GIXRF

Materials (2014) **7(4)**, 3147-3159

Characterization of nanoparticle depositions

Reference-free GIXRF is also suitable for both a chemical and a dimensional characterization of nanoparticle depositions on flat substrates. By means of the reference-free quantification, an access to deposition densities and other dimensional quantitative measureands is possible.

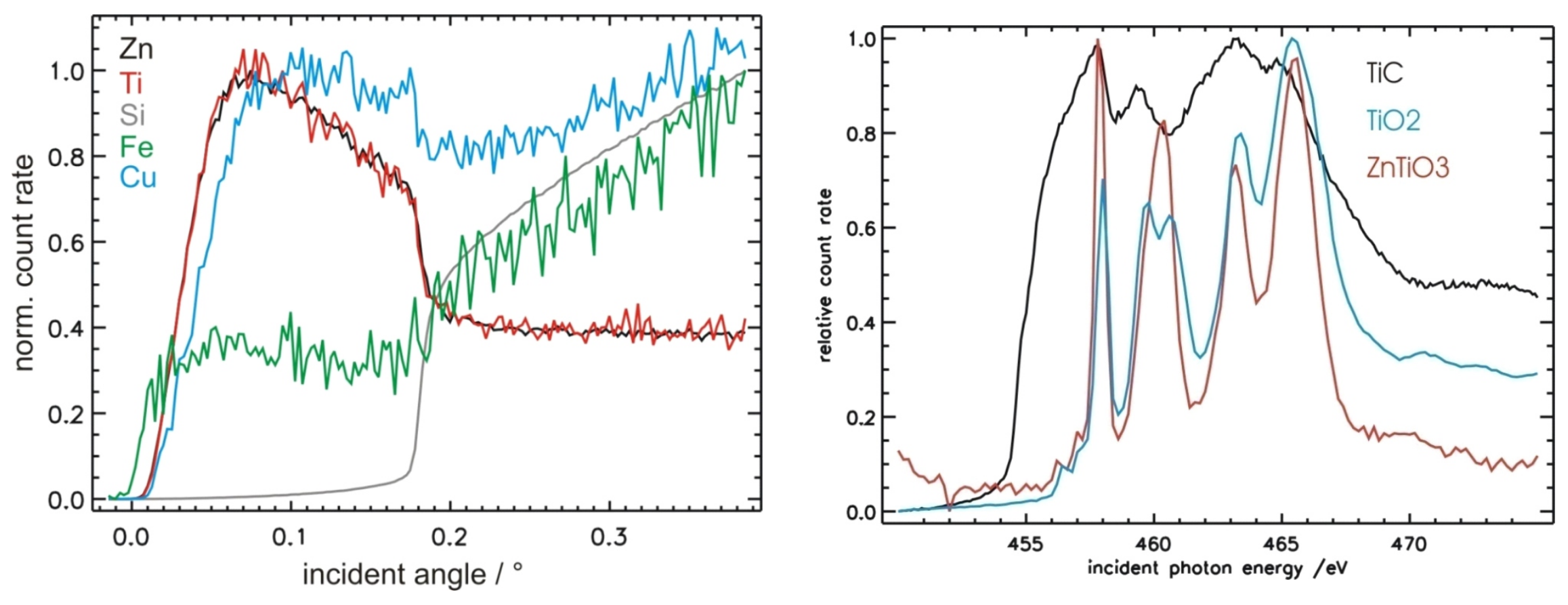
By employing also X-ray absorption spectroscopy (XAFS), also a chemical speciation of the nanoparticles or a compound within can be performed.

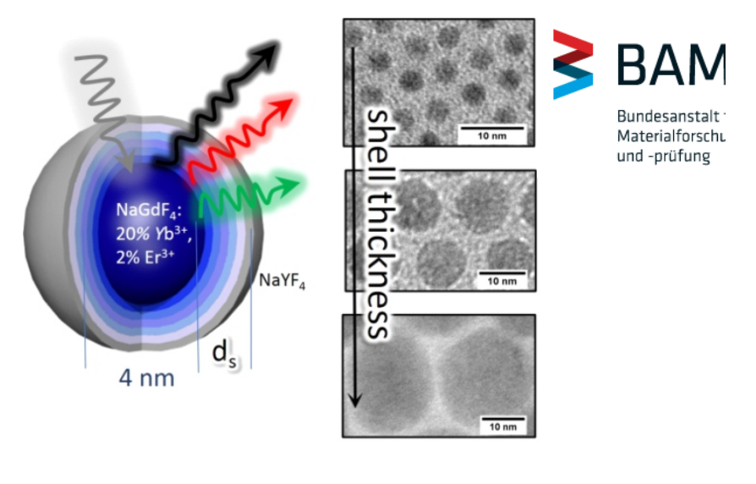


Ag nanoparticles
Si substrate
E_0 = 3.5 keV

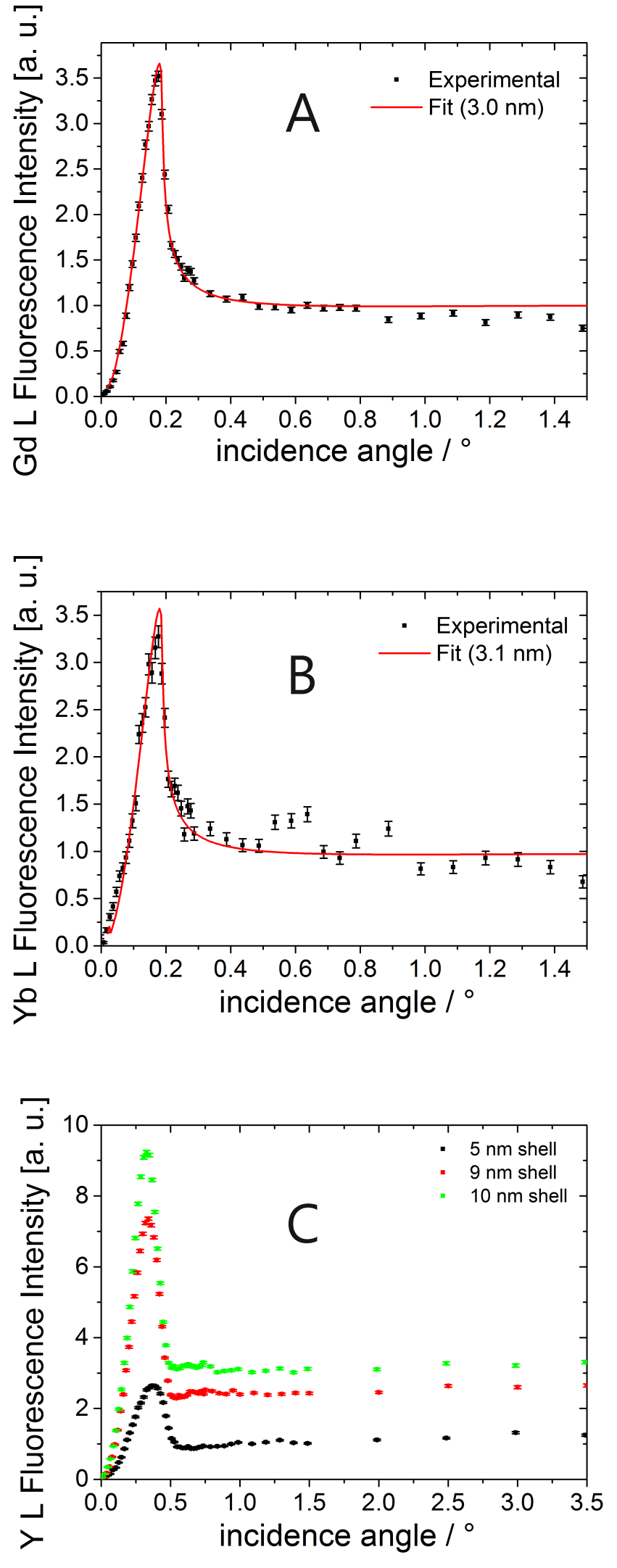
80% with 9.5 nm diameter
20% with 24.2 nm diameter
0.5 nm capping layer

Nominal 30 nm ZnTiO3 particles: Ti and Zn GIXRF reveals homogeneous particles, Chemical speciation XAFS

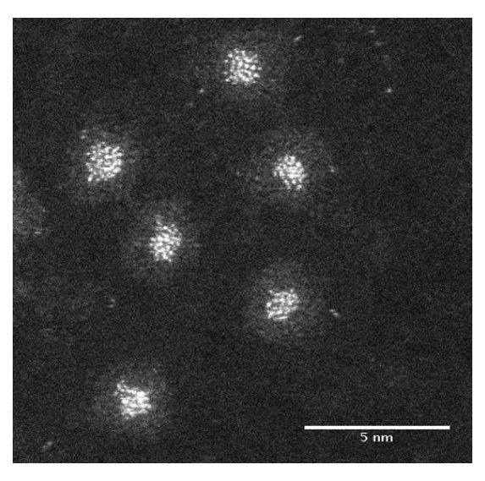




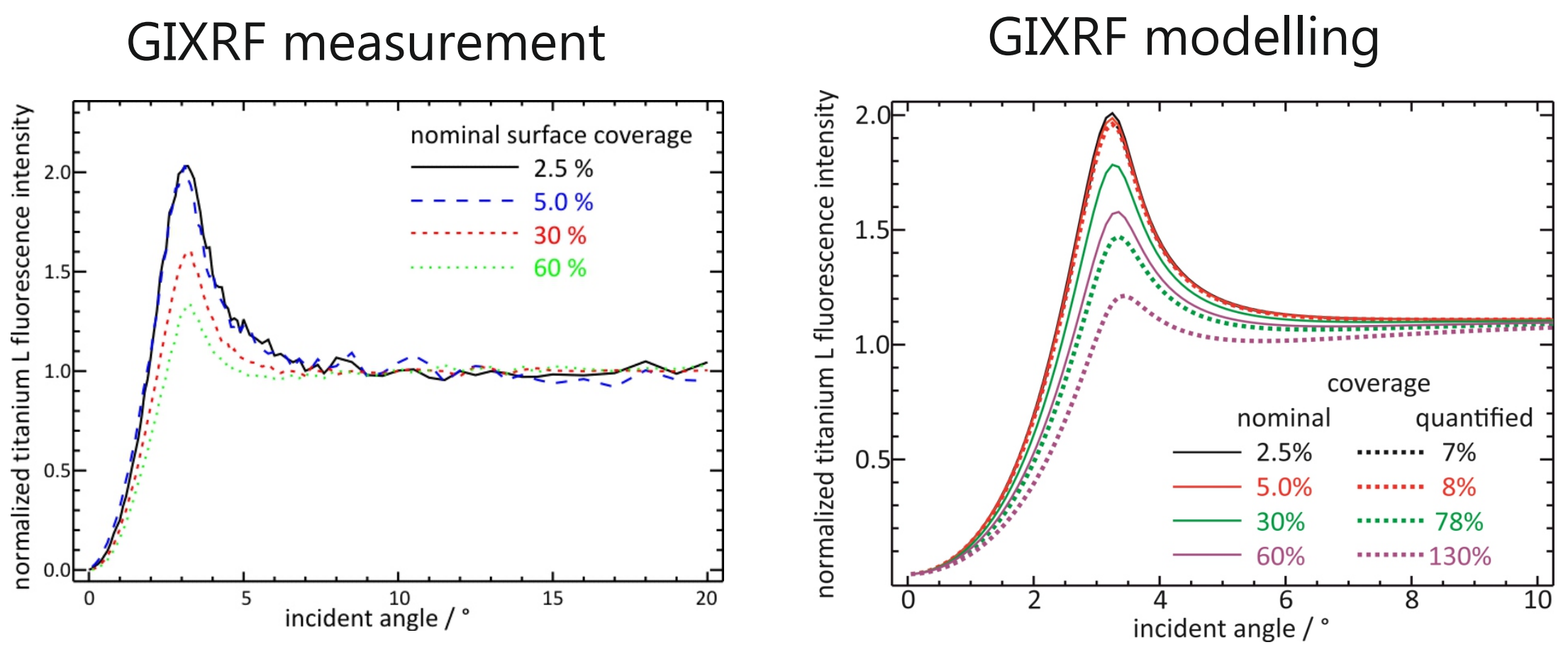
Core-shell nanoparticles measured at 9.5 keV and 3.7 keV: A and B from core only particles, C for core-shell particles with different shell thickness



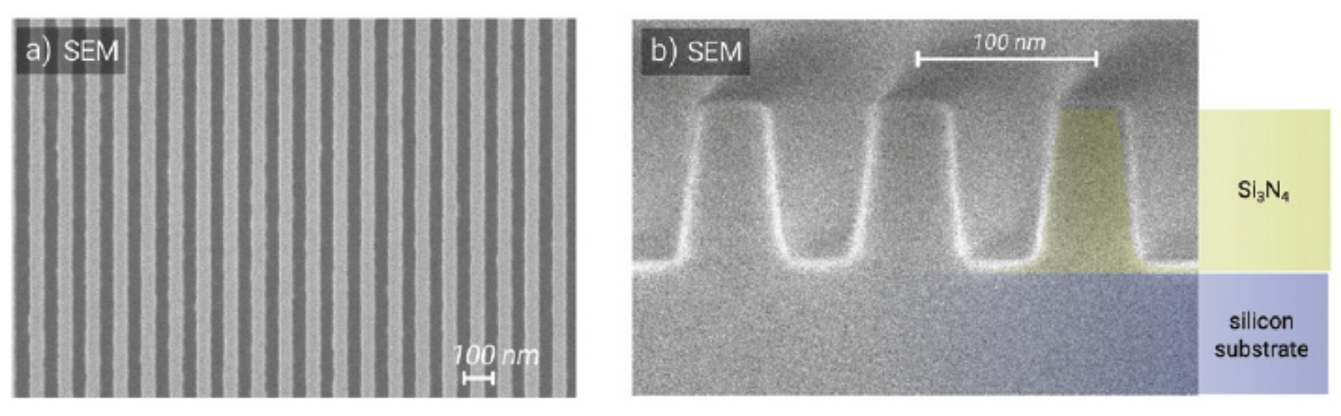
Reference-free GIXRF quantification of Pt-TiO$_2$ core-shell nanoparticle depositions with different deposition densities.



STEM Image

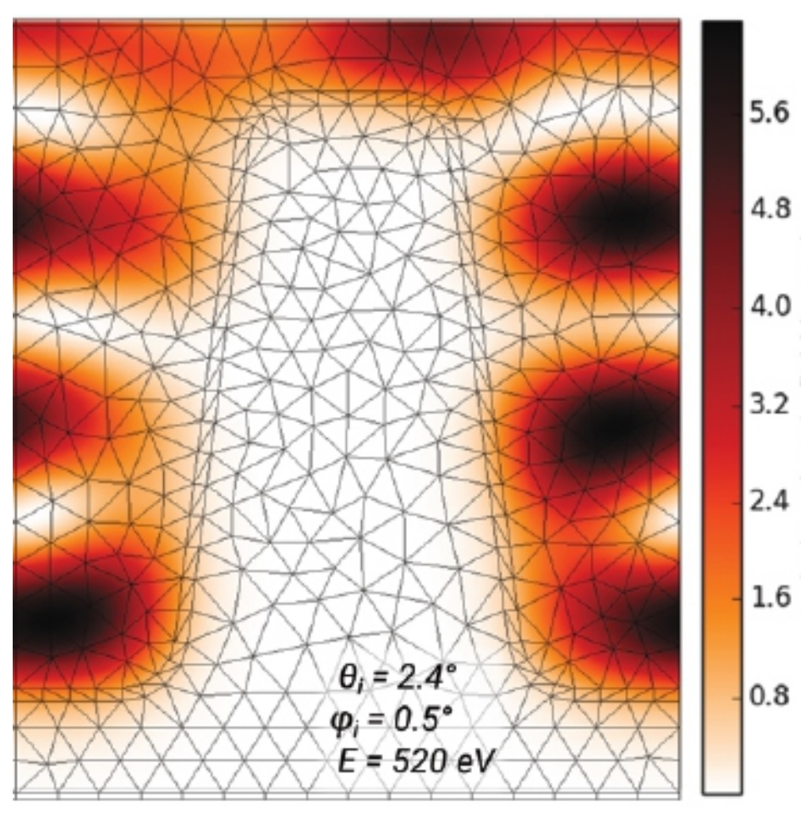


Characterization of artificial 2D nanostructures

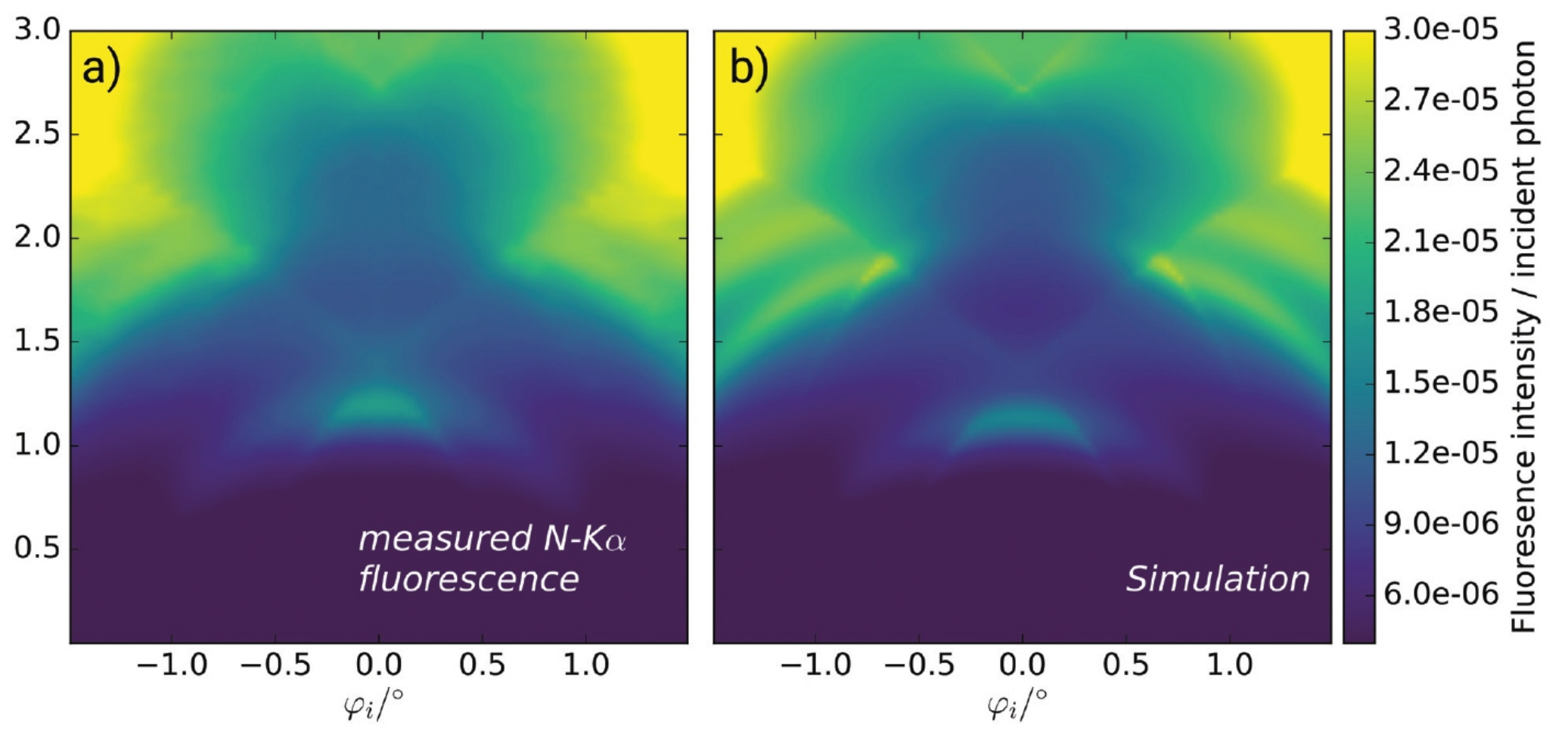


SEM images of the characterized Si$_3$N$_4$ grating structure

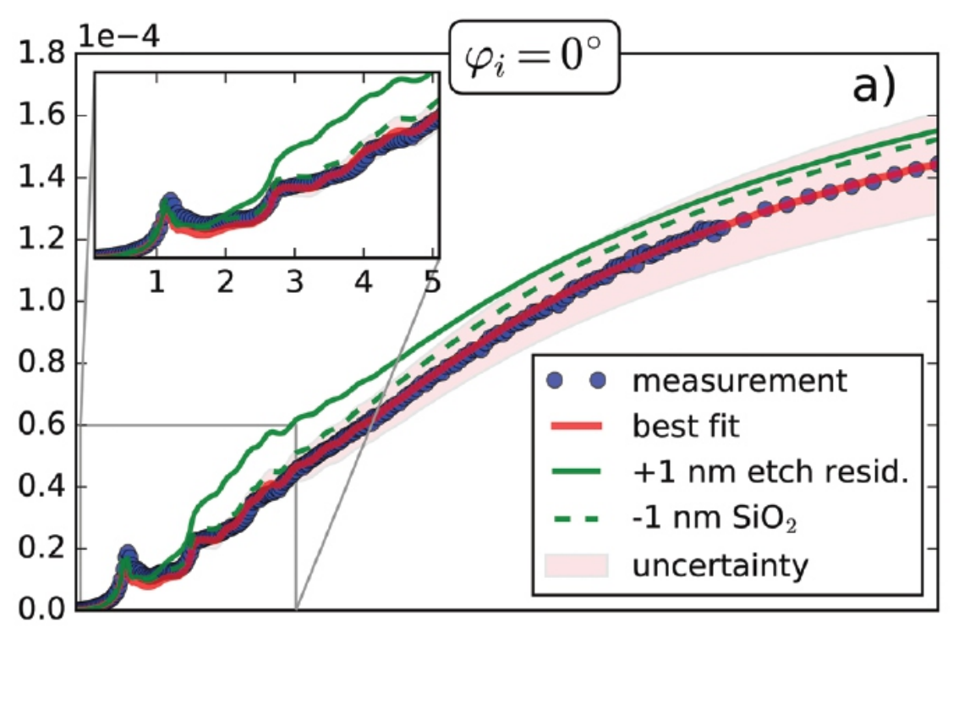
In a second example, we work on the development of nanostructures as calibration samples. Several lithographic 2D grating structures have been fabricated and characterized using the reference-free GIXRF methodology of PTB. Here, an advanced calculation scheme based on the finite element method for the intensity distributions within the X-ray standing wave field (XSW) is required. In addition to the traceable quantification of elemental mass depositions, this allows for a determination of in-depth elemental distributions and the dimensional properties of the nanostructures.



FEM calculation of the XSW intensity distribution



Comparison of an FEM calculated fluorescence intensity map to the experimental data as a function of the incident and the azimuthal angle



Comparison of the experimental data to the FEM calculated data

Nanoscale (2018) 10, 6177-6185

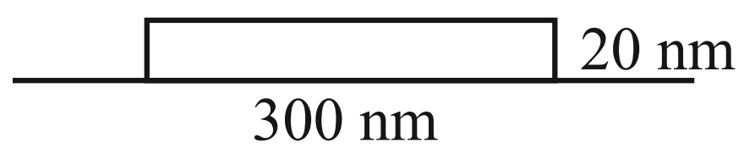
Characterization of 3D artifical particle-like nanostructures

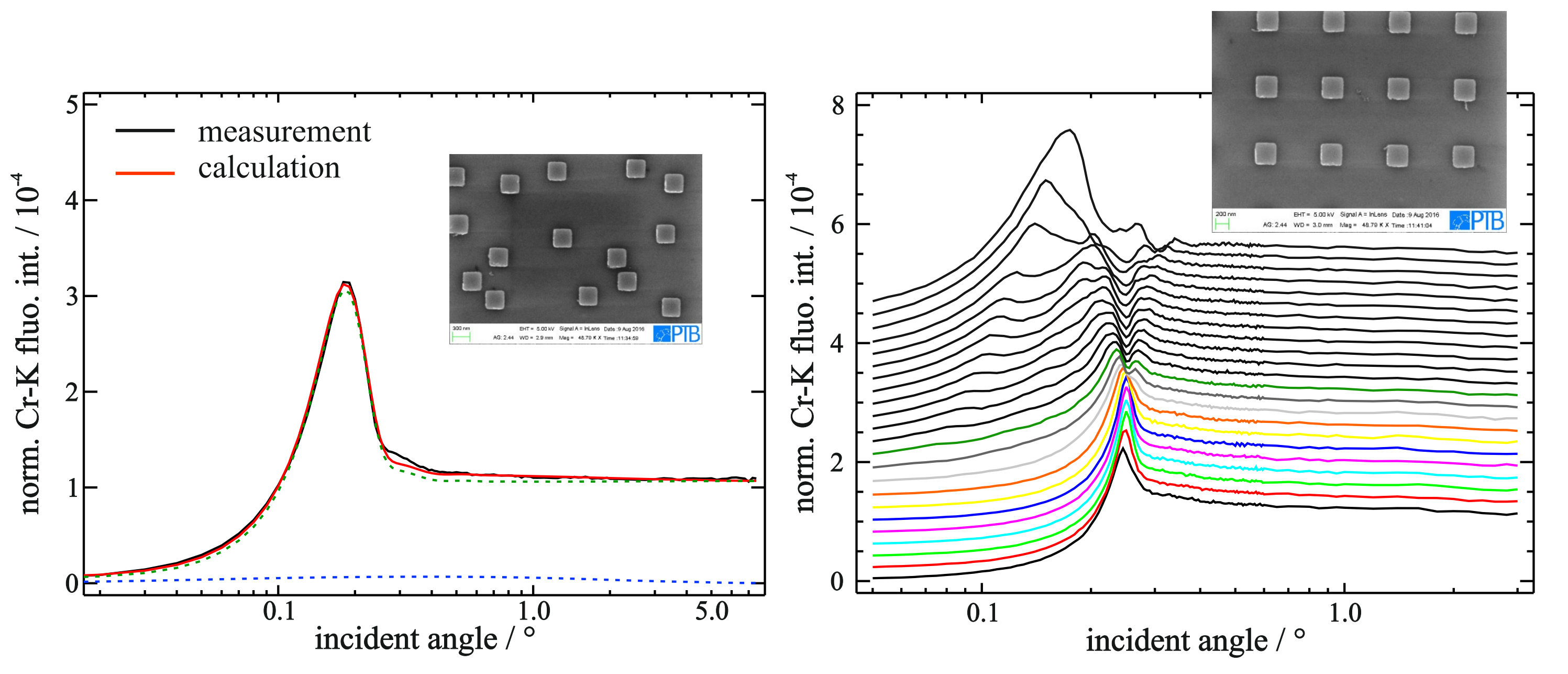
In principle, the methodology is also well suited to characterize 3D nanostructures for calibration sample applications. Here, electron beam lithography was used to fabricate regular and irregular ordered chromium pads with nominal sizes of 300 x 300 x 20 nm^3. They were also characterized using the reference-free GIXRF methodology of PTB.

Here, the experimental data from the irregular sample is modeled using the effective density approach. The nanostructures are approximated as a layer of Cr with reduced density. The density can be calculated as a function of the dimensional parameters of the structures.

The regular structures also show a strong dependence on the azimuthal angle. However, they cannot be modeled using the effective density approach requiring also the FEM based technique. As this results in a much larger computational effort as compared to the 2D gratings, it could not be performed so far. Due to the high amount of features in the data, we expect a high sensitivity for both the dimensional parameters and the elemental distributions.

Schematic view of nano-squares





Comparison of an experimental GIXRF curve for irregularly and regularly ordered chromium nanoblocks (see insets). For the irregular blocks also a calculated GIXRF signal assuming ideally shaped rectangles is shown.

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