X-ray spectrometry

SI traceable characterization of nanomaterials by X-ray xpectrometry

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Materials characterisation by X-ray spectrometry

PTB
X-ray spectrometry

- analytical challenges for nanotechnologies
- reference-free x-ray spectrometry
- surface contamination and nanolayer characterization
- depth profiling at grazing incidence
- chemical speciation at buried interfaces
- operando speciation of bulk-type films
- high energy and spatial resolution spectrometry
- atomic fundamental parameter determinations

Analytical challenges for nanotechnologies

X-ray spectrometry

- dozens of new nanoscaled materials appear every month
- technology R&D cycles for new materials down to 4 months
- need for correlation of material properties with functionality
- requirements on sensitivity, selectivity and information depth
- most analytical methodologies rely on reference materials or calibration standards but there are only few at the nanoscale
- usage of calibrated instrumentation and knowledge on atomic data enables reference-free techniques such as SR based XRS

Challenges for nanotechnologies – nano-scaled reference materials

X-ray spectrometry

Nanoscaled Reference Materials (in line with ISO/TC 229 Nanotechnologies)

‚Reference materials are the key to guaranteeing realiability and correctness for results of chemical analyses and technical measurements.‘

Categories:

- flatness
- film thickness
- single step , periodic step, step grating
- lateral X-Y-axis, 1-dim
- lateral X-Y-axis, +2-dim,
- critical dimensions
- 3-dimensional
- nanoobjects/nanoparticles/nanomaterial
- nanocrystallite materials
- porosity
- depth profiling resolution

Every month several tens new nanoscaled materials appear.

The number of nanoscaled reference materials is considerably lower.

Reference-free / first principles based methodologies can address this increasing gap.

www.nano-refmat.bam.de/en/

Challenges for nanotechnologies – nano-scaled reference materials

X-ray spectrometry

Nanoscaled Referenc

‚Reference materials a

for results of chemical

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- nanocrystallite materi
- porosity
- depth profiling resolution

Description	Certified values (nm)	RM name	RM type	RM no.
Ti-Al multilayer 100/250 nm on 100Cr6 steel substrate	100	BAM L-100	CRM	12
Thickness standards, tantalum pentoxide film Calibration of depth-resolving surface analysis	30	BCR-261	CRM	13
Thickness standard, silicon dioxide film NIST traceable	(2, 4.5, 7.5, 12, 25, 50, ...)	FTS	RM	3
Thickness standards, silicon nitride film NIST traceable	20	NFTS	RM	10
Thickness standards, tungsten film For best performance with sonar technology, an oxide layer 100 nm thick is added between the silicon substrate and the metal film, traceable to NIST	200	WFTS	RM	11
GaAs/Al/As-superlattice Calibration of depth resolution	23	CRM 5201-a	CRM	32
SiO2/Si multilayer film reference material Consist of five layers with SiO2 and Sigrown using r.f. magnetron sputtering method on aSi substrate. The thickness of each layer is certified in units of length via X-ray reflectometry, control the precision of analysis and to regulate measurement condition in depth profile analysis by ion	20	NMIJ CRM 5202-a	CRM	54
GaAs/AlAs super lattice The CRM has six-layer-structure and the certified values for the thickness from the second to sixth layer are given; control the precision of analysis and to regulate measurement condition in depth profile analysis by ion sputtering	9,51	NMIJ CRM 5203-a	CRM	55
Ultrathin silicon dioxide film 3.49 nm (0.19 nm); control the precision of analysis and to regulate measurement condition in depth profile analysis by ion sputtering	3,49	NMIJ CRM 5204-a	CRM	56

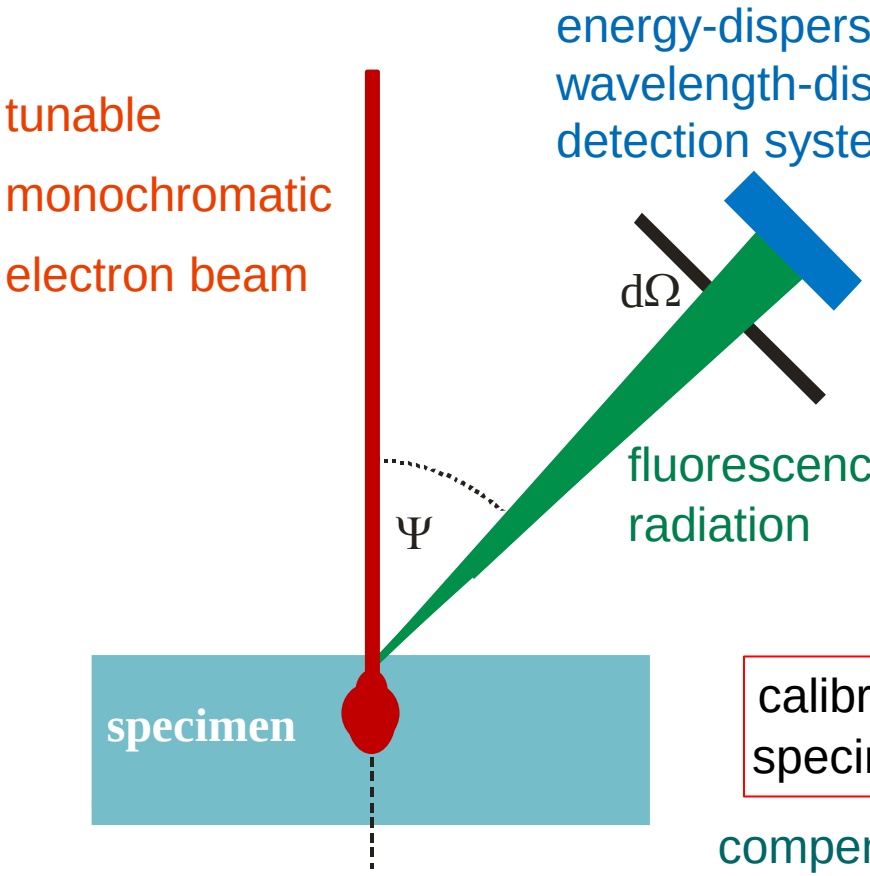
www.nano-refmat.bam.de/en/

X-ray emission spectrometry:

electron beam excitation - X-ray beam excitation

PTB
X-ray spectrometry

EDS

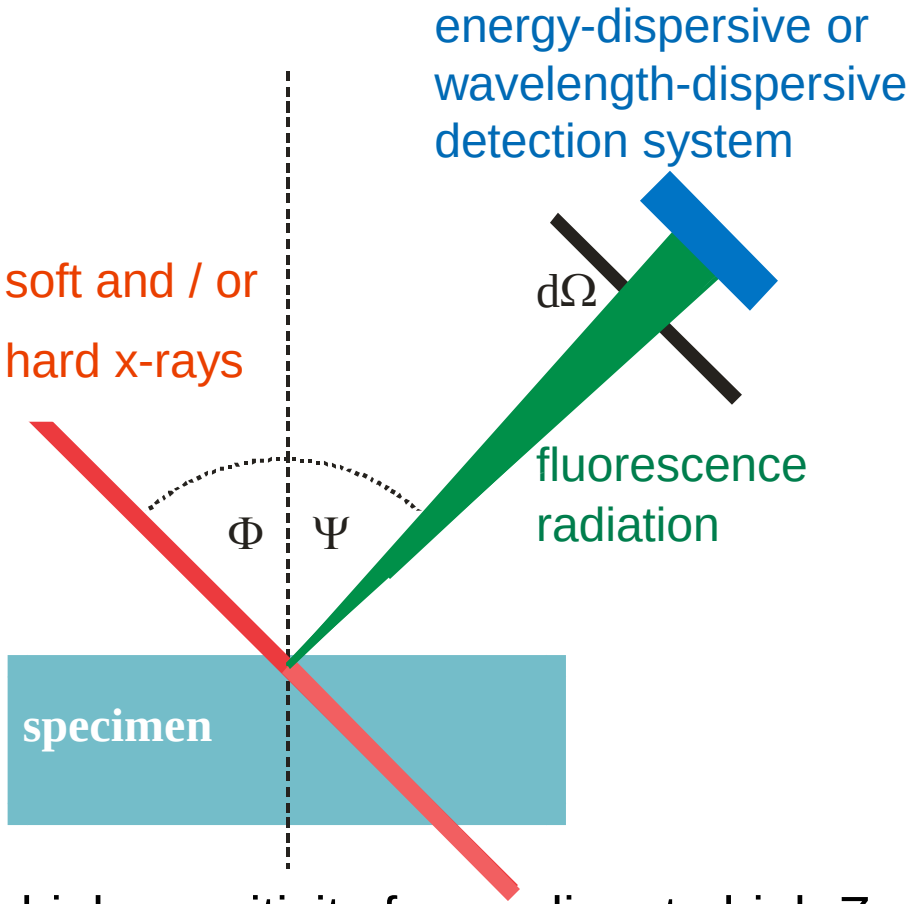


high sensitivity for low Z
small beam profiles
small penetration depth

calibration
specimens

compensation
for missing
knowledge

XRS



high sensitivity for medium to high Z
moderate beam profiles
moderate to large penetration depth

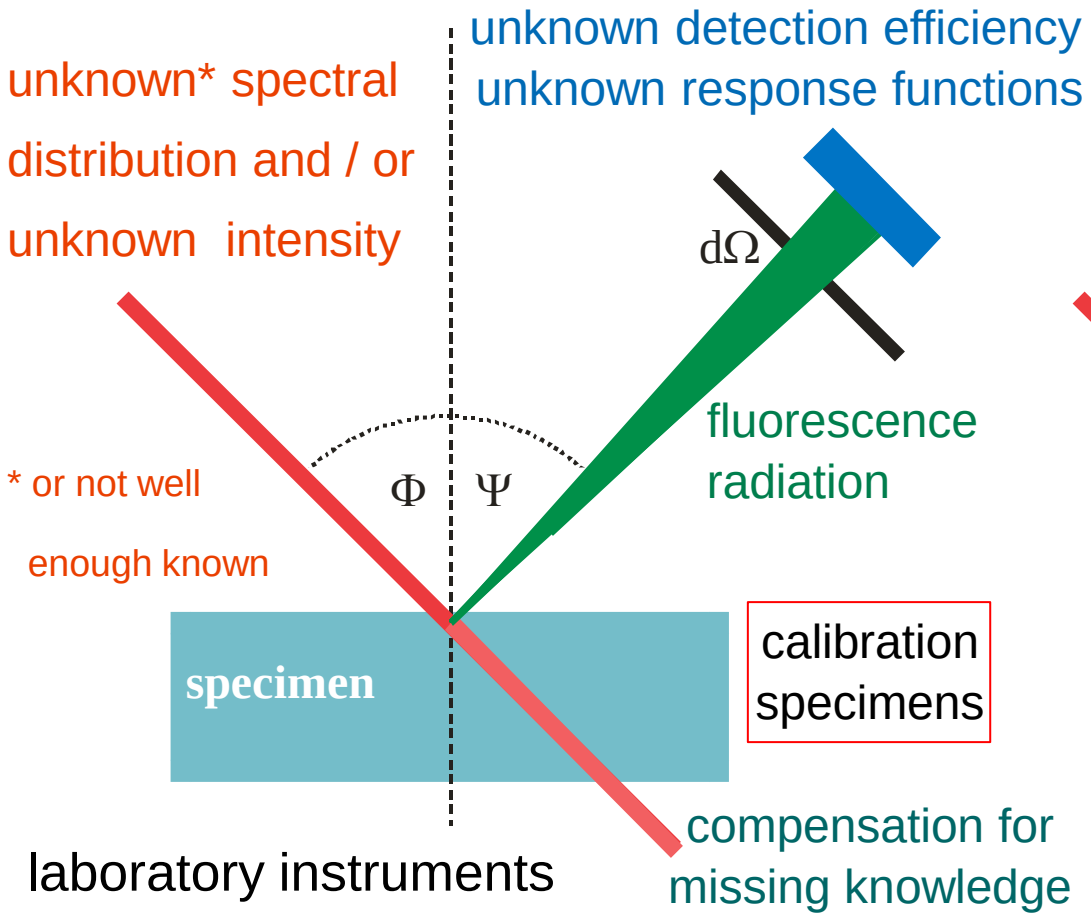
X-Ray Fluorescence (XRF) analysis:

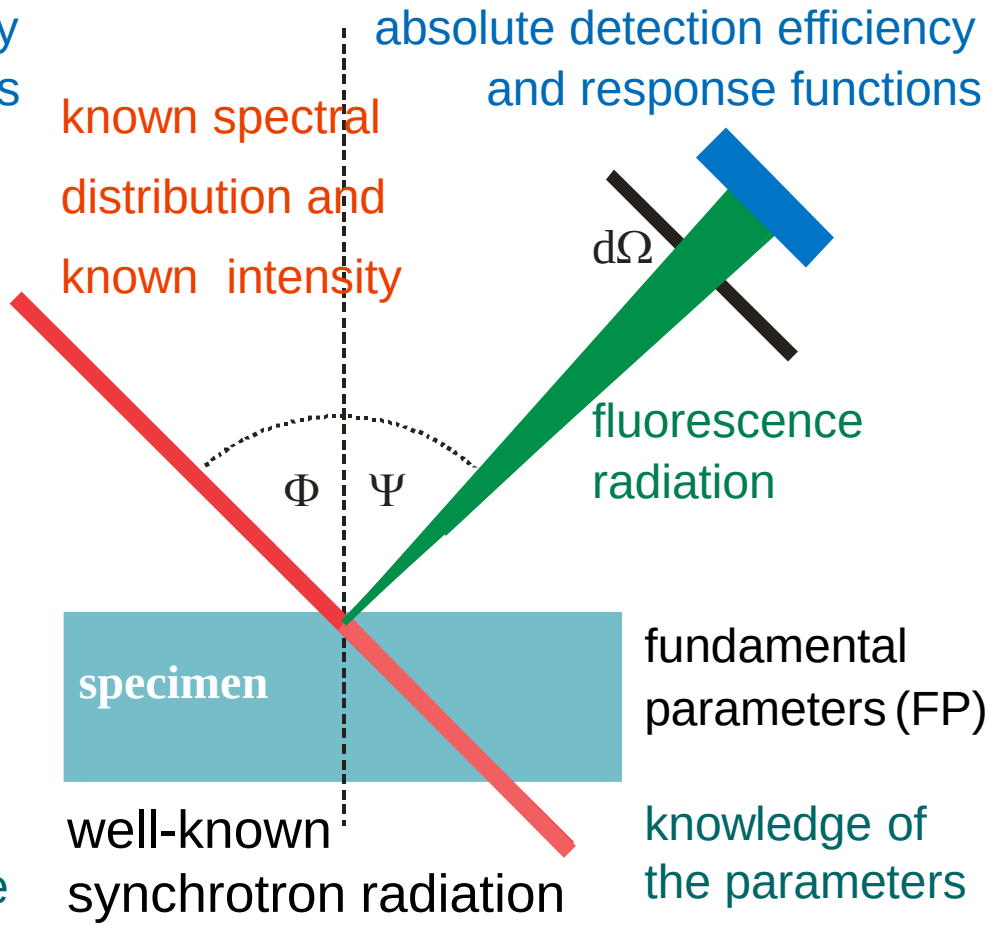
reference material based - reference-free approaches

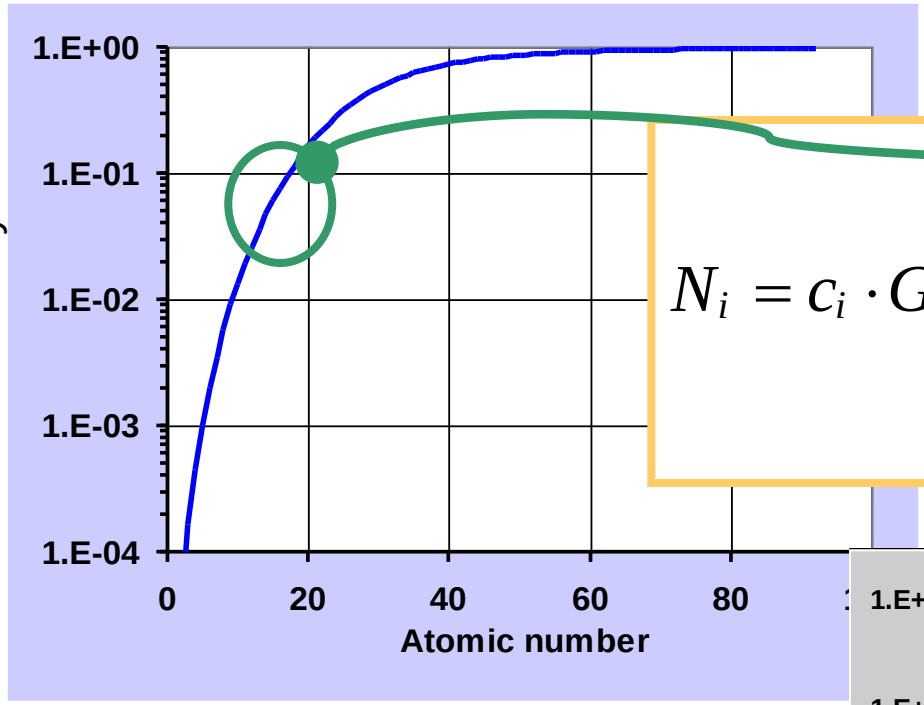
X-ray spectrometry

conventional technique based on calibration or reference materials

reference-free technique based calibrated instrumention and FPs

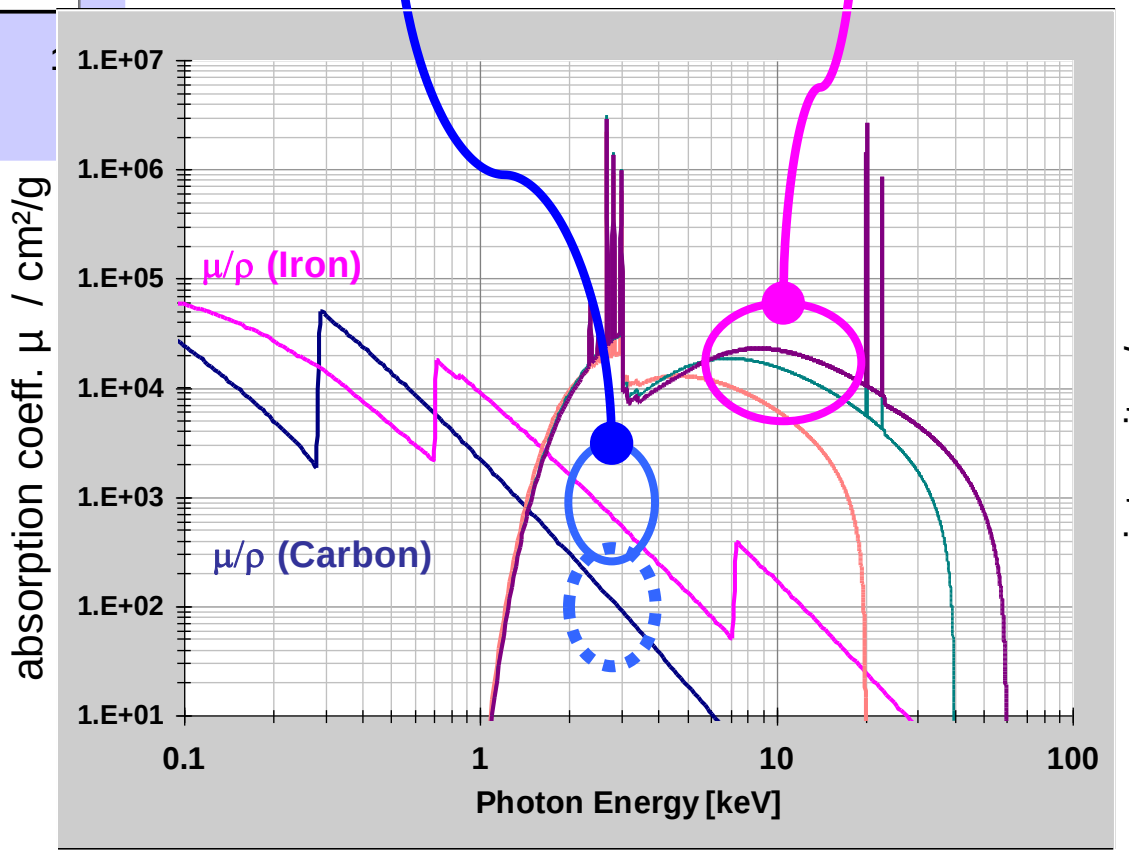






$$N_i = c_i \cdot G \cdot \int_E \frac{\frac{S-1}{S} \cdot p_i \cdot \omega_i \cdot \tau_i(E)}{\frac{\mu(E)}{\sin\psi_1} + \frac{\mu(i)}{\sin\psi_2}} \cdot N_0(E) \cdot dE$$

Fundamental parameter approach in XRF analysis



courtesy of M.Mantler, TU Vienna

Quantification concepts in X-Ray Fluorescence analysis

PTB
X-ray spectrometry

Typical XRF quantification variants:

α- coefficients	reference material based	reference-free methodology
	(chemical traceability)	(physical traceability to SI system)
- empirical coefficients	- pre-calibration of instrumentation e.g. by thin *standards*	- good knowledge on both instrumental and fundamental parameters (FP)
- interpolation regime for main matrix elements or traces in constant matrices	- additional calibration by reference materials for specific *applications*	- increasing relevance for complex sample systems, e.g. nano-scaled specimens or operando studies
- extrapolation restricted	- interpolation by good knowledge of FP data	- reason: lack of appropriate reference materials or calibration standards

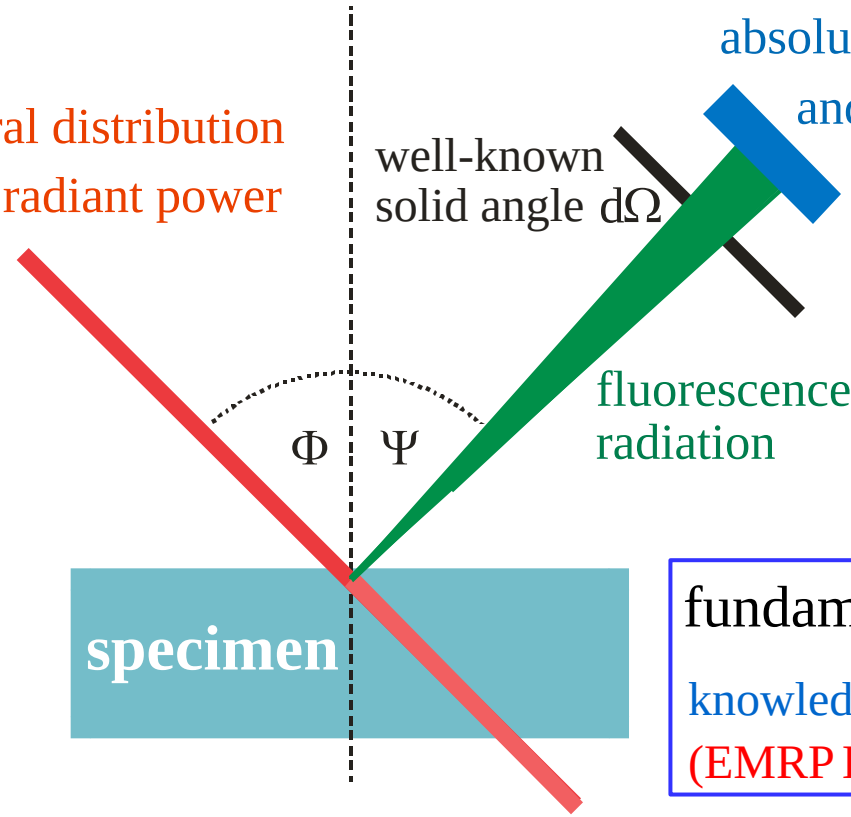
→ *Relevant contribution of knowledge on FP on the uncertainty of the analytical results*

Synchrotron radiation based x-ray spectrometry

X-ray and IR spectrometry

XRS excitation channel:

XRS detection channel:



PTB capabilities:

→ characterized beamlines

→ calibrated photodiodes

→ calibrated diaphragms

→ calibrated Si(Li) detectors

fundamental parameters

knowledge of atomic parameters
(EMRP IND07, NEW01, ENG53)

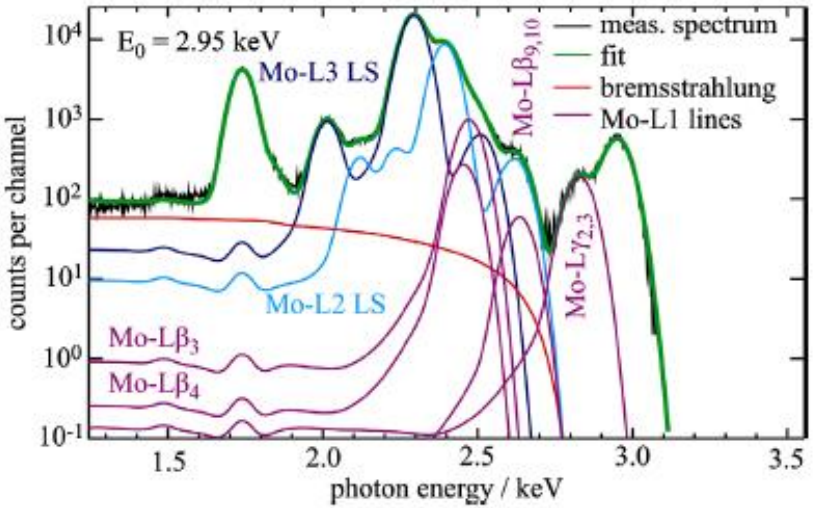
transmission measurements

absorption correction factors

Phys. Rev. Lett **113**, 163001 (2014)

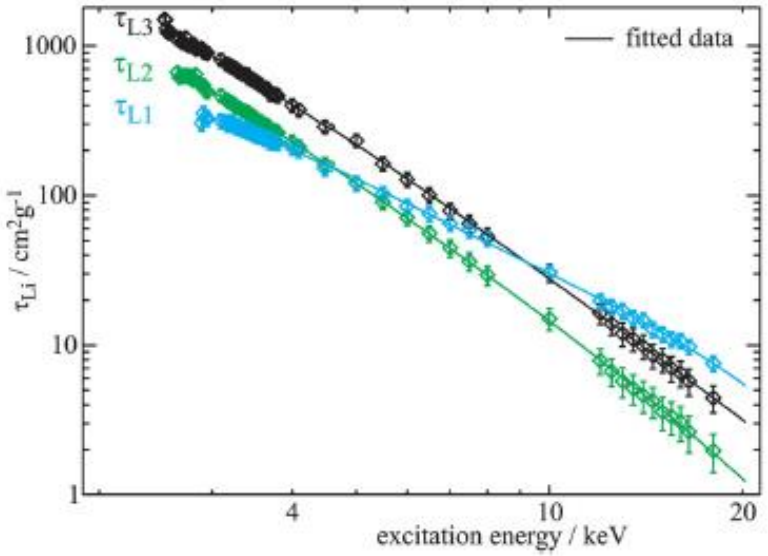
Determination of L-shell photoionization cross sections

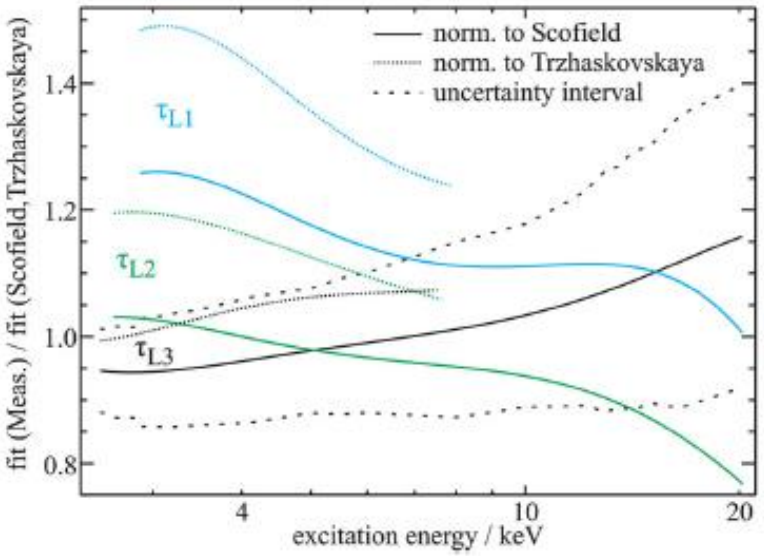
X-ray spectrometry



Response function based deconvolution of a Mo layer XRF spectrum for each L-shell.

Experimentally determined PCS for the Mo-L subshells and the comparison to calculated data.



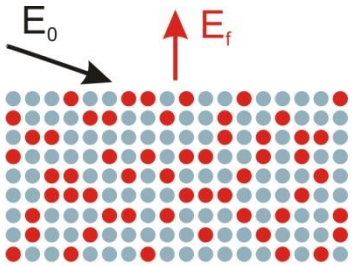


Phys. Rev. Lett **113**, 163001 (2014)

Tuning the analytical sensitivity and information depth by means of appropriate operational parameters

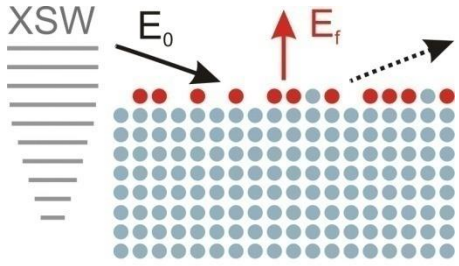
X-ray spectrometry

excitation conditions



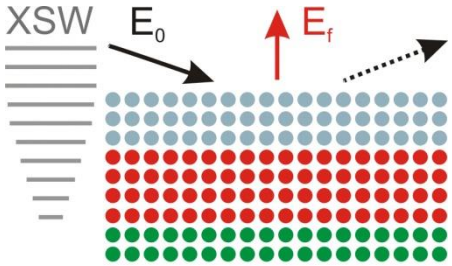
concentration

total-reflection



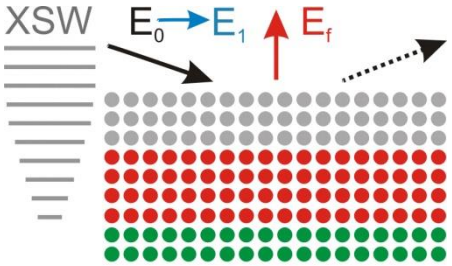
contamination

tunable incident angle



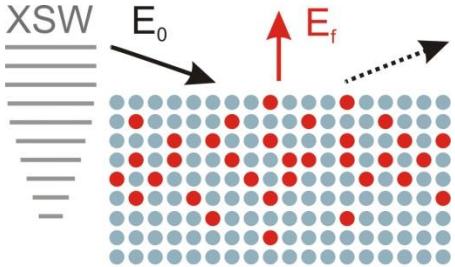
nanolayer

tunable photon energy



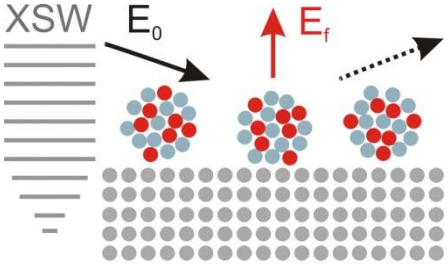
nanolayer speciation

tunable incident angle



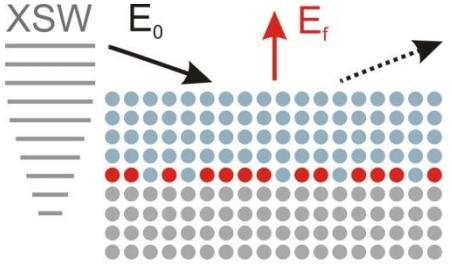
depth profile

total-reflection



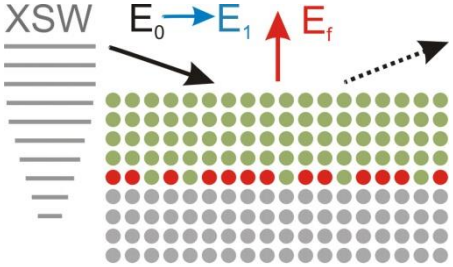
nanoparticles

tunable incident angle



interface

tunable photon energy



interface speciation

E_0 = photon energy of excitation radiation

E_1 = photon energy above absorption edge

E_f = photon energy of fluorescence radiation

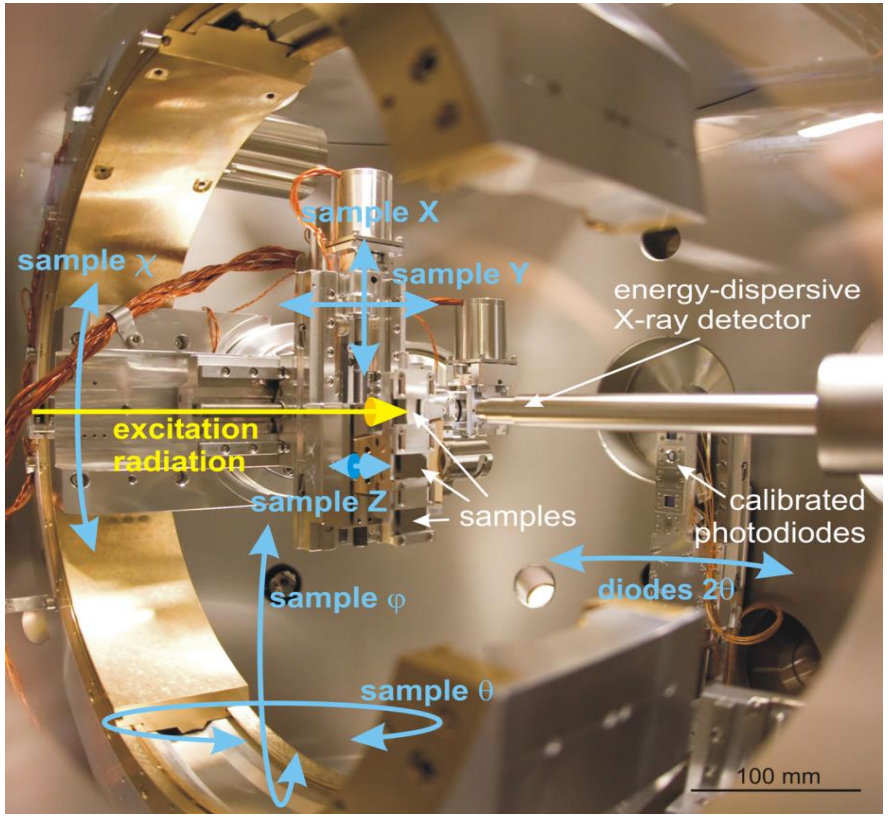
XSW = X-ray Standing Wave field

J. Anal. At. Spectrom. **23**, 845 (2008)

Novel XRS instrumentation for advanced materials characterizations with synchrotron radiation

X-ray spectrometry

PTB XRS intrumentation at BESSY



9-axis manipulator and chamber ensuring

- the entire TXRF, GIXRF and XRF regime
- polarization-dependent speciation by XAFS
- combined GIXRF and XRR investigations
- movable aperture system for reference-free XRF and atomic FP determinations

→ µm- and nm-beam forming optics options

Transfer of modified instrumentation to

- TU Berlin for a **laboratory plasma source**
- LNE/CEA-LNHB for **SOLEIL storage ring**
- IAEA (UN) for **ELETTRA storage ring**

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

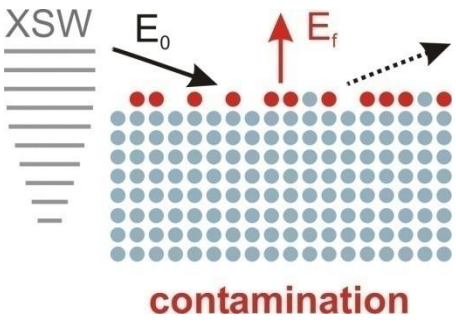
AIP **1741**, 030011 (2016)

Reference-free quantitation in TXRF analysis on Si wafers

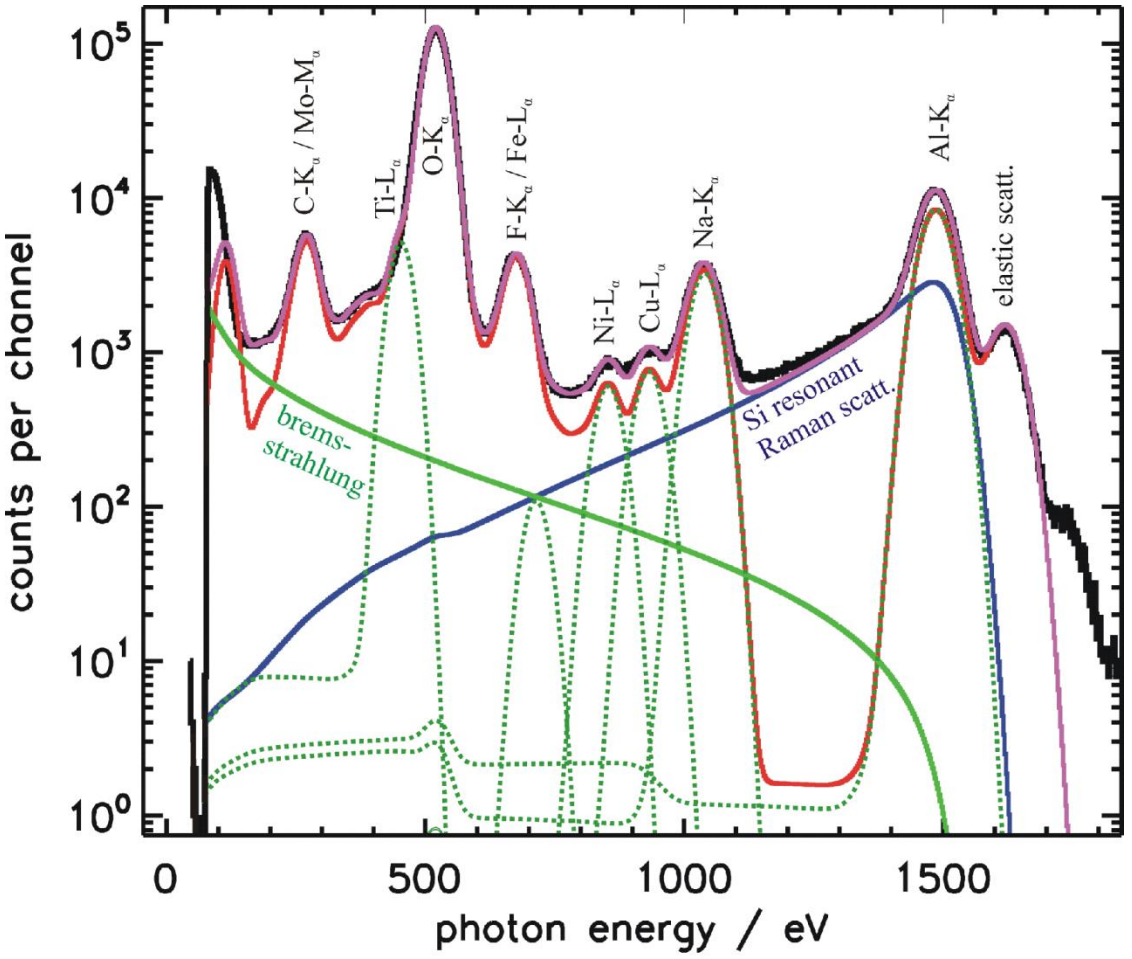
X-ray spectrometry

TXRF **spectra deconvolution** including SDD detector response functions, RRS, and bremsstrahlung contributions.

reference-free TXRF **quantitation**: known incident flux, detector efficiency and solid angle.



spin-coated wafer with 10^{12} cm^{-2} of various transition metals



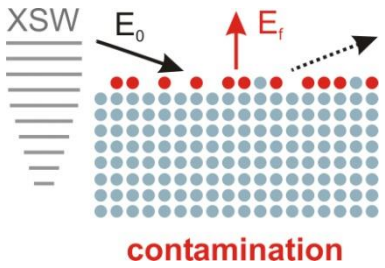
Anal. Chem. **79**, 7873 (2007) Phys. Stat. Sol. B **246**,1415 (2009)

Reference-free quantitation in SR-TXRF analysis

mass deposition m_i / F_I of the element i with unit area F_I

$$\frac{m_i}{F_I} = \frac{-1}{\mu_{tot,i}} \ln\left\{1 - \frac{P_i}{P_{0,Wsurf}\,\tau_{i,E_0}\,Q\,\frac{\Omega_{det}}{4\pi}\,\frac{1}{\sin\psi_{in}}\,\frac{1}{\mu_{tot,i}}}\right\}$$

E_0	photon energy of the incident (excitation) radiation
$P_0 = S_0 / \sigma_{diode,E_0}$	radiant power of the incident radiation
S_0	signal of the photodiode measuring the incident radiation
σ_{diode,E_0}	spectral responsitivity of the photodiode



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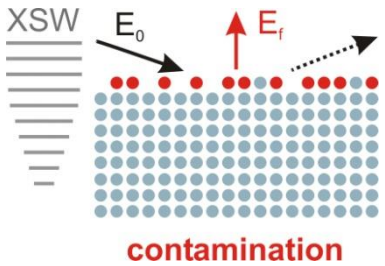
I_{Wsurf} relative intensity of the X-ray standing wave field[1] at the wafer surface

$P_{0,Wsurf} = P_0 I_{Wsurf}$

1 software package IMD: D. Windt, Computers in Physics **12**, 360-370 (1998)

ψ_{in} angle of incidence with respect to the wafer surface

E_i photon energy of the fluorescence line l of the element i



Anal. Chem. **79**, 7873 (2007)

Reference-free quantitation in SR-TXRF analysis

X-ray spectrometry

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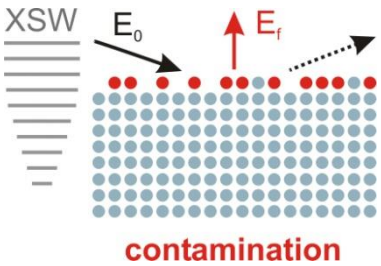
R_i detected count rate of the fluorescence line l of the element i

ε_{det,E_i} detection efficiency of the Si(Li) detector at the photon energy E_i

$P_i = R_i / \varepsilon_{det,i}$

Ω_{det} effective solid angle of detection



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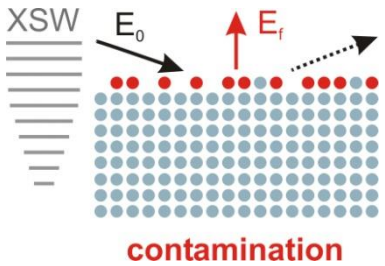
ψ_{out} angle of observation which equals 90 ° in a typical TXRF geometry

τ_{i,E_0} photo electric cross section of the element i at the photon energy

$\mu_{i,E}$ absorption cross section of the element i at the photon energy E

$$\mu_{tot,i} = \mu_{i,E_0} / \sin\psi_{in} + \mu_{i,E_i} / \sin\psi_{out}$$



Anal. Chem. **79**, 7873 (2007)

Reference-free quantitation in SR-TXRF analysis

X-ray spectrometry

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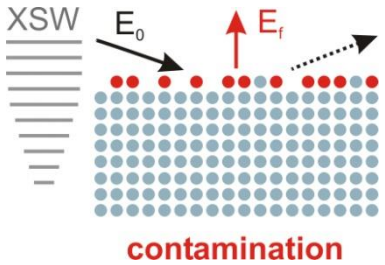
ω_{Xi} fluorescence yield of the absorption edge Xi (of the element i)

$g_{l,Xi}$ transition probability of the fluorescence line l belonging to Xi

j_{Xi} jump ratio at the absorption edge Xi

$$Q = \omega_{Xi}\, g_{l,Xi}\, (j_{Xi}\text{-}1) / j_{Xi}$$



Analysis of contamination on novel materials (Ge, SOI, InGaAs, …) or of nanolayered systems (buried interfaces – photovoltaics)

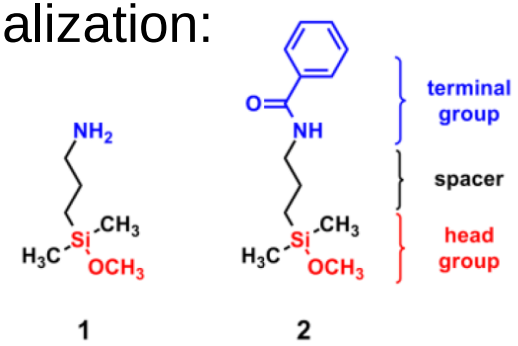
→ calculation of the x-ray standing wave field

Anal. Chem. **79**, 7873 (2007)

Traceable quantification of functionalized surfaces by means of reference-free TXRF analysis

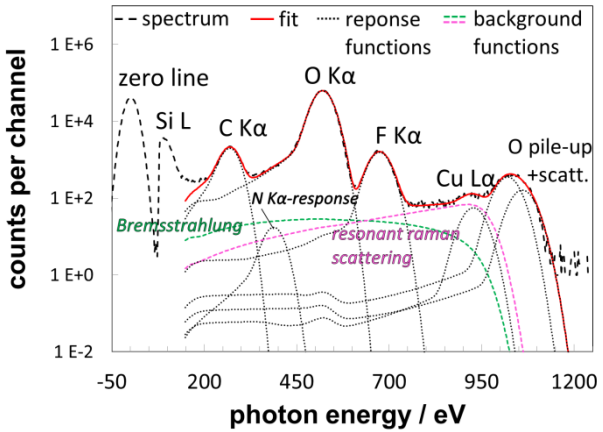
PTB
X-ray spectrometry

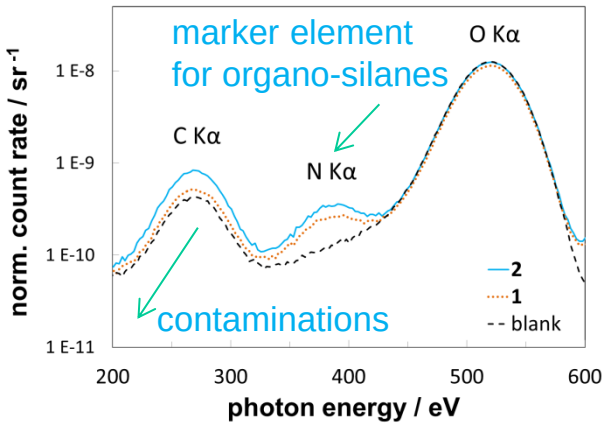
- Single organo-silanes for surface functionalization:

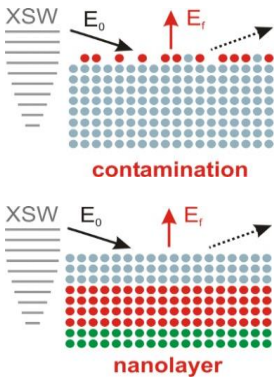


- molecular surface density as revealed by reference-free TXRF
- traceable quantification based on specific elements as marker (nitrogen)

Spectral deconvolution:

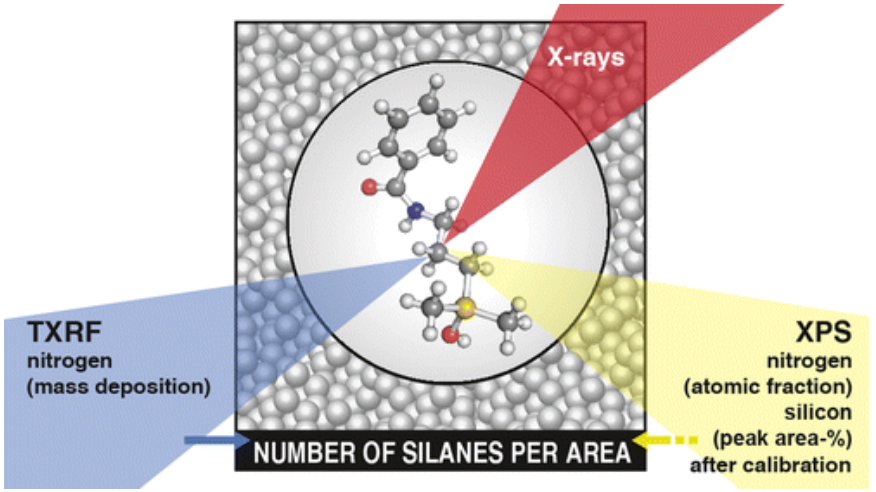






layer	TXRF nitrogen $\left[\frac{ng}{cm}\right]$	TXRF silane areic density $\left[\frac{molecules}{nm^2}\right]$	thickness[1] $[nm]$
1	5.9±1.8	2.5±0.8	0.6±0.2
2	8.9±2.7	3.8±1.1	1.4±0.5

C. Streeck, A. Nutsch

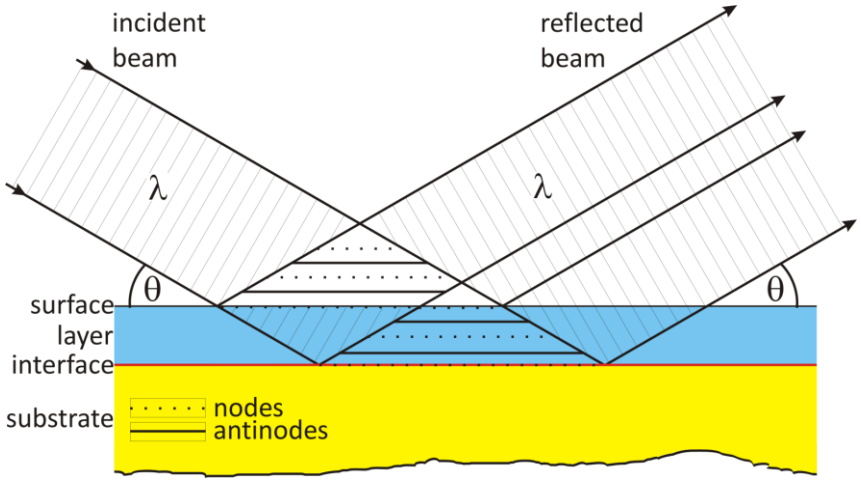


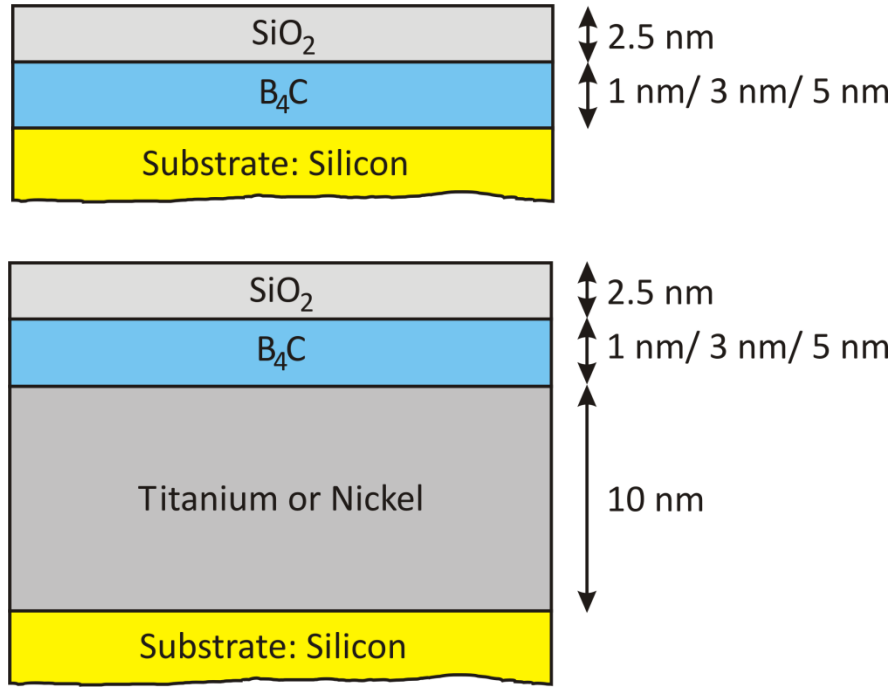
Anal. Chem. **87**, 10117 (2015)

Reference-free XRF and grazing-incidence XRF of buried nanolayers - layer composition and thickness

X-ray spectrometry

X-ray standing wave field (XSW)



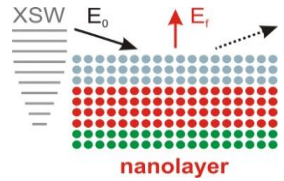


design of samples: total-reflection of the incident beam at silicon or at the metal

→ occurrence of the XSW in boron carbide layer

objective: determination of the boron carbide layer composition and thickness

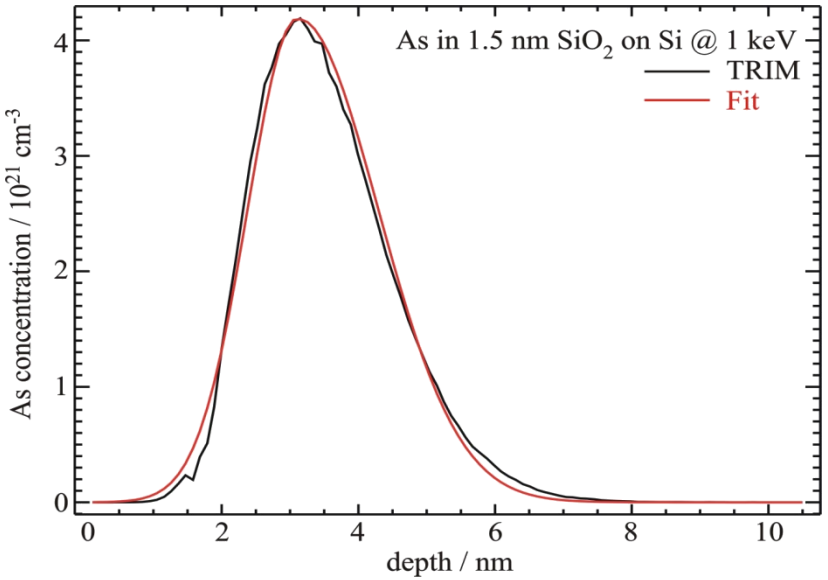
→ comparison of XRF and GIXRF quantification

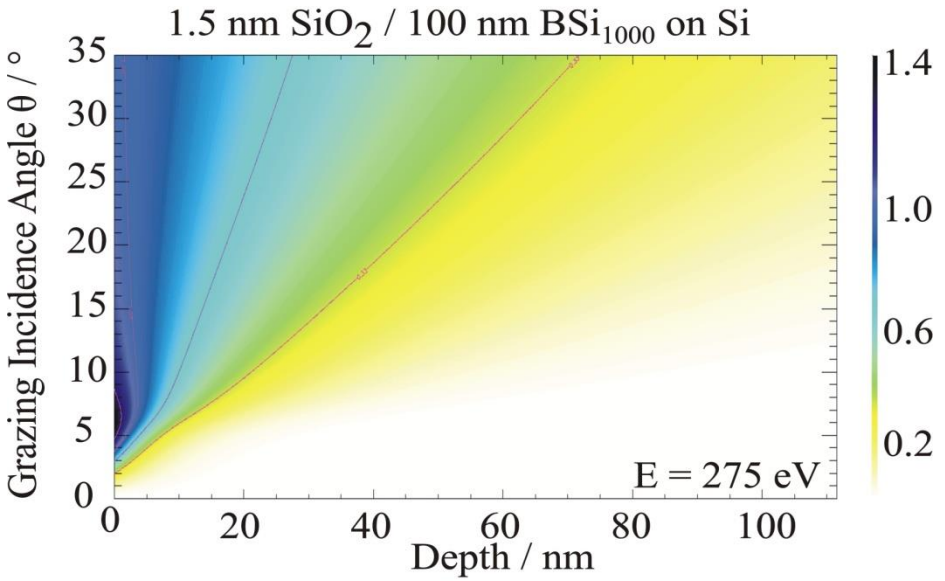


Anal. Chem. **83**, 8623 (2011)

GIXRF analysis of B and As implantation profiles

X-ray spectrometry





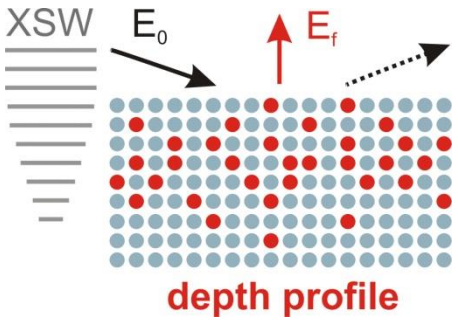
fundamental and instrumental parameters

depth distribution of the implant

X-ray Standing Wave field distribution

absorption term

$$F_{Imp}(\theta) = G \int_0^{t_{max}} P_{Imp}(t) \cdot I_{XSW}(t, \theta, E_0) \cdot \left(e^{-\frac{t\rho\mu_{tot}(t)}{\sin\theta_{det}}} \right) dt$$



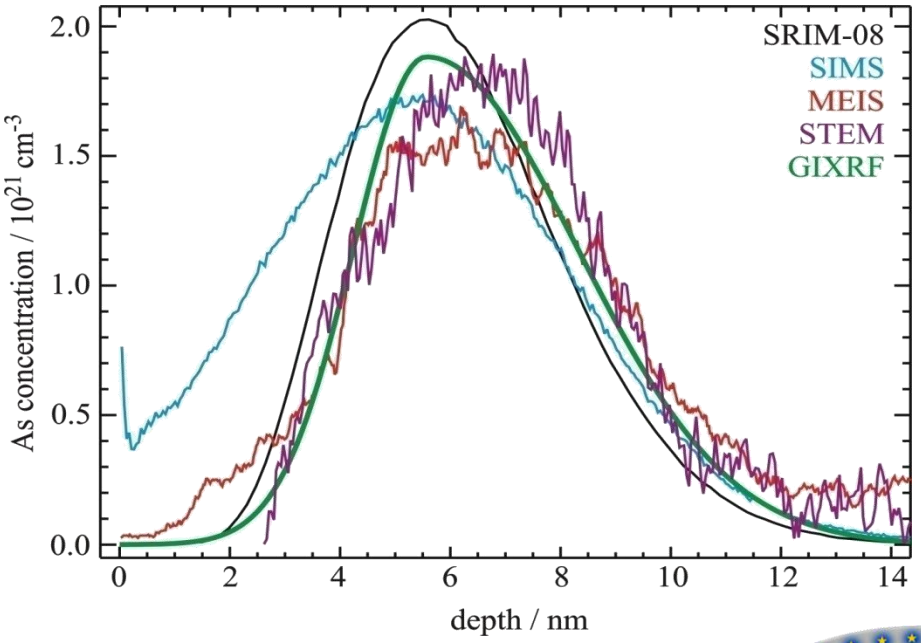
P. Hönicke

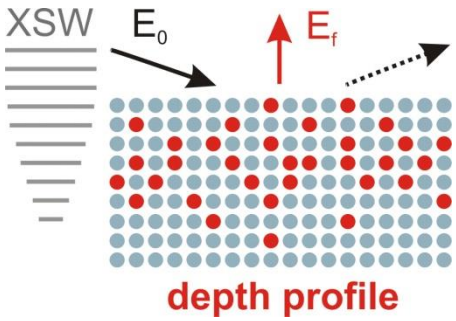
Anal. Bioanal. Chem. **396**, 2825 (2010)

GIXRF analysis of B and As implantation profiles

X-ray spectrometry

Comparison of GIXRF results on arsenic samples to SIMS, MEIS and STEM



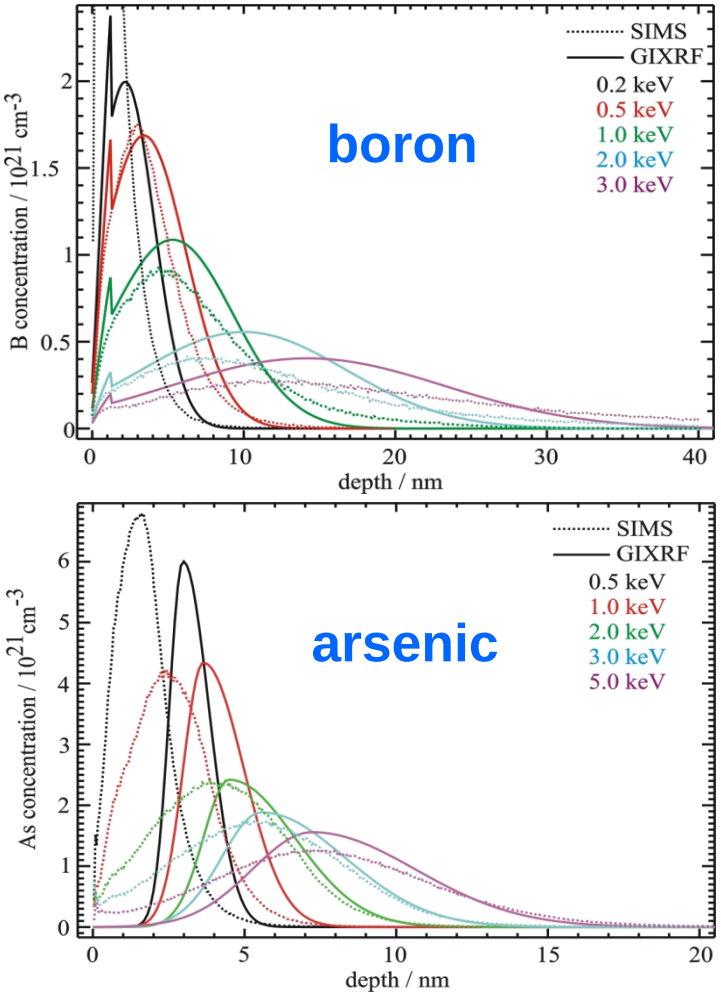


D. Giubertoni (FBK)

J. van den Berg (Univ. Salford)

P. Hönicke

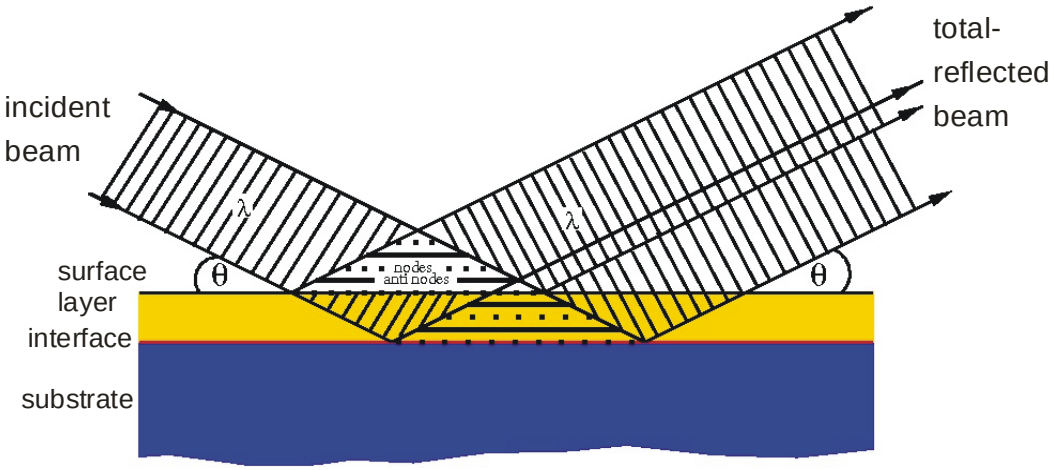
Comparison of GIXRF results to SIMS



Anal. Bioanal. Chem. **396**, 2825 (2010)

Speciation of buried nanolayers by GIXRF-NEXAFS

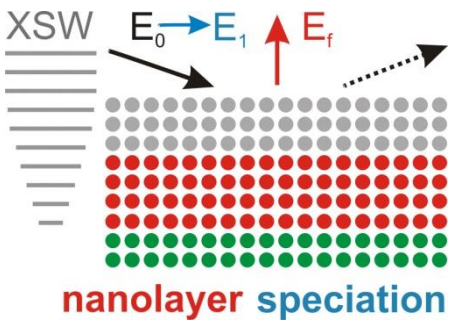
X-ray spectrometry



→ **composition and speciation of buried nanolayers**

→ **higher information depth (>> 5nm) than XPS**

→ **parallel variation of incident angle and photon energy**

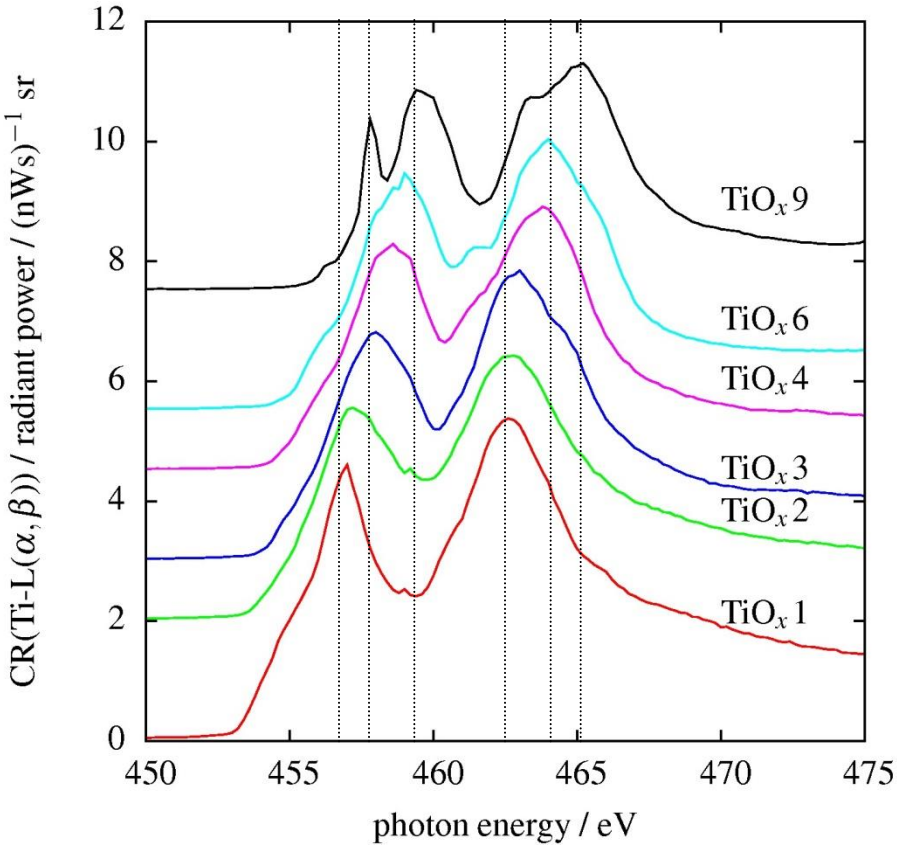


B. Pollakowski

Phys. Rev. B **77**, 235408 (2008)

Anal. Chem. **85,** 193 (2013)

GIXRF-NEXAFS at the Ti-$L_{iii,ii}$ edges

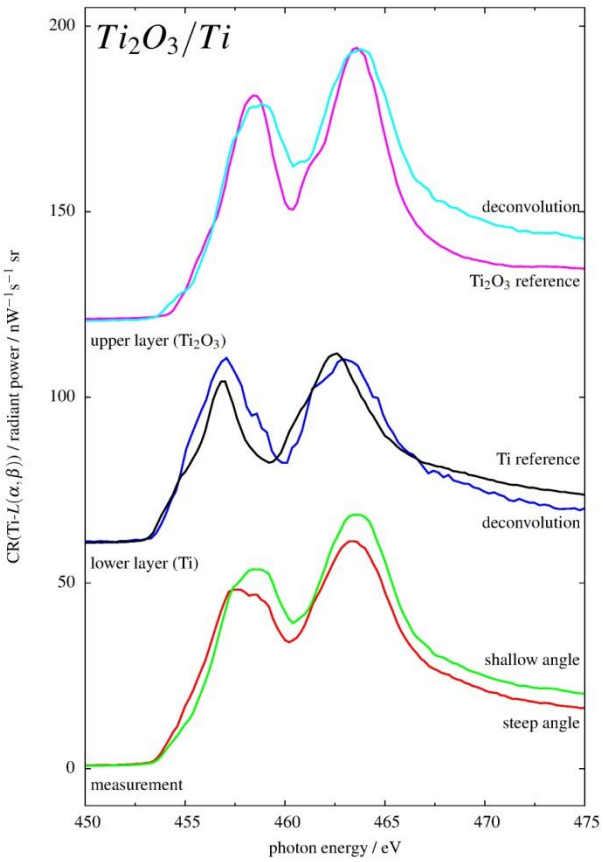


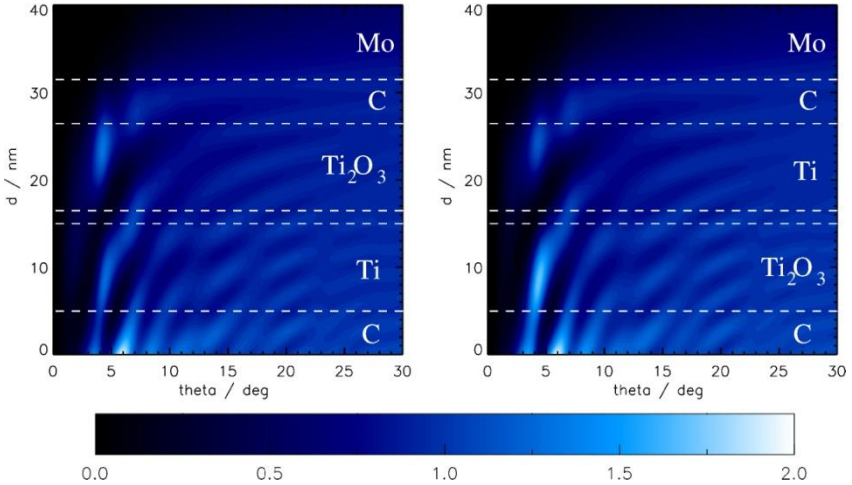
speciation of buried Ti oxide nanolayers

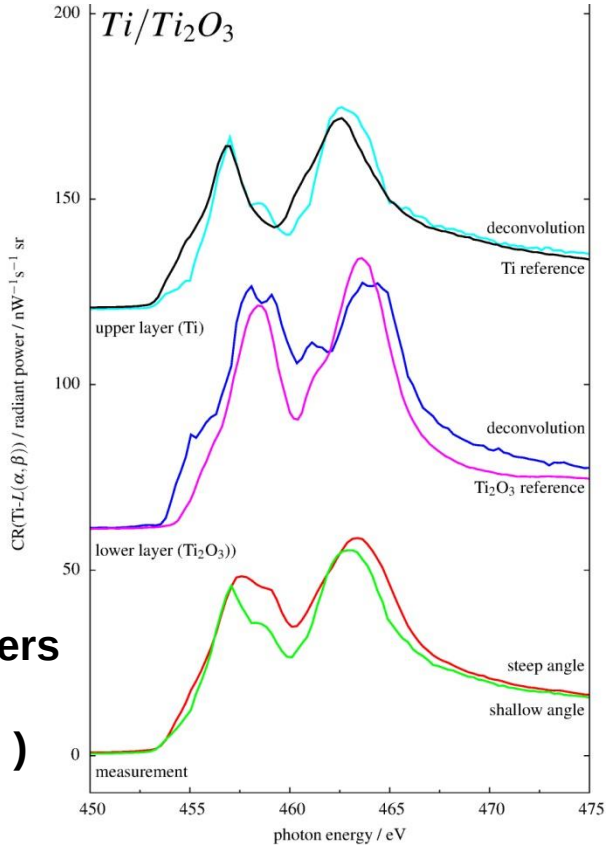
(the degree of oxidation scales with indices)

Speciation depth profiling by GIXRF-NEXAFS

X-ray spectrometry



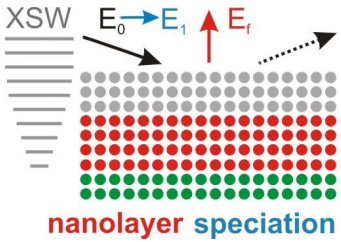




→ **speciation of $Ti_{x1}O_{y1}$ /$Ti_{x2}O_{y2}$ nanolayers**

→ **high information depth (up to 500 nm)**

→ **simultaneous variation of angle of incidence and of the photon energy**



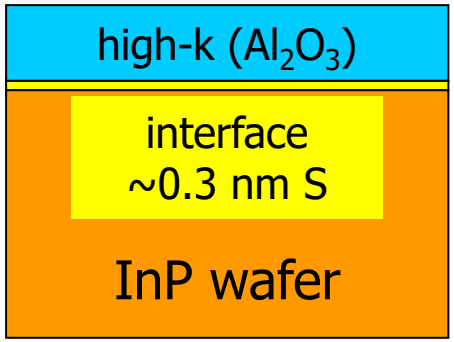
B. Pollakowski

Anal. Chem. **87,** 7705 (2015)

Quantitative characterization of nanoelectronics

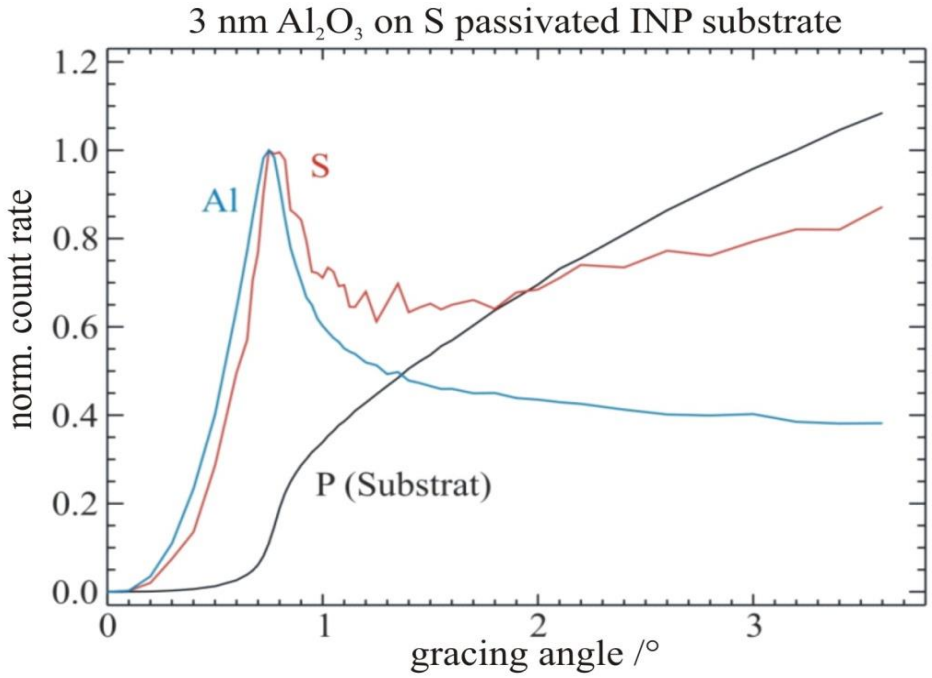
X-ray spectrometry

Optimization of high-k nanolayer fabrication

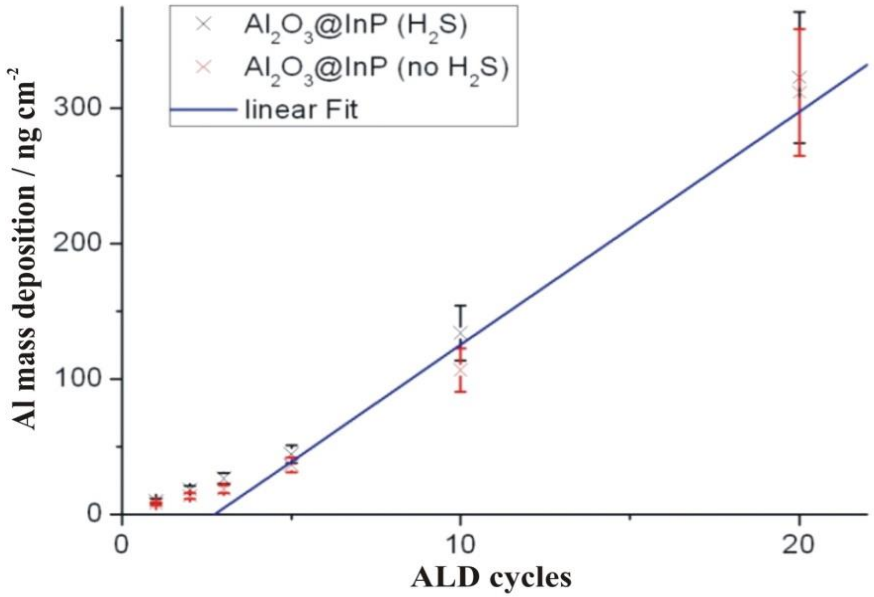


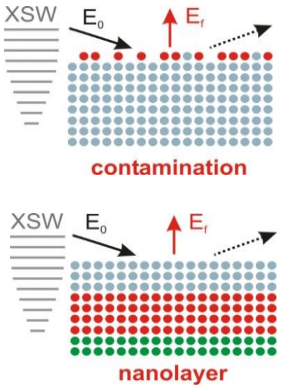
imec
aspire invent achieve

KATHOLIEKE UNIVERSITEIT
LEUVEN



Quantification of the ALD growth rate





linear growth on S passivated InP substrate after the 3rd ALD cycle

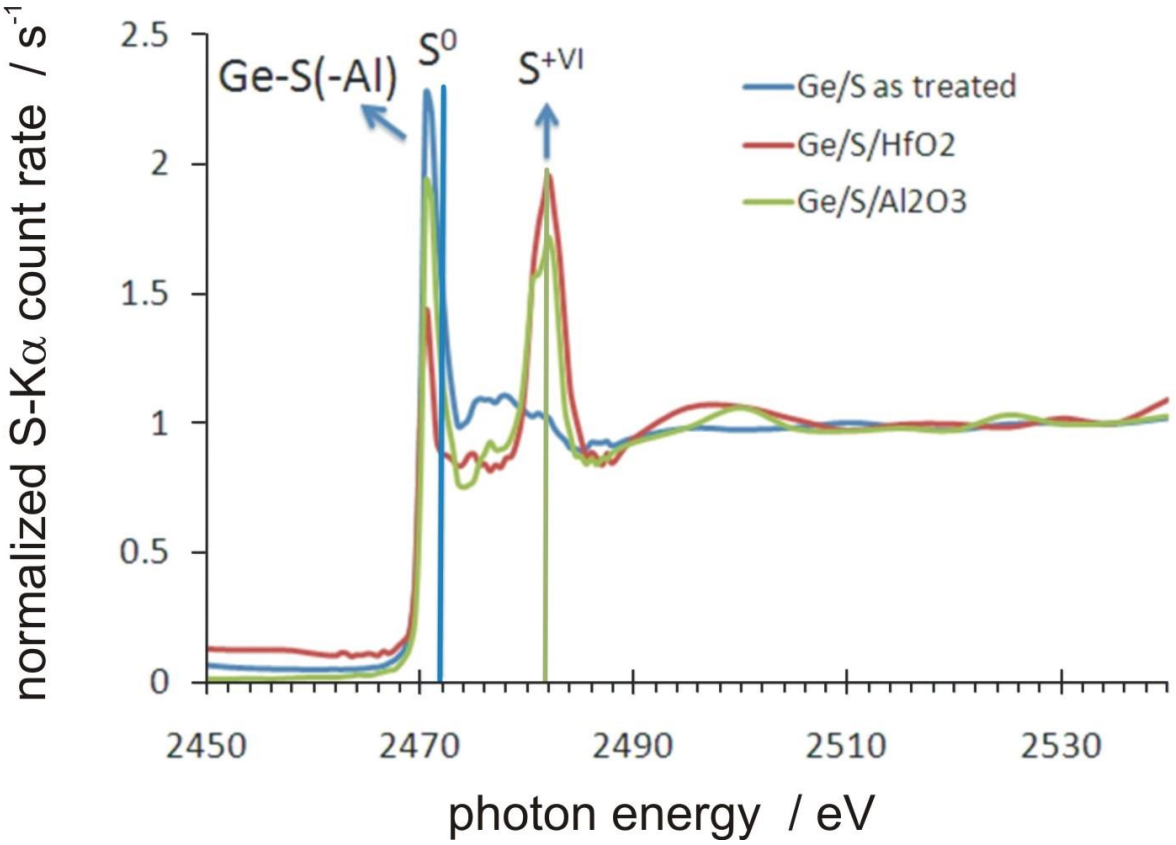
M. Müller

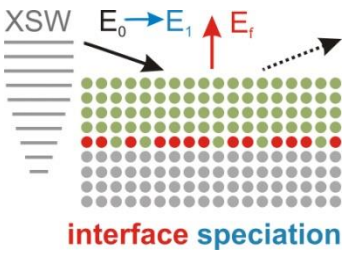
J. Vac. Sci. Technol. A **30**, 01A127 (2012)

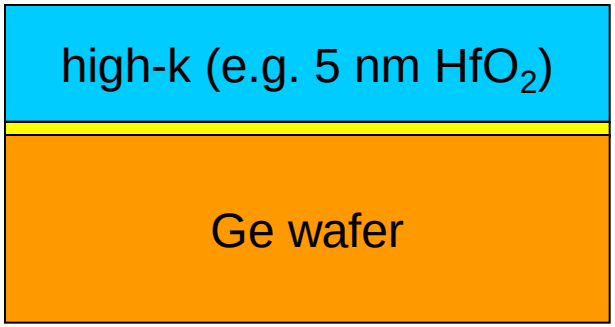
Quantitative interface characterization and speciation

X-ray spectrometry

XAFS speciation of the S passivated interface as treated and for two high k cap layer







passivated interface
(S monolayer ~0.3 nm)

M.Müller

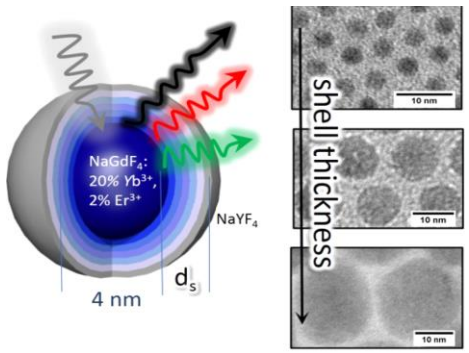
J. Electrochem. Soc. **158**, H1090 (2011)

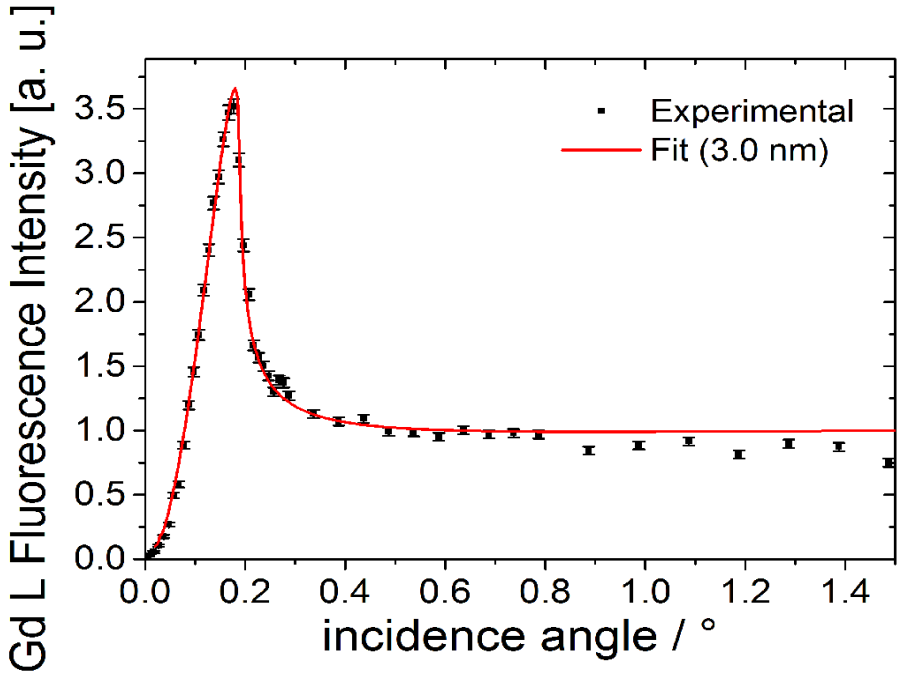
GIXRF based characterization of nanostructures - nanoparticles -

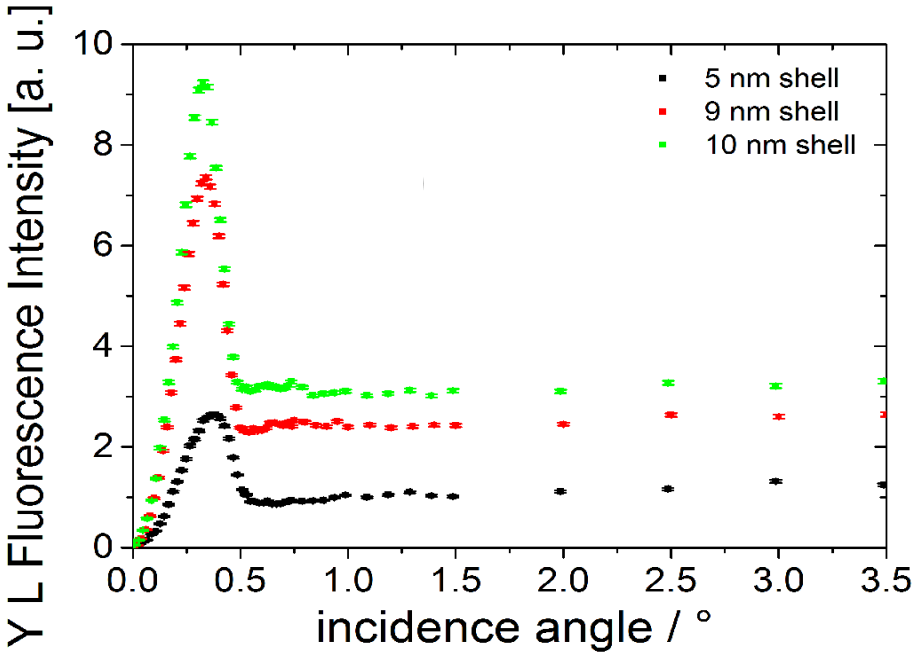
X-ray spectrometry

BAM Bundesanstalt für Materialforschung und -prüfung

- **Core-shell nanoparticle depositions on Si**
  - Determination of deposition densities using reference-free quantification
  - modeling of GIXRF data to determine e.g. core size



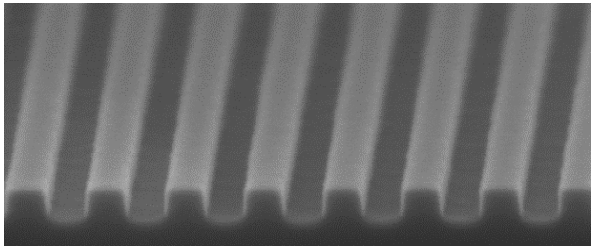




Y. Kayser

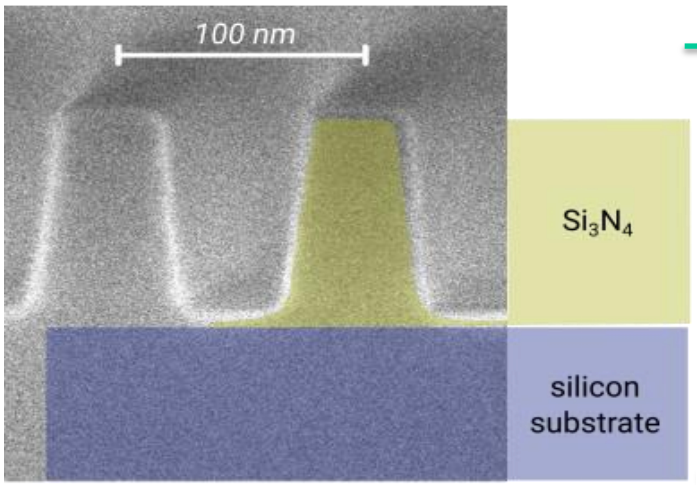
GIXRF based characterization of nanostructures - well-ordered 2D nanostructures -

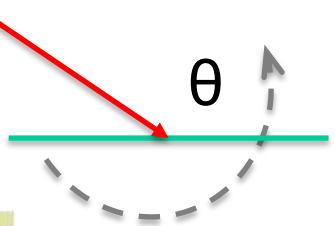
X-ray spectrometry

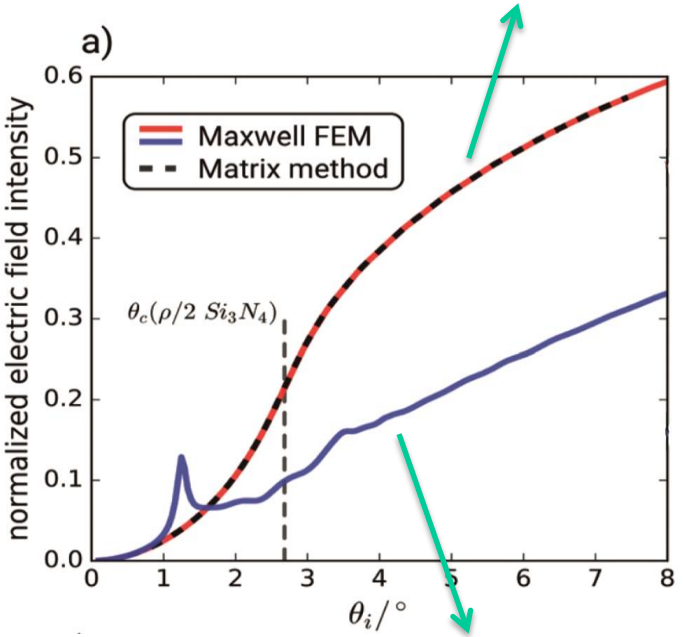


- **Si_3N_4 patterned grating on Si**
  - grating with pitch, height and width
  - GIXRF at 520 eV to detect nitrogen fluoresence

Effective density layer calc.





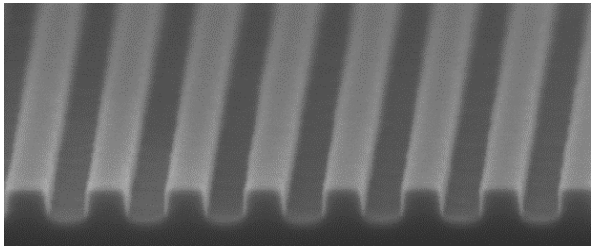


FEM calc. of real structure

P. Hönicke, V. Soltwisch (EUV radiom.) Nanoscale **10**, 6177 (2018)

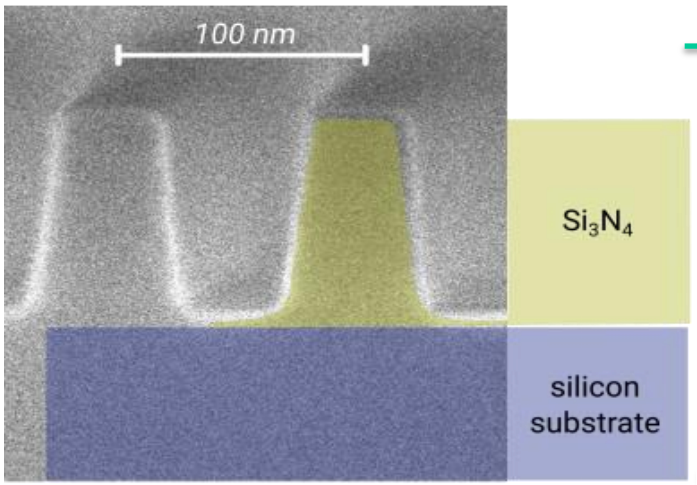
GIXRF based characterization of nanostructures - well-ordered 2D nanostructures -

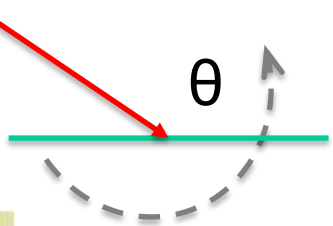
X-ray spectrometry

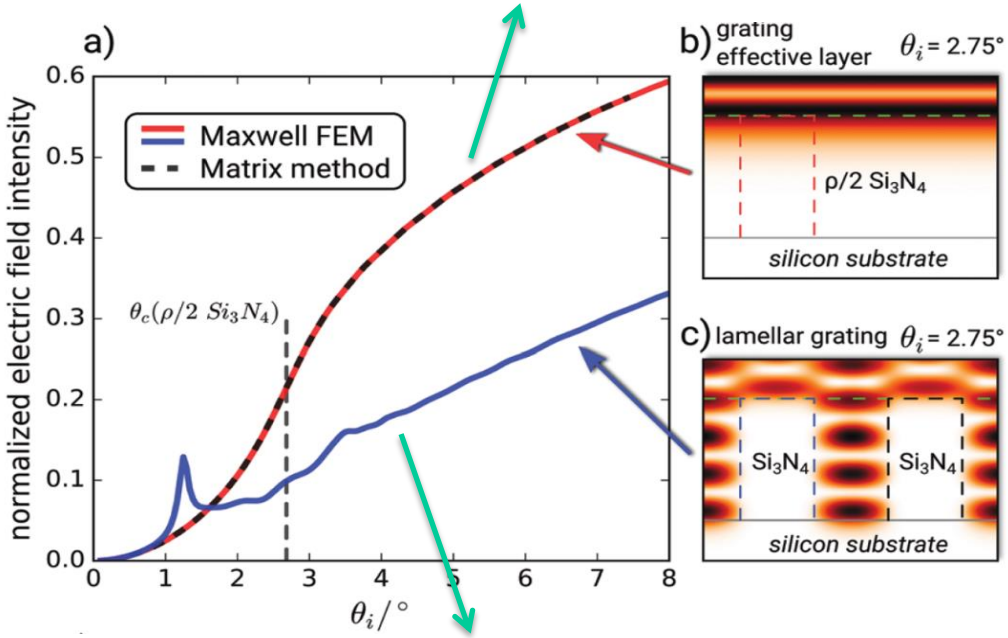


- **Si_3N_4 patterned grating on Si**
  - grating with pitch, height and width
  - GIXRF at 520 eV to detect nitrogen fluoresence

Effective density layer calc.





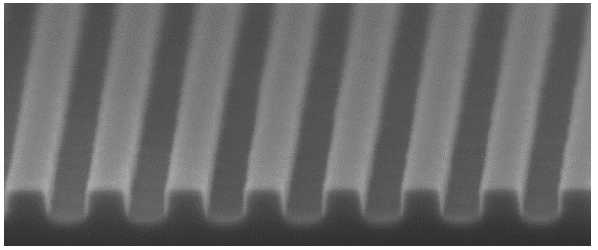


FEM calc. of real structure

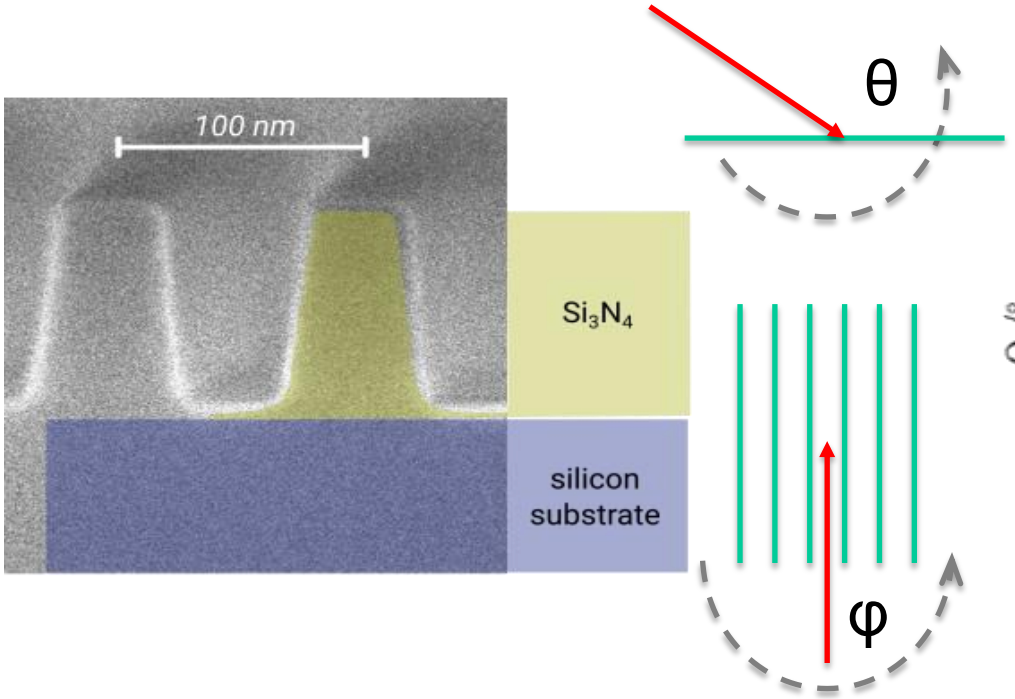
P. Hönicke, V. Soltwisch (EUV radiom.) Nanoscale **10**, 6177 (2018)

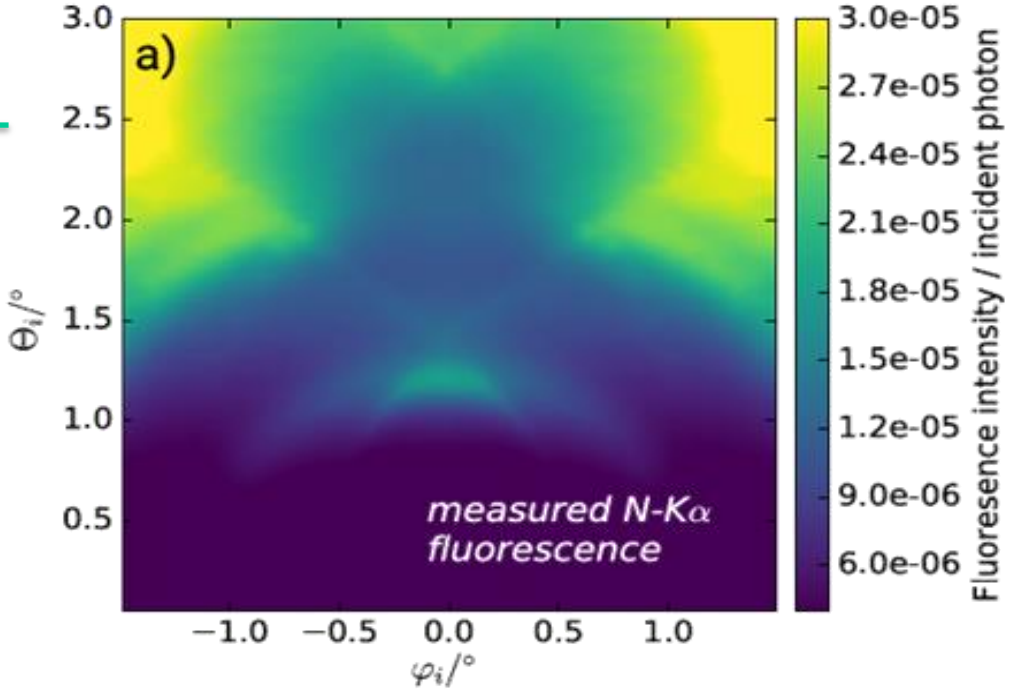
GIXRF based characterization of nanostructures - well-ordered 2D nanostructures -

X-ray spectrometry



- **Si_3N_4 patterned grating on Si**
  - grating with pitch, height and width
  - GIXRF at 520 eV to detect nitrogen fluorescence
  - θ (beam and surface) and φ (beam and grating) are varied





P. Hönicke, V. Soltwisch (EUV radiom.) Nanoscale **10**, 6177 (2018)

GIXRF based characterization of nanostructures - well-ordered 2D nanostructures -

X-ray spectrometry

model parameters

- width, heigth and pitch
- oxide thickness and groove edge residue

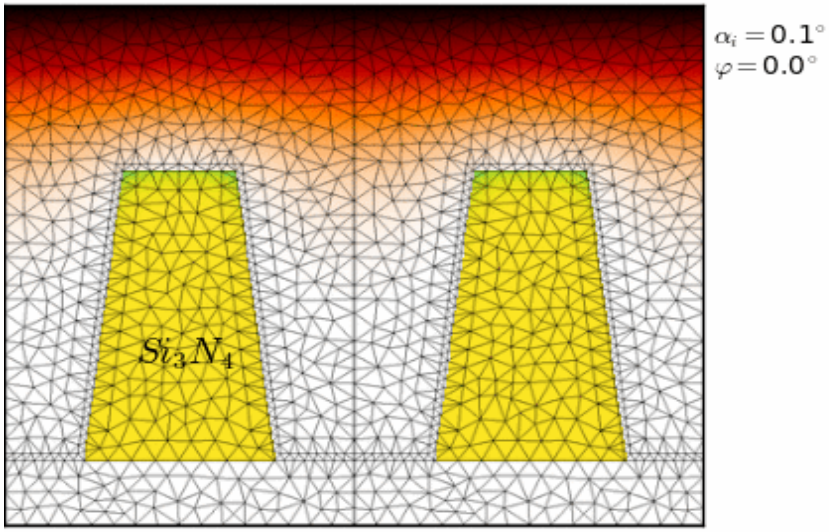
FP's

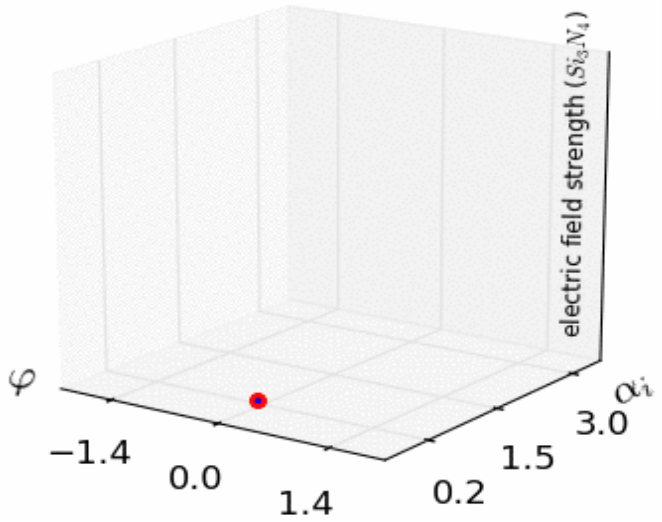
Electric field int.

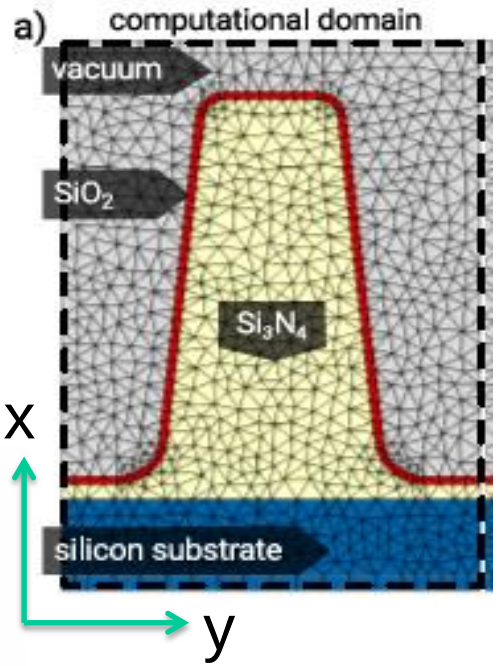
$$\frac{4\pi \sin\theta_i}{\Omega}\frac{F(\theta_i,E_i)}{N_0\varepsilon_{E_f}} = \frac{W_i\rho\tau(E_i)\omega_k}{\sum dx}\cdot\sum_x\sum_y |E(x,y)|^2\cdot\exp\left[-\rho\mu_{E_i}y_{dis}\right].$$

Norm. fluorescence

Atten. correction







JCMwave

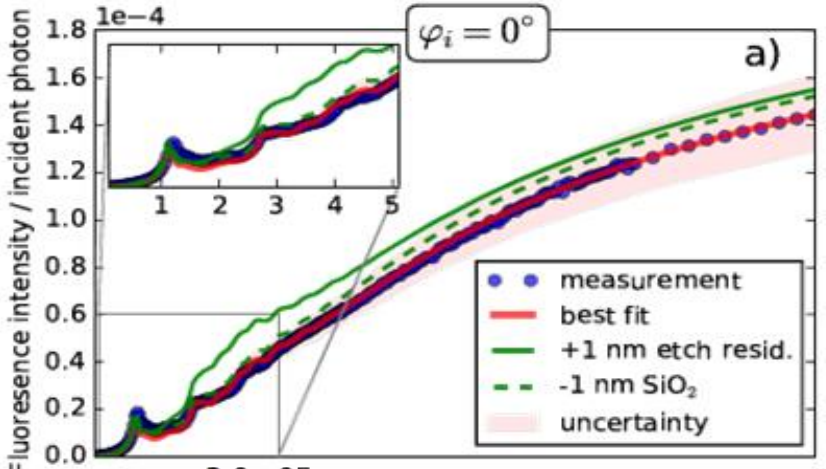
3D Maxwell Solver

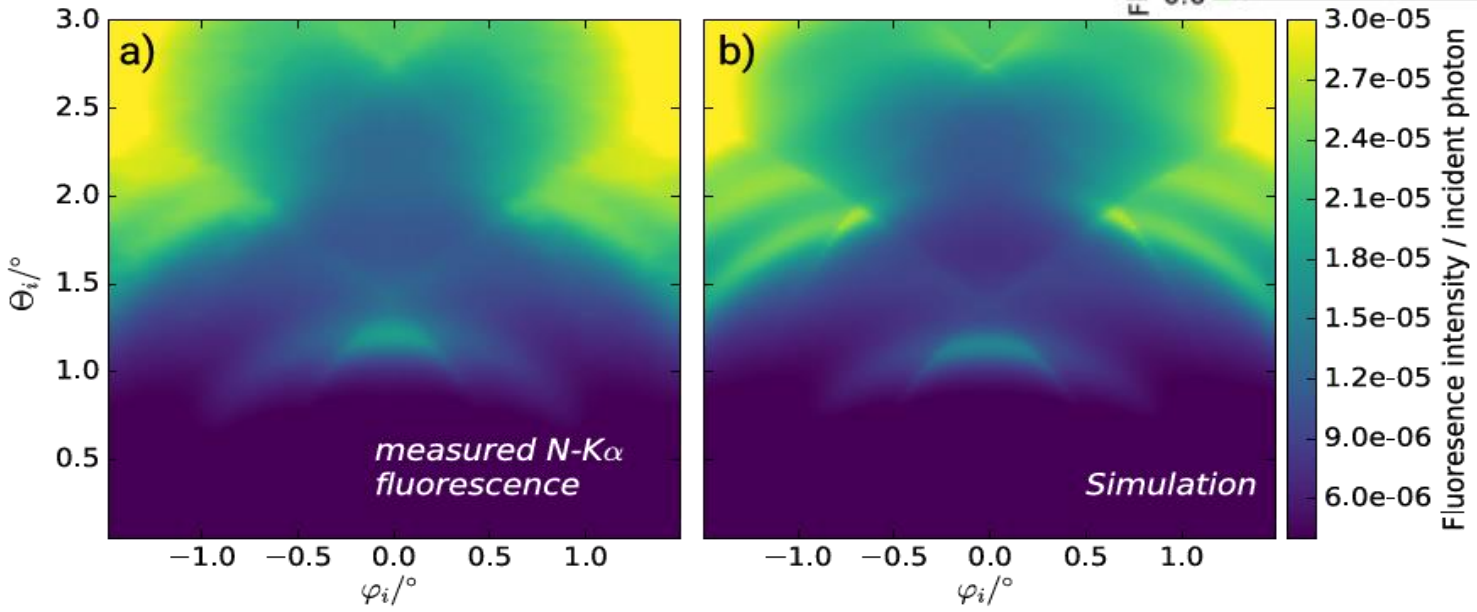
P. Hönicke, V. Soltwisch (EUV radiom.) Nanoscale **10**, 6177 (2018)

GIXRF based characterization of nanostructures - well-ordered 2D nanostructures -

X-ray spectrometry

- **Results Si_3N_4 grating**
  - Very sensitive for deviations of etch residue or oxide thickness
  - Determination of dimensional properties and elemental distributions





JCMwave

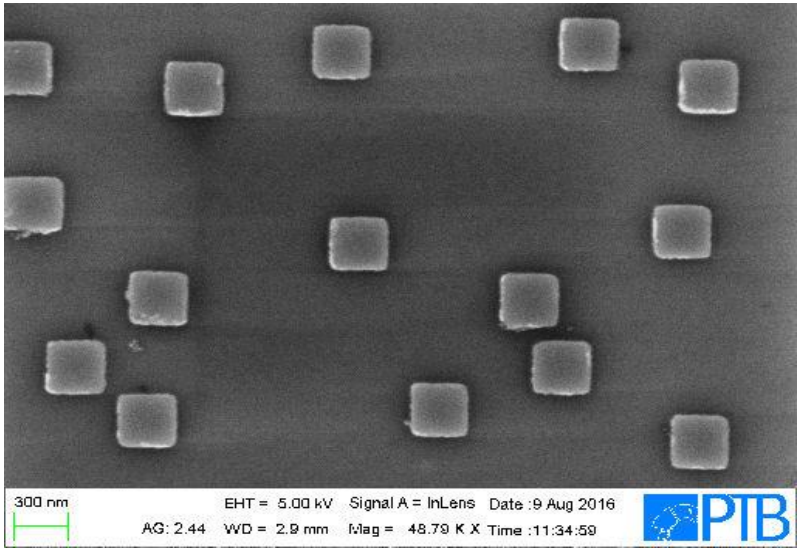
3D Maxwell Solver

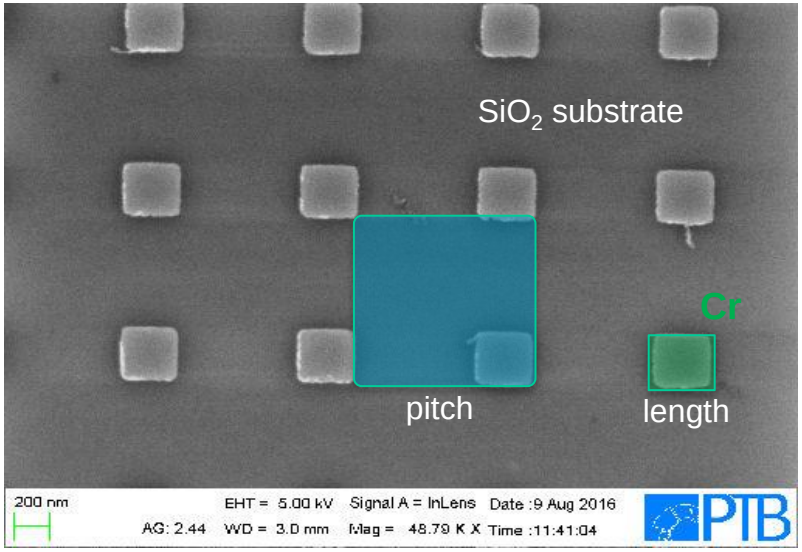
P. Hönicke, V. Soltwisch (EUV radiom.) Nanoscale **10**, 6177 (2018)

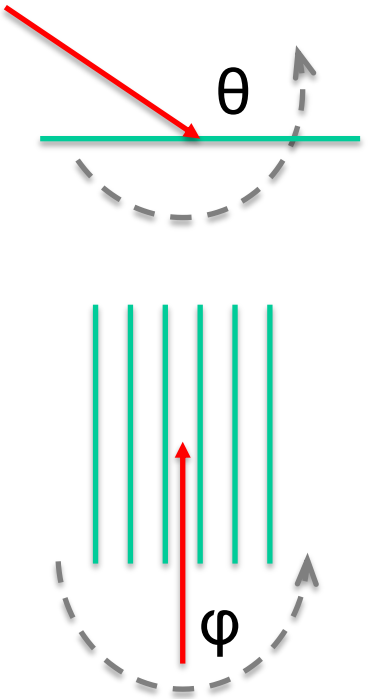
GIXRF based characterization of nanostructures - 3D nanostructures -

X-ray spectrometry

- **Cr rectangular nanostructures on SiO_2:** 300x300x20 nm³ blocks
  - 1000 nm pitch and 300 nm width
  - ordered array and non-ordered patterns (identical average pitch)
  - GIXRF experiments performed with varying phi excitation







Phys. Status Solidi A **215**, 1700866 (2018)

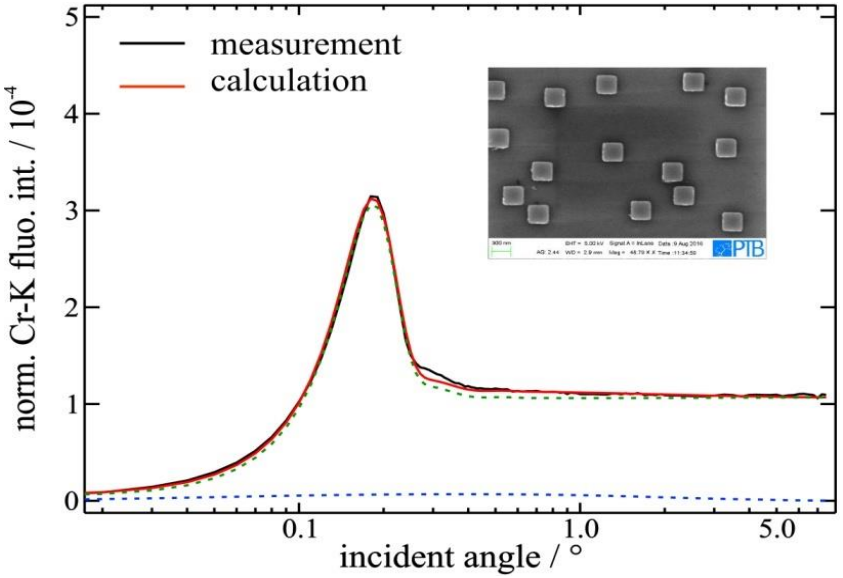
GIXRF based characterization of nanostructures - 3D nanostructures -

X-ray spectrometry

- **Cr rectangular nanostructures on SiO_2:** 300 x 300 x 20 nm³ blocks

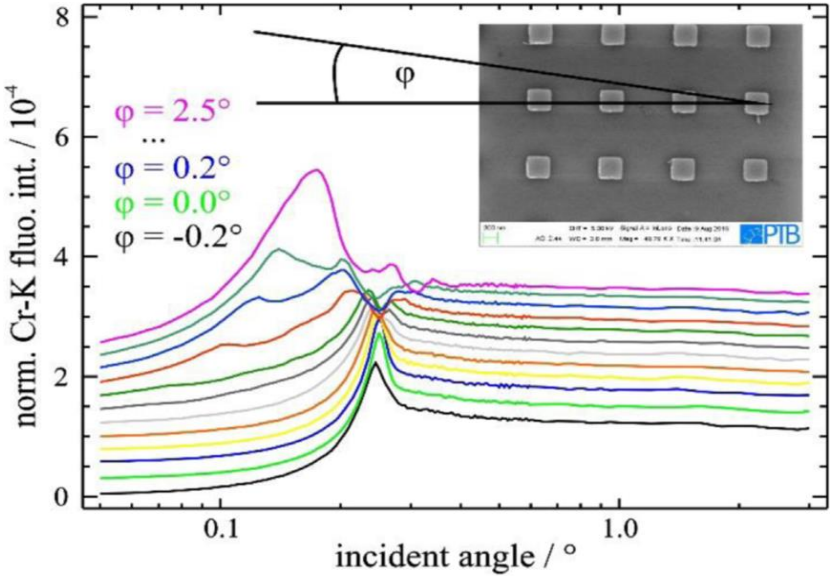
Non-ordered pattern:

- no phi dependence of the signal
- modeling of GIXRF based on effective density layer



Ordered pattern:

- Strong phi dependence
- FEM based modeling is computationally challenging



	SEM	GIXRF
length / nm	295 ± 12	288 ± 29
pitch / nm	992 ± 41	996 ± 99

Phys. Status Solidi A **215**, 1700866 (2018)

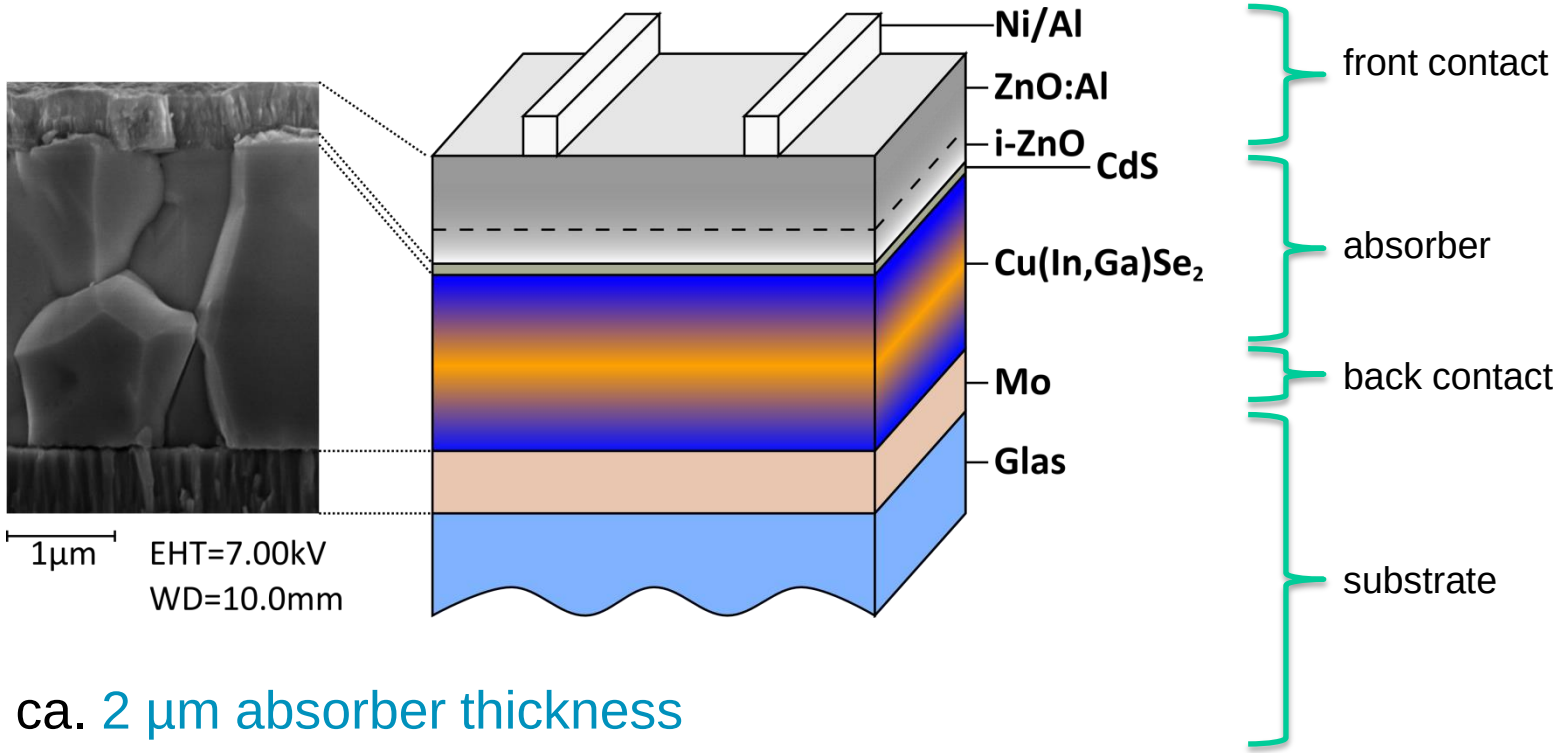
P. Hönicke

Elemental depth profiling of CIGS photovoltaics by GIXRF using calibrated instrumentation

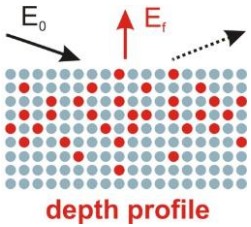
X-ray spectrometry

HELMHOLTZ ZENTRUM BERLIN für Materialien und Energie

Cu(In,Ga)Se2 absorber for thin film solar cells



- ca. 2 µm absorber thickness
- inhomogeneous element depth distribution of In and Ga influences the efficiency



C. Streeck

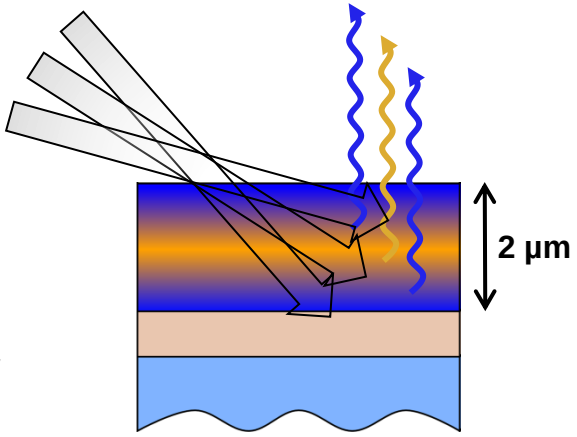
Appl. Phys. Lett. **103**, 113904 (2013)

Elemental depth profiling of CIGS photovoltaics by GIXRF using calibrated instrumentation

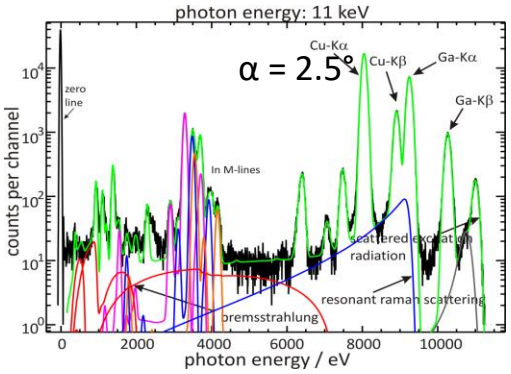
X-ray spectrometry

HELMHOLTZ ZENTRUM BERLIN für Materialien und Energie

Increasing information depth with increasing incidence angle

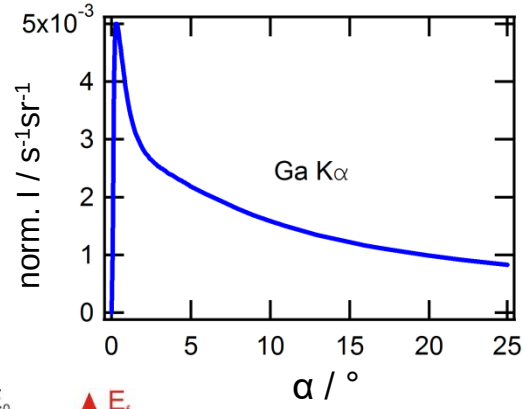


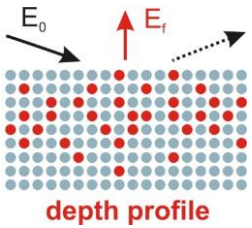
XRF-spectrum



Fluorescence intensity in dependence of the angle of incidence

GIXRF

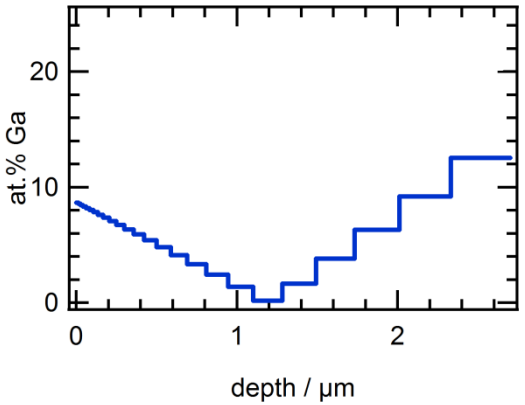




Non-destructive access to the elemental depth profile

Fundamental parameter-based quantification

Elemental depth profile



C. Streeck

Appl. Phys. Lett. **103**, 113904 (2013)

Comparison of in-depth resolving techniques

HELMHOLTZ ZENTRUM BERLIN für Materialien und Energie

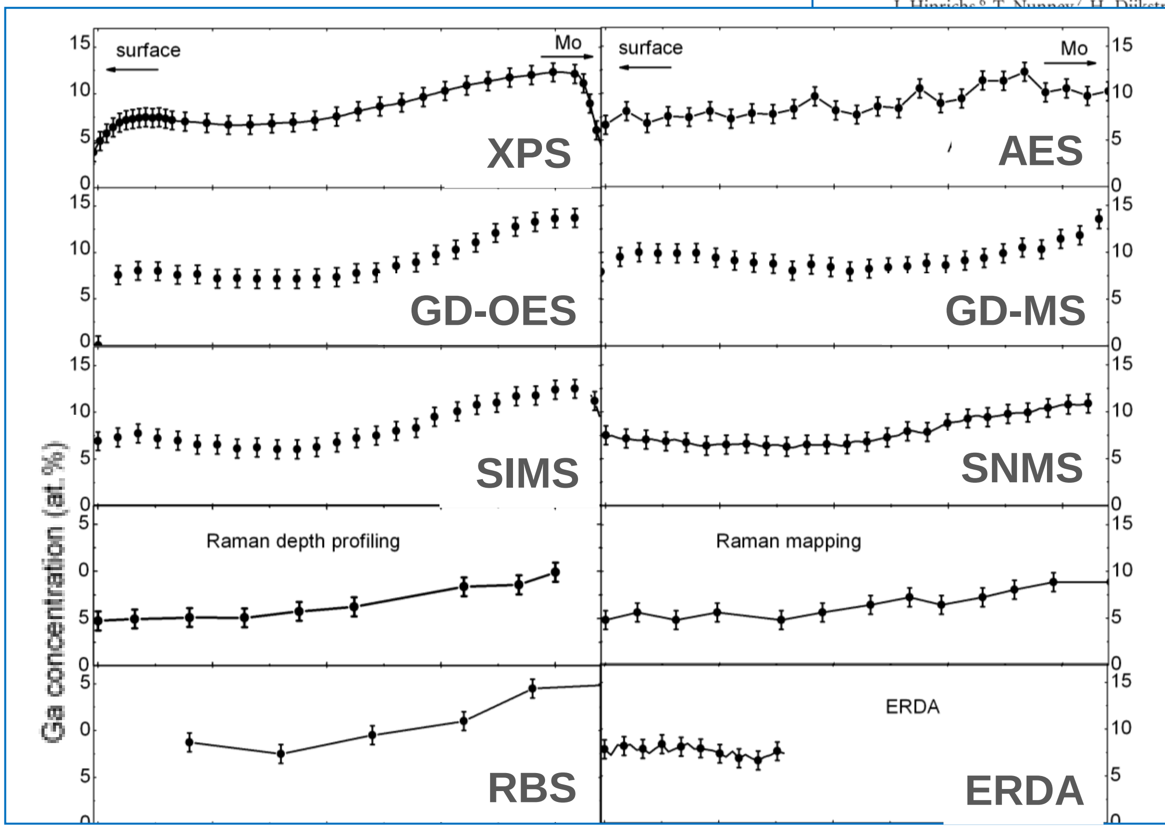
Non-destructive traceable technique:
reference-free XRF analysis

Microsc. Microanal. 17, 728–751, 2011
doi:10.1017/S1431927611000523

Microscopy AND Microanalysis

Comprehensive Comparison of Various Techniques for the Analysis of Elemental Distributions in Thin Films

D. Abou-Ras,[1,*] R. Caballero,[1] C.-H. Fischer,[1] C.A. Kaufmann,[1] I. Lauermann,[1] R. Mainz,[1]
H. Mönig,[1] A. Schöpke,[1] C. Stephan,[1] C. Streeck,[1] S. Schorr,[2] A. Eicke,[3] M. Döbeli,[4] B. Gade,[5]
V. Hoffmann,[9] D. Klemm,[9] V. Efimova,[9] A. Bergmaier,[10]
A.A. Rockett,[12] A. Perez-Rodriguez,[13,14] J. Alvarez-Garcia,[15]
P. Choi,[17] M. Müller,[18] F. Bertram,[18] J. Christen,[18]
llac,[19] and I. Kötschau[20]



- more then 20 analytical techniques
- On sections of a laterally homogeneous sample
- Quantitative differences larger than uncertainties of single techniques
- Most methods require a calibration sample

.

D. Abou-Ras (HZB) et al.

Microscopy & Microanalysis **17**,728 (2011)

Elemental depth profiling of CIGS photovoltaics by GIXRF using calibrated instrumentation

X-ray and IR spectrometry

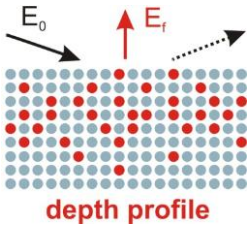
BIPM pilot-study CCQM-P140:

Quantitative surface analysis of multi-element alloy films

SURFACE ANALYSIS

Measurement of atomic fractions in $Cu(In,Ga)Se_2$ Films

Composition / at.%	Certified values KRISS	Reference-free GIXRF PTB
Cu	**23.8** ± 0.6	**24.0** ± 1.3
In	**19.1** ± 0.6	**19.3** ± 1.1
Ga	**6.6** ± 0.3	**6.3** ± 0.4
Se	**50.6** ± 1.5	**50.4** ± 2.8
d / µm	ca. **2**	**2.06** ± 0.09



C. Streeck

Metrologia **52**, Tech. Supp. 08017 (2015)

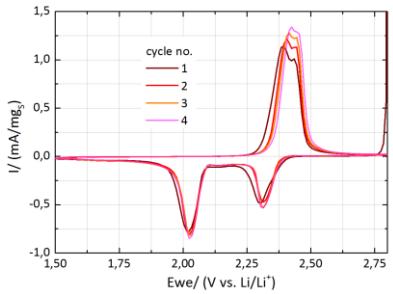
In-situ / operando battery characterization by means of Near-Edge X-ray Absorption Fine Structure (NEXAFS)

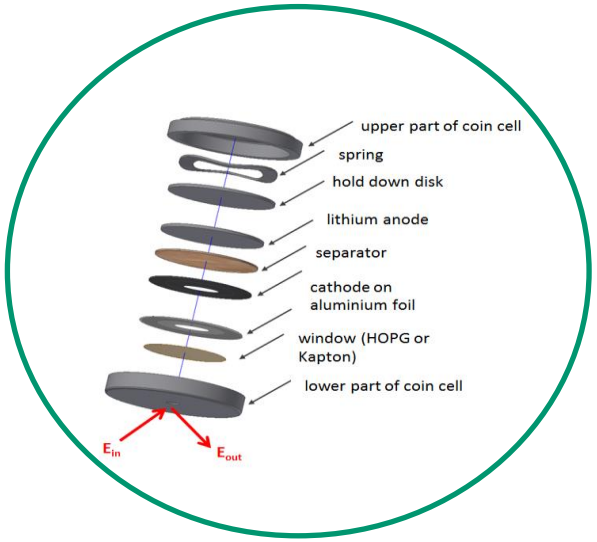
X-ray spectrometry

combination of morphologic, structural, and performance probing investigation

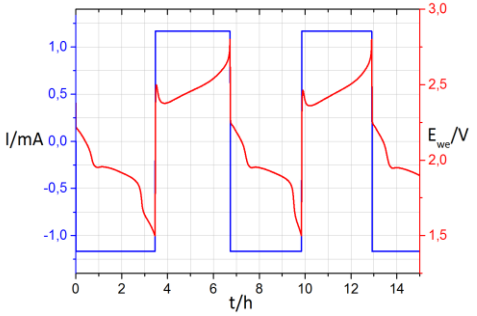
to reveal a most complete unterstanding of the battery degradation mechanism

cyclovoltammetry

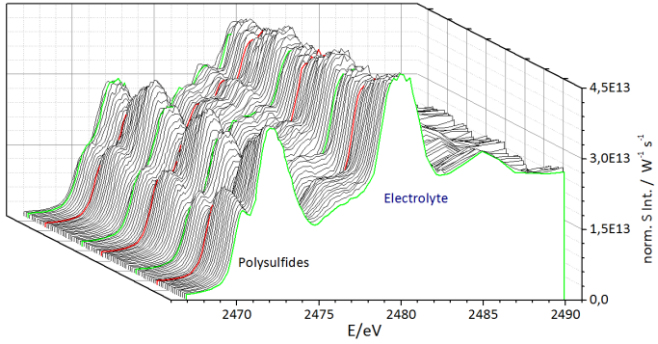




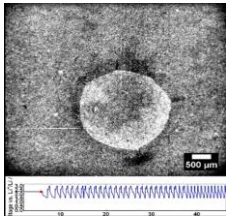
electrochemical characterization



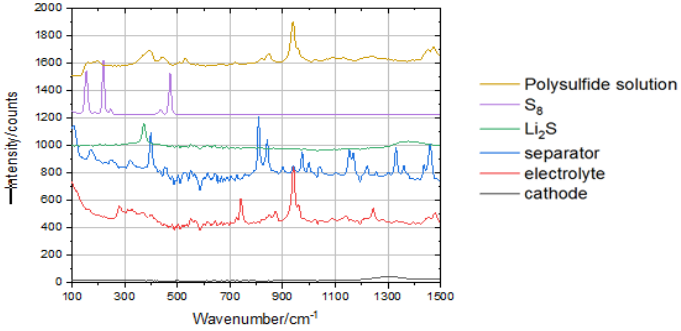
operando NEXAFS at the sulfur K edge



operando X-ray radiography (HZB Wannsee)



operando Raman spectroscopy (IFP Dresden)



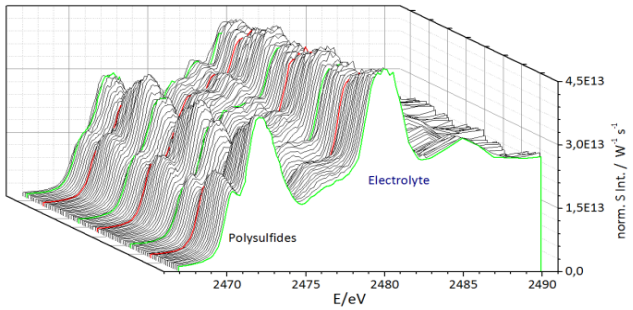
C. Zech

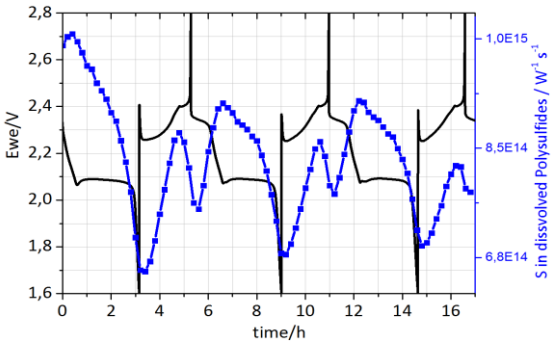
DFG project ISIBAT with IFP Dresden

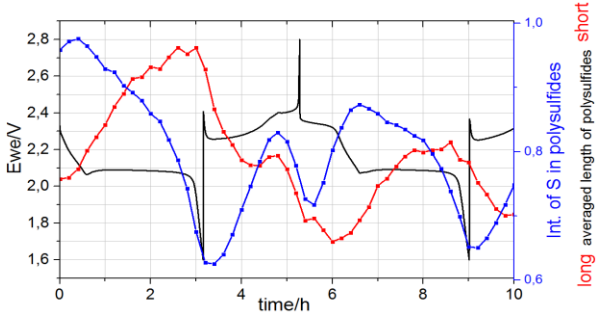
Operando NEXAFS investigations of Li-S batteries from 2 sides

X-ray spectrometry

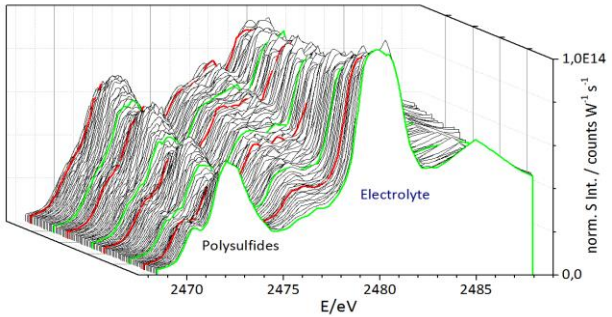
cathode side

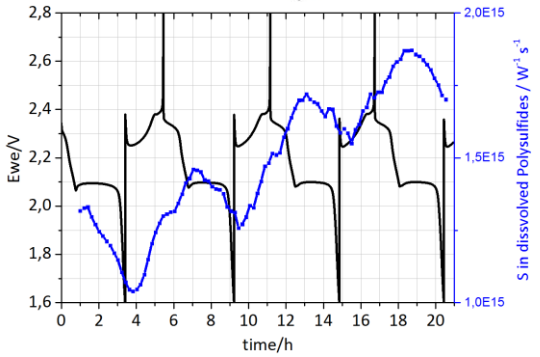


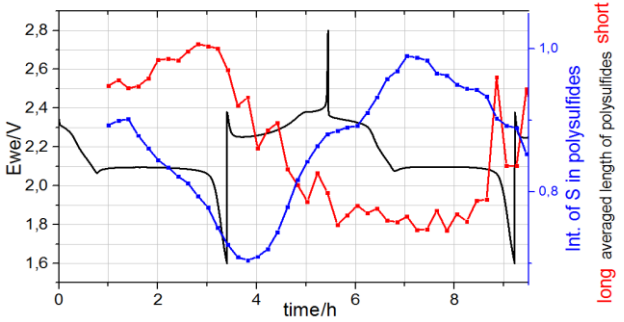




anode side







operando NEXAFS spectra

↓

spectral deconvoltution

↓

Variation of the polysulfide concentration across three charging/discharging cyles

↓

Deduction of the length of polysulfide chain lengths

↓

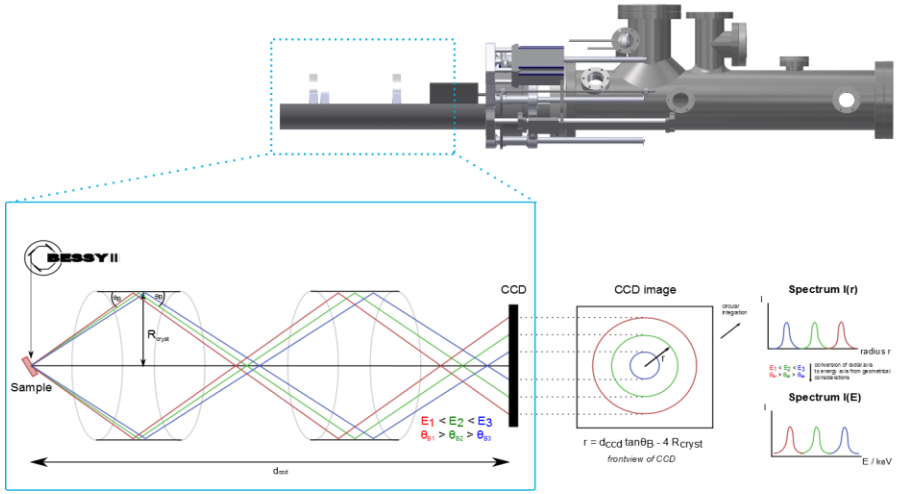
Better understanding of the polysulfide shuttle in LiS batteries

DFG project ISIBAT with IFP Dresden

Compact von Hamos spectrometer for high-resolution x-ray emission – FP determination and chem. speciation

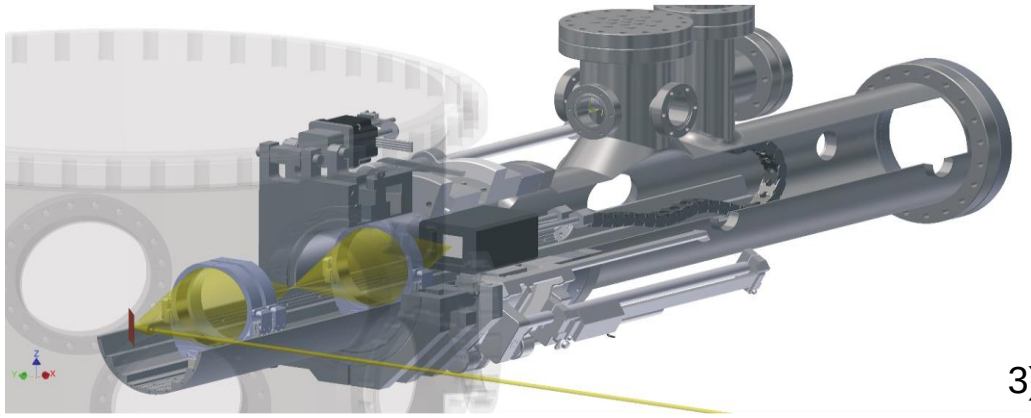
X-ray spectrometry

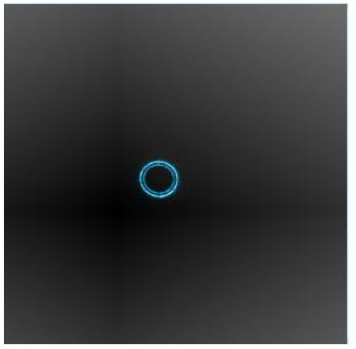
- Commissioning of the new spectrometer and development of CCD data analysis software
- Robust calibration concepts for reference-free XRS and XES



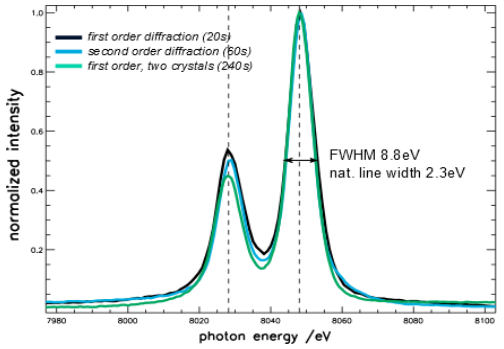
2) schematical arrangement and principle

1) Side view of the spectrometer





3) recorded CCD data



4) spectra deduced from CCD data

I. Holfelder

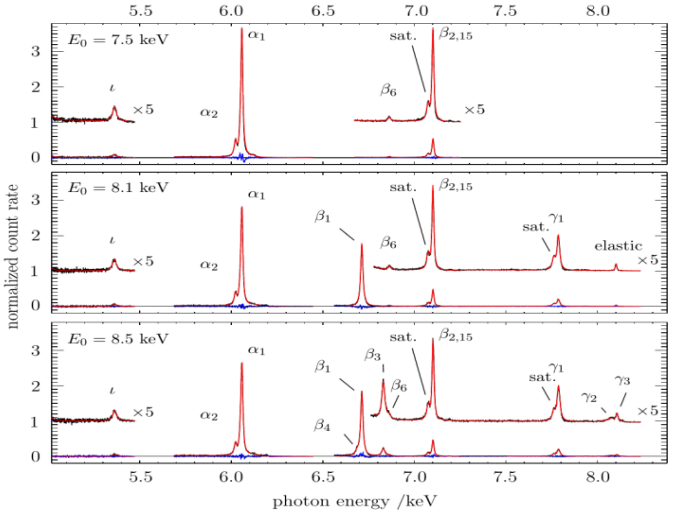
M. Wansleben

Compact von Hamos spectrometer for high-resolution x-ray emission – FP determination and chem. speciation

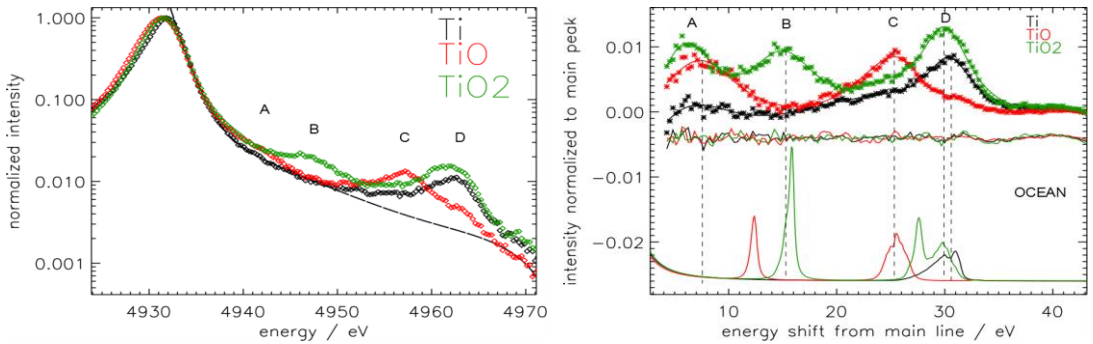
X-ray spectrometry

Fields of application

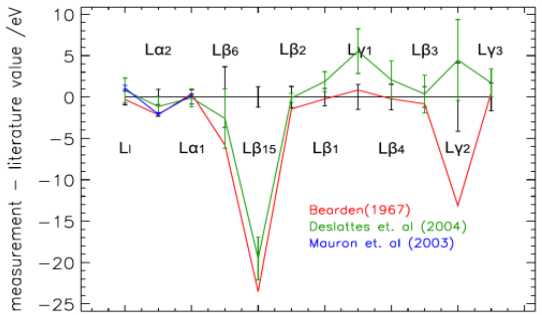
- Chemical speciation (reference-free de-termination of species mass depositions)
- Determination of x-ray fundamental parameters (FP) using the calibration
  - line energies
  - line intensities (transition and CK propabilities)



6) gadolinium L emission spectra for subshell selective photon excitations



5) Valence-to-Core XES of titanium compounds and comparison to calculations (OCEAN) in cooperation with the US NMI NIST



7) Comparison of measured gadolinium L line energies with NIST reference data

X-Ray Spectr. **48**, 102 (2019)

M. Wansleben

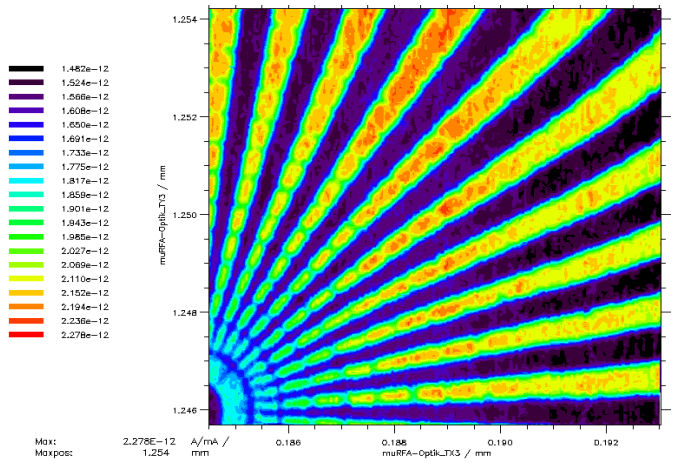
Traceable X-ray fluorescence analysis with spatial resolutions in the 100 nm range

X-ray spectrometry

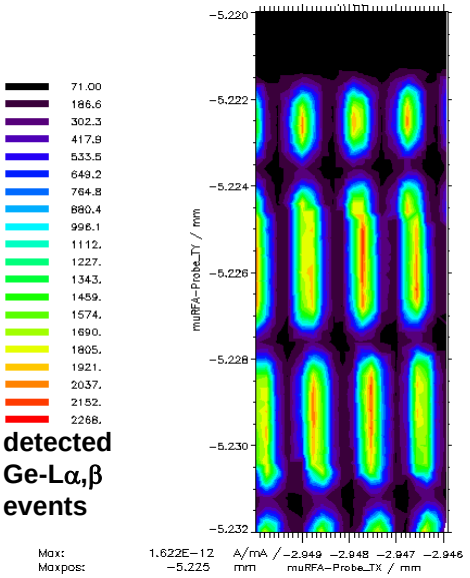
Vibration reduced approach in existing XRF instrumentation of PTB

for nanoanalytics by means of a joint optics-sample platform

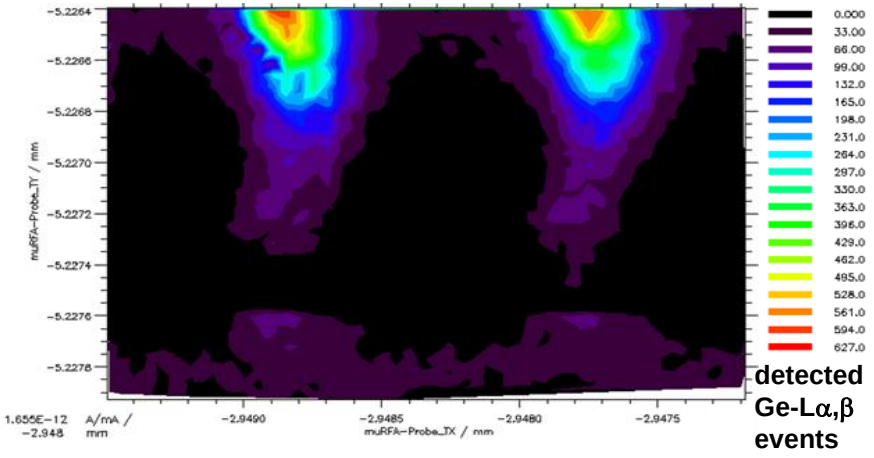
90 nm spatial resolution



450 nm spatial resolution



140 nm spatial resolution



Transmittance of a Siemens star at the PGM-U49 beamline (50 µm pinhole at PGM focus)

1st reference-free XRF analysis of 150 nm wide, 3 µm long SiGe structures

Reference-free XRF at the end zones of two 150 nm wide SiGe structures (100 µm pinhole at the PGM focal plane)

photon energy of 1500 eV

Microsc. Microanal. **24** (Suppl 2), 158 (2018)

AEROMET

Aerosol metrology for atmospheric science and air quality

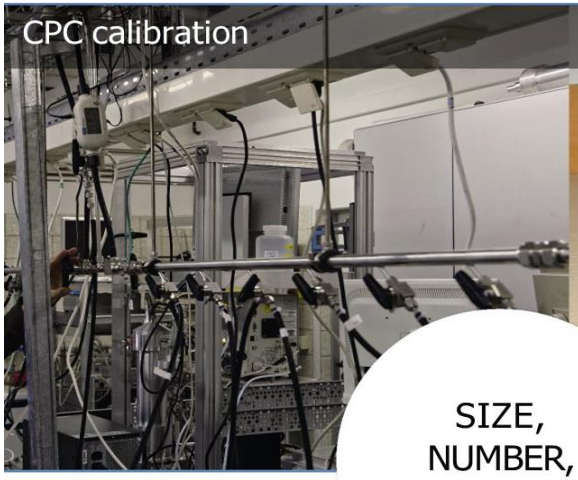
EURAMET
European Association of National Metrology Institutes

Dimensional metrology

AEROMETPROJECT.COM

Analytical metrology

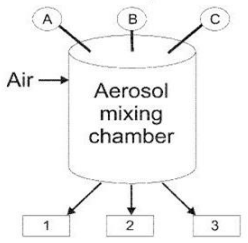
CPC calibration



In-field aerosol sampler

SIZE, NUMBER, MASS

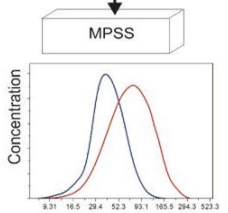
Test aerosol generation



Comparison of aerosol instruments at outlets 1, 2 and 3

MPSS calibration

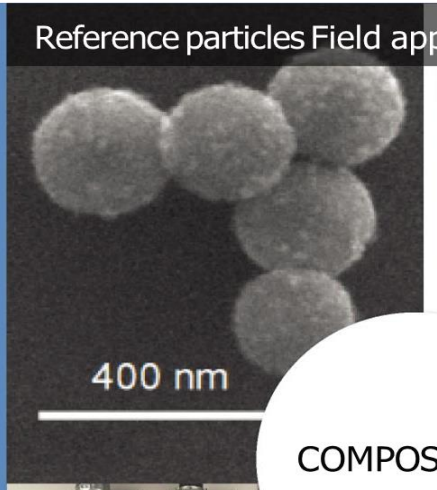
Reference test aerosol, d_T



displayed particle size, d_M

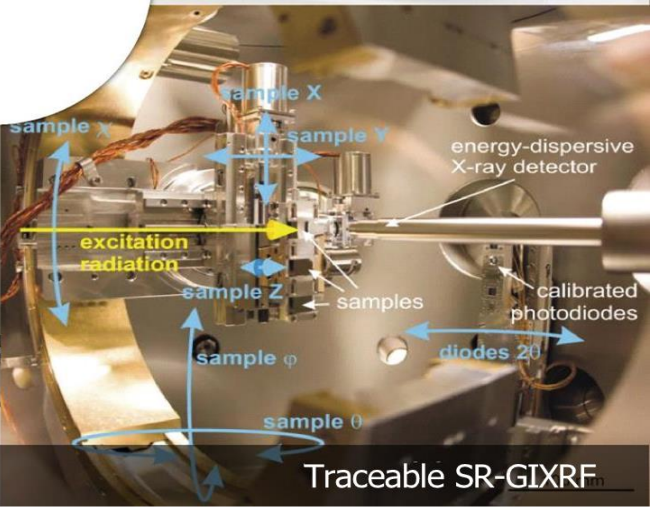
Mixing chamber MPSS calibration

Reference particles Field applicable XRF



COMPOSITION

New ICP-QQQ-MS

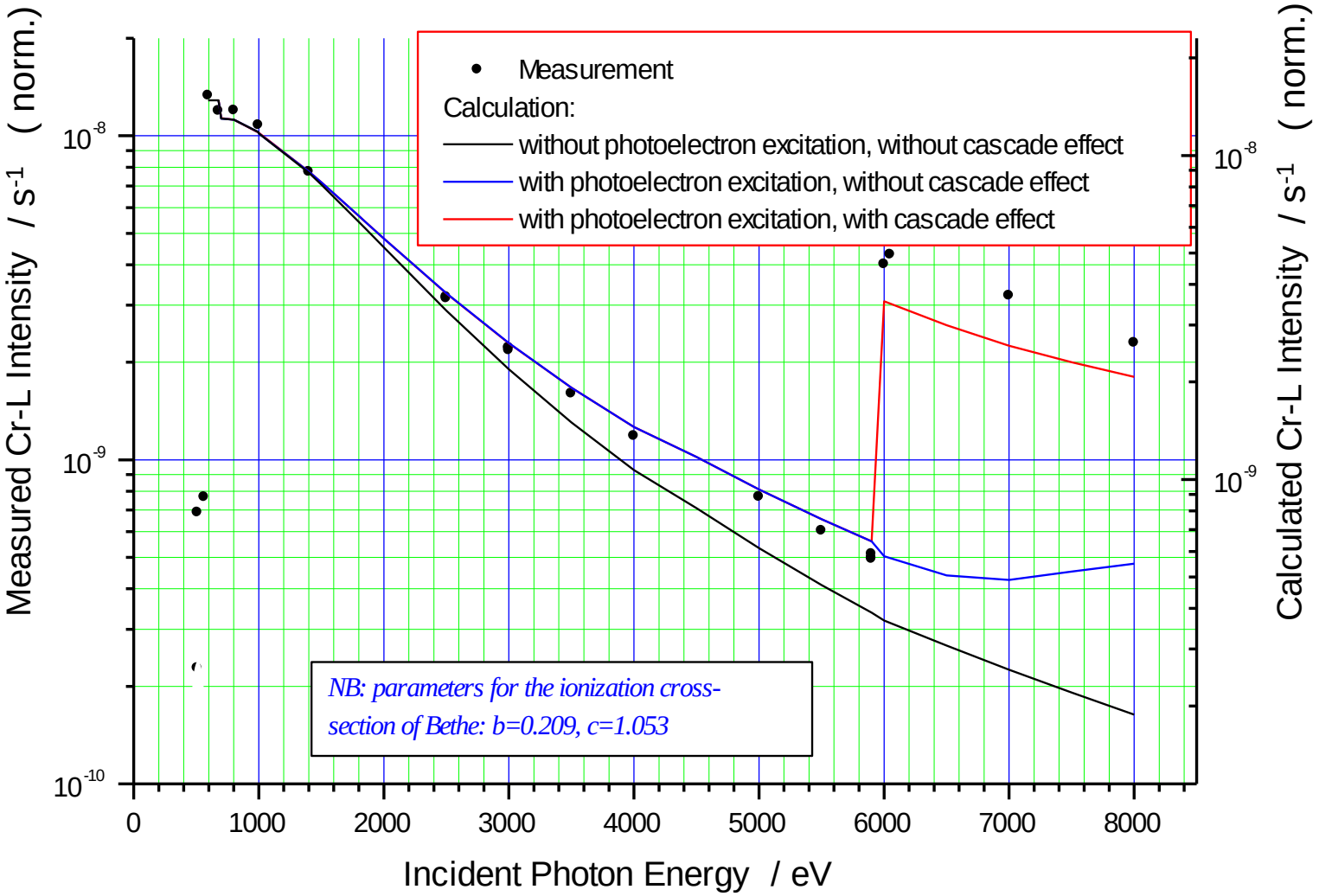


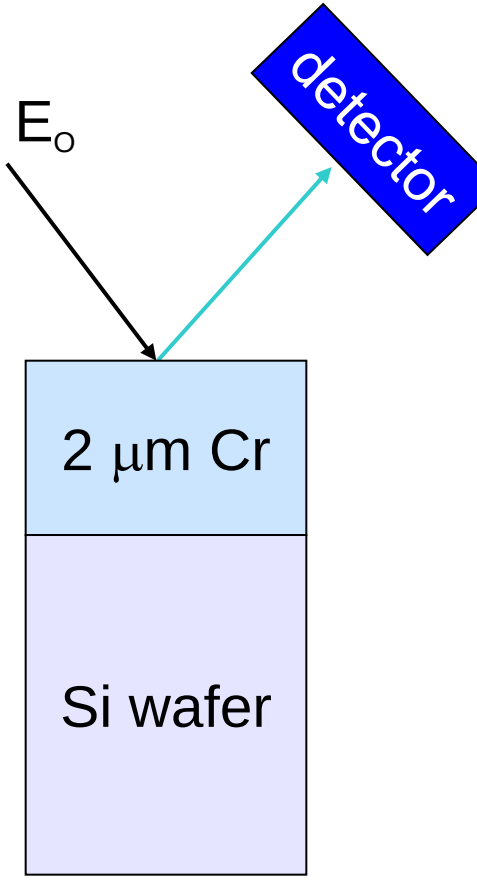
Traceable SR-GIXRF

NILU · UPO · BRUKER · LUND UNIVERSITY · TROPOS Leibniz Institute for Tropospheric Research · DANISH TECHNOLOGICAL INSTITUTE · NTUA · NPL National Physical Laboratory · DFM Danish National Metrology Institute · LNE · PTB · BAM · SP · CMI Czech Metrology Institute · METAS · IRSN · INRiM · FORCE Technology · MTA-EK

photoelectron and cascade effects: Cr L-lines

X-ray spectrometry





Adv. X-Ray Anal. **45**, 511 (2002)

Phys. Rev. A 83, 052511 (2011)

Summary

X-ray spectrometry

- Reference-free analysis of contamination on Si and of functionalized surfaces
- Quantitative characterization of nanostructured and gradient systems (~2 µm)
- Depth profiling (~500 nm) and interfacial analysis of nanoscaled materials
- High-resolution x-ray emission spectrometer and battery operando NEXAFS
- Determinations of atomic fundamental parameters (cross sections, yields, …)

Further information on **EMRP ENG51, ENG53, IND07, IND56, NEW01, SIB03** and **EMPIR 14IND01, 14IND07, 14IND12, 15HLT01, 16ENG03, 16ENG05, 16ENV07** at **EURAMET.org**

Acknowledgements: IMEC, KU Leuven, IPF, LETI, LNHB, HZB, NPL, IWS, AXO, MEMC, Numonyx, BAM, Technical Universities Berlin, Darmstadt, Dresden and Ilmenau, & industrial partners of PTB

E-MRS symposia ‚Analytical Techniques for Precise Characterization of Nanomaterials' 2014 - 2020

International initiative on x-ray fundamental parameters

METHODOLOGICAL APPROACH

- Initiate new measurements taking advantage of technical improvements
- Perform similar measurements in different institutes to establish reliabilty and associated uncertainties of the experimental values
- Perform calculation for selected cases (use calculations for interpolations and validation purposes)
- Compare calculation to experiment
- Provide reliable practical tables to users

www.exsa.hu/fpi.php

International initiative on x-ray fundamental parameters

Participants and events

- **Active participation from :**

  4 National Metrology Institutes

  > 14 Research institutes

  10 Industrial companies

  > 100 members

- **10 international workshops (2008 – 2018)**

- **2018: Denver X-Ray Conference FP session**

- **2019: FP workshop in Lisbon (see www.exsa.hu)**

www.exsa.hu/fpi.php

International initiative on x-ray fundamental parameters

international meetings and objectives:

www.EXSA.hu

1st workshop LNE (M.-C. Lépy)	Oct. 2008	→ definition of expert groups
2nd workshop PTB (B. Beckhoff)	May 2009	→ road map generation
3rd workshop LNE (M.-C. Lépy)	Nov. 2010	→ project options
4th workshop NIST (T. Jach)	July 2011	→ def. of new expert groups
at the EXRS2012 conference	June 2012	→ FP roadmap document online
5th workshop PTB (B. Beckhoff)	Febr. 2013	→ new expert group meetings
6th workshop NIMS (K. Sakurai)	Sept. 2013	→ dissemination of information
7th workshop LNE (M.-C. Lépy)	Mar. 2014	→ road map updates by new EGs
8th workshop UNL (J.-P. Santos)	Apr. 2015	→ road map updates by new EGs
9th workshop UNL (Ch. Jeynes)	Oct. 2016	→ new FP roadmap discussion
10th workshop PTB (B. Beckhoff)	Oct. 2017	→ new FP roadmap approved

International initiative on x-ray fundamental parameters

Tenth FP workshop - Round table discussion on FPs

Are there any recommendations for the most reliable data bases ?

- **ionisation cross sections**

  (including sub-shell values) – ***best:*** **recent experiments**

  second-best: Scofield (Cullen) data

- **fluorescence yields and CK**

  transition probabilities – ***best:*** **recent experiments, second-best: Krause data**

- **line energies** – ***best:*** **recent experiments, second-best: NIST phys. ref. data**

www.exsa.hu/fpi.php

International initiative on x-ray fundamental parameters

2nd FP roadmap document released December, 2017

Roadmap document on atomic Fundamental Parameters for X-ray methodologies

Version 2.0

December 2017

Contents

www.exsa.hu/news/wp-content/uploads/IIFP_Roadmap_V2.pdf

www.exsa.hu/fpi.php