X-ray and IR spectrometry

Materials characterization at the nanoscale by X-ray spectrometry

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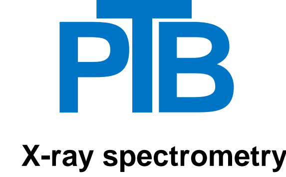
Materials characterisation by X-ray spectrometry



- analytical challenges for nanotechnologies
- reference-free x-ray spectrometry
- surface contamination and nanolayer characterization
- depth profiling at grazing incidence
- chemical speciation at buried interfaces
- towards in-situ speciation of bulk-type films
- high-resolution spectrometry

Analytical challenges for nanotechnologies

- 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 and IR 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 and IR spectrometry

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- 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/

Synchrotron radiation based x-ray spectrometry

XRS excitation channel: XRS detection channel:

well-known spectral distribution
and a well-known radiant power

well-known
solid angle dΩ

absolute detection efficiency
and response functions

derived from
x-ray radiometry

Φ Ψ

fluorescence
radiation

specimen

fundamental parameters

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

transmission measurements

absorption correction factors

PTB capabilities:

→ characterized beamlines

→ calibrated photodiodes

→ calibrated diaphragms

→ calibrated Si(Li) detectors

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

Determination of L-shell photoionization cross sections

X-ray and IR spectrometry

τ_{L3}

τ_{L2}

τ_{L1}

Jump ratio approx.

Scofield data

Trzhaskovskaya data

fitted Scofield

$E_{L1} = 2866$ eV

$E_{L2} = 2625$ eV

$E_{L3} = 2520$ eV

1000

100

10

τ_{Li} / cm^2g^{-1}

3

10

excitation energy / keV

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

Comparison of different PCS data for Mo

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

excitation conditions	total-reflection	tunable incident angle	tunable photon energy
E_0 E_f	XSW E_0 E_f	XSW E_0 E_f	XSW $E_0 \rightarrow E_1$ E_f
concentration	contamination	nanolayer	nanolayer speciation

tunable incident angle	total-reflection	tunable incident angle	tunable photon energy
XSW E_0 E_f	XSW E_0 E_f	XSW E_0 E_f	XSW $E_0 \rightarrow E_1$ E_f
depth profile	nanoparticles	interface	interface speciation

E_0 = photon energy of excitation radiation

E_1 = photon energy above absorption edge

E_f = photon energy of fluorescence radiation

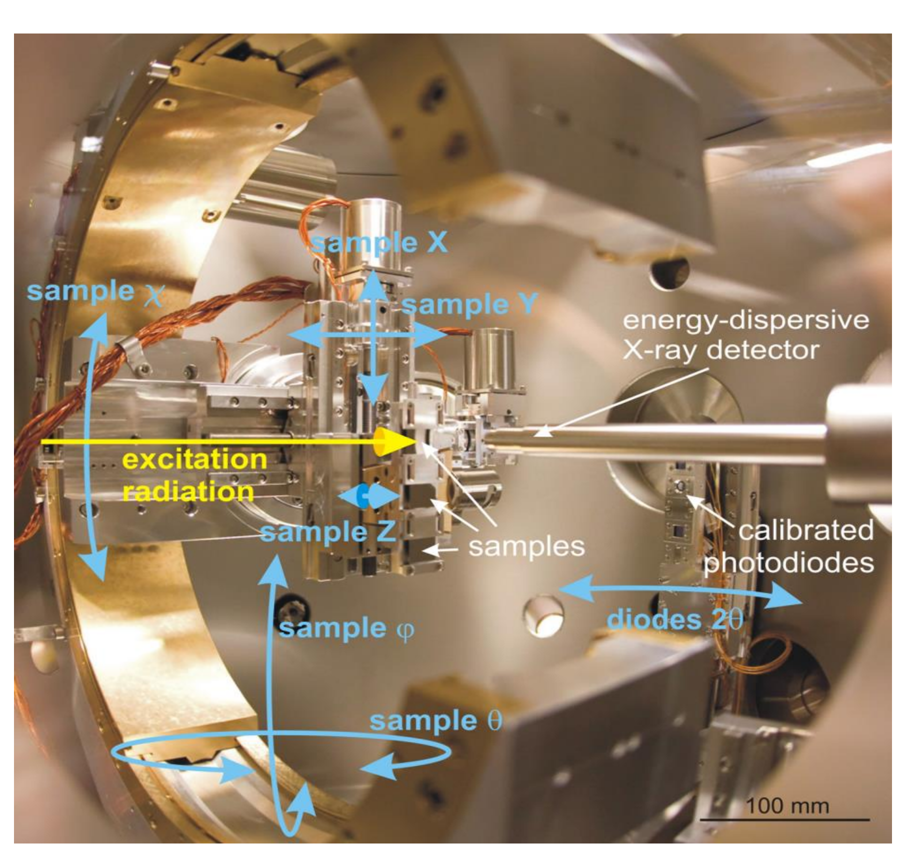
XSW = X-ray Standing Wave field

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

Novel XRS instrumentation for advanced materials characterizations with synchrotron radiation

X-ray and IR spectrometry

PTB XRS intrumentation at BESSY

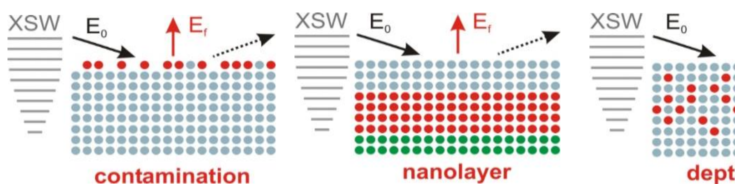


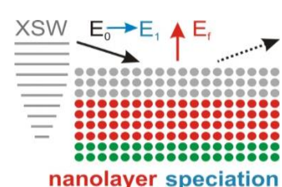
9-axis manipulator and chamber ensuring

- 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

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**





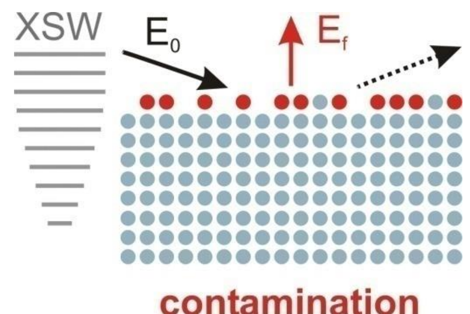
Janin Lubeck et al.,

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

Quantitation in SR-TXRF routine analysis on Si wafers

TXRF **spectra deconvolution** including Si(Li) 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

counts per channel: 10^0, 10^1, 10^2, 10^3, 10^4, 10^5

C-K_α / Mo-M_α, Ti-L_α, O-K_α, F-K_α / Fe-L_α, Ni-L_α, Cu-L_α, Na-K_α, Al-K_α, elastic scatt.

brems-strahlung

Si resonant Raman scatt.

photon energy / eV: 0, 500, 1000, 1500

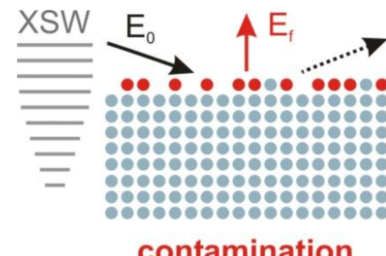
Anal. Chem. **79**, 7873 (2007)   Phys. Stat. Sol. B **246**,1415 (2009)

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



Analytical Chemistry **79**, 7873 (2007)

Reference-free quantitation in SR-TXRF analysis

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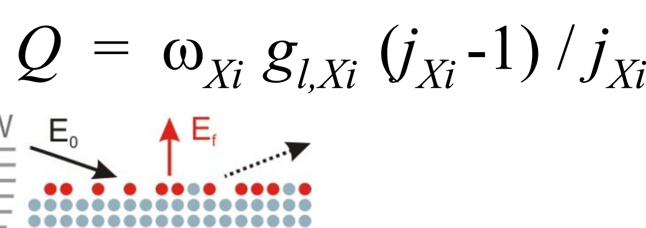
ω_{Xi} fluorescence yield of the absorption edge Xi (of the element i)

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

j_{Xi} jump ratio at the absorption edge Xi

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



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

→ calculation of the x-ray standing wave field

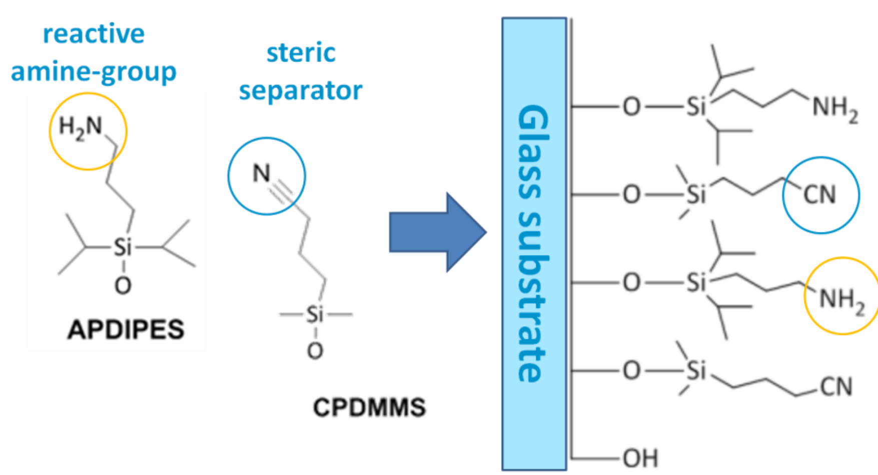
Anal. Chem. **79**, 7873 (2007)

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

X-ray and IR spectrometry

- Organo-silanes for surface functionalization : aminated monolayers with a controlled density of functional and reactive groups
- determination of molecular surface density by means of reference-free TXRF analysis
- traceable quantification based on usage of specific elements as markers (here: nitrogen)
- validation of other methods, e.g. XPS

Organo-silanes for surface functionalization:



Samples	Silane density molecules/nm²
100 % APDIPES	2.3
1:1 CPDMMS / APDIPES	2.4
100 % CPDMMS	2.1
pure glass	-

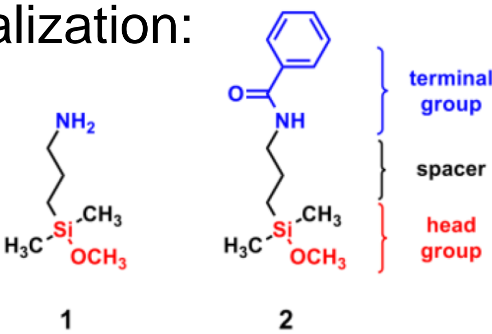
C. Streeck, A. Nutsch

Anal. Chem. **87**, 2685 (2015)

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

X-ray and IR spectrometry

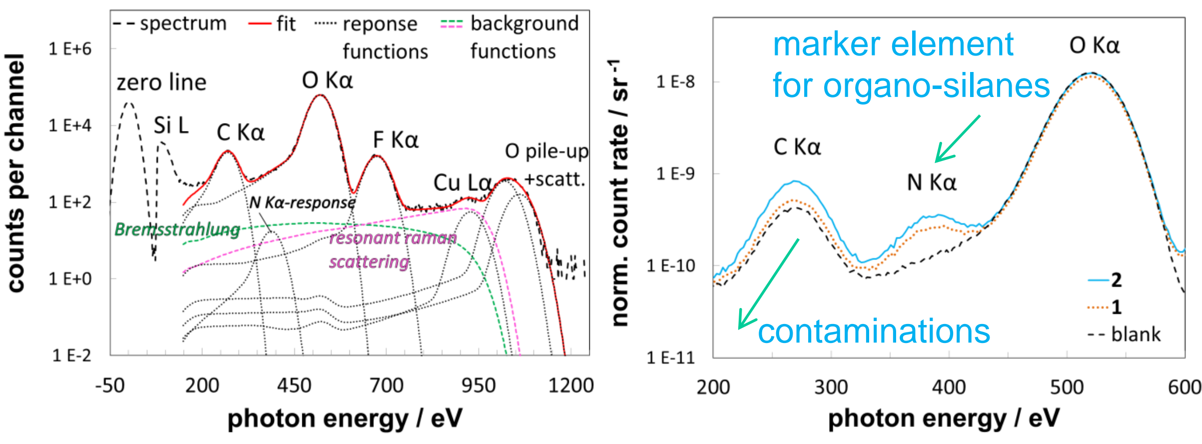
- Single organo-silanes for surface functionalization:

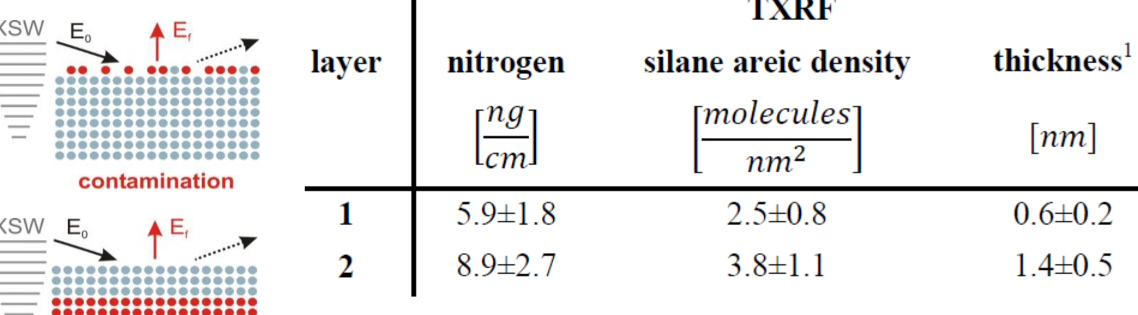


- molecular surface density as revealed by reference-free TXRF

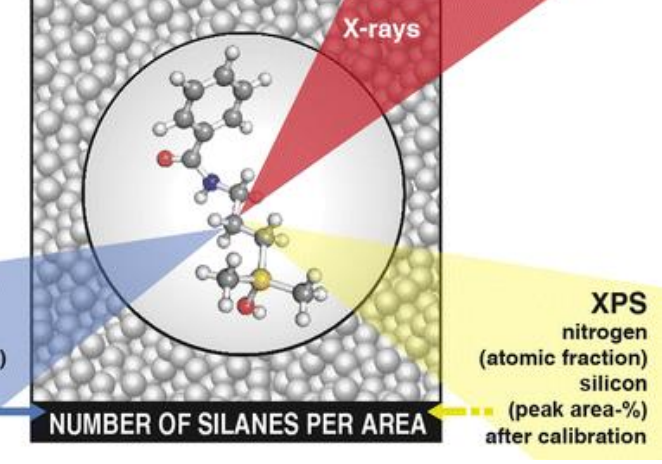
- traceable quantification based on specific elements as marker (nitrogen)

Spectral deconvolution:





layer	TXRF nitrogen $\left[\frac{ng}{cm}\right]$	TXRF silane areic density $\left[\frac{molecules}{nm^2}\right]$	TXRF 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



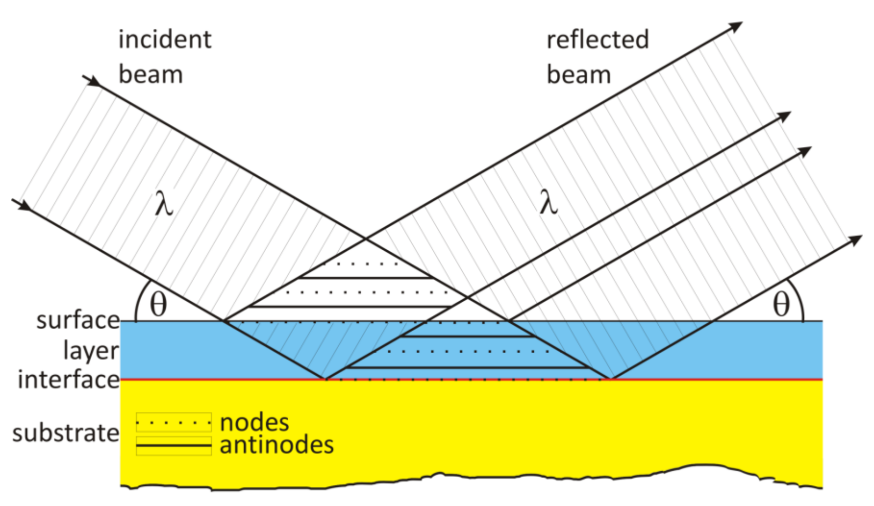
C. Streeck, A. Nutsch

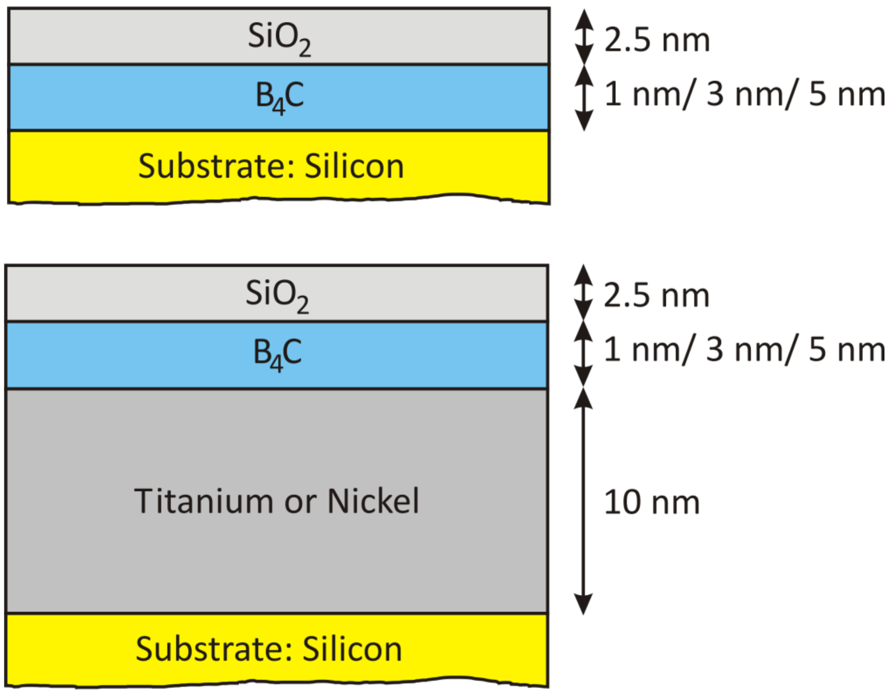
Anal. Chem. **87**, 10117 (2015)

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

X-ray and IR spectrometry

X-ray standing wave field (XSW)



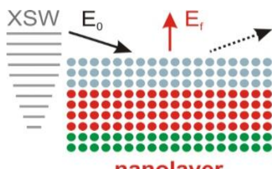


design of samples: total-reflection of the incident beam at silicon or at the metal

→ 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)

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

photon energy: 1060 eV

5nm B_xC

1.19°
1.28°
1.39°

O Kα
C Kα
B Kα
Si Ll

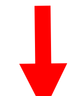
relative count rate /solid angle *sin(inc. angle)

incident angle / °

XSW E_0 E_f contamination

XSW E_0 E_f nanolayer

depth-dependent modification of the excitation radiation due to XSW



reveal information about the sequence of the layers

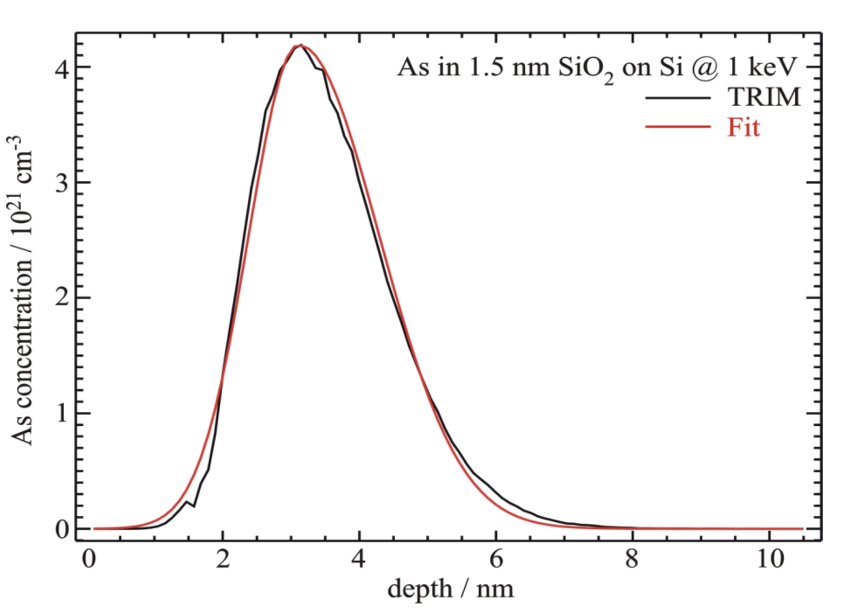
1. oxygen
2. carbon
3. boron
4. silicon (substrate)

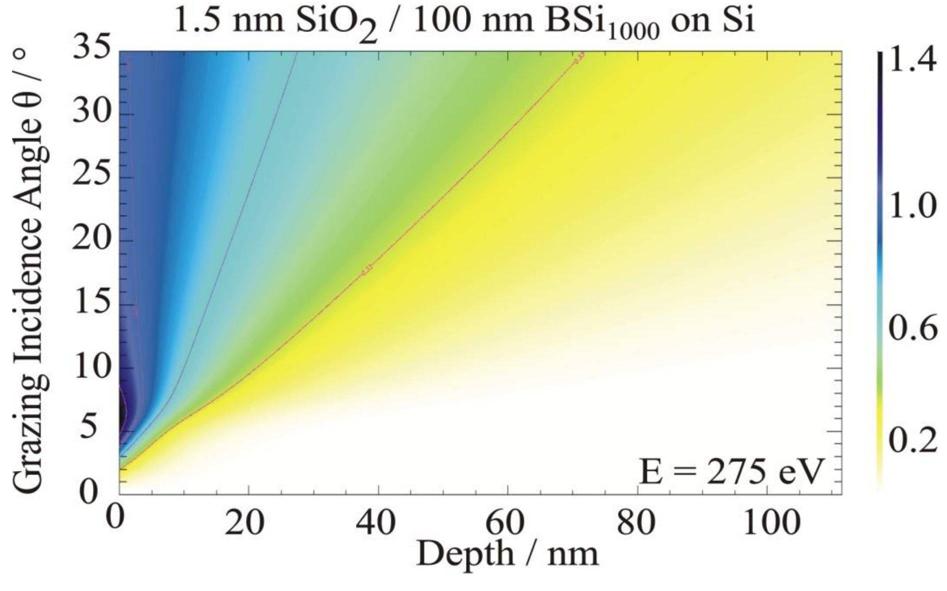
carbon contamination at surface recorded

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

GIXRF analysis of B and As implantation profiles

X-ray and IR spectrometry



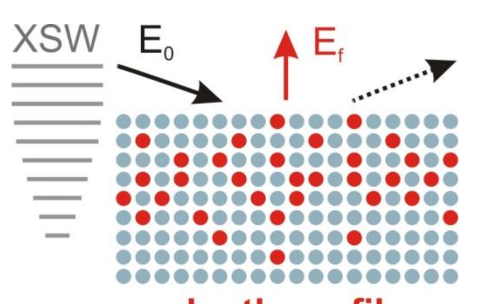


fundamental and instrumental parameters

depth distribution of the implant

X-ray Standing Wave field distribution

absorption term



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

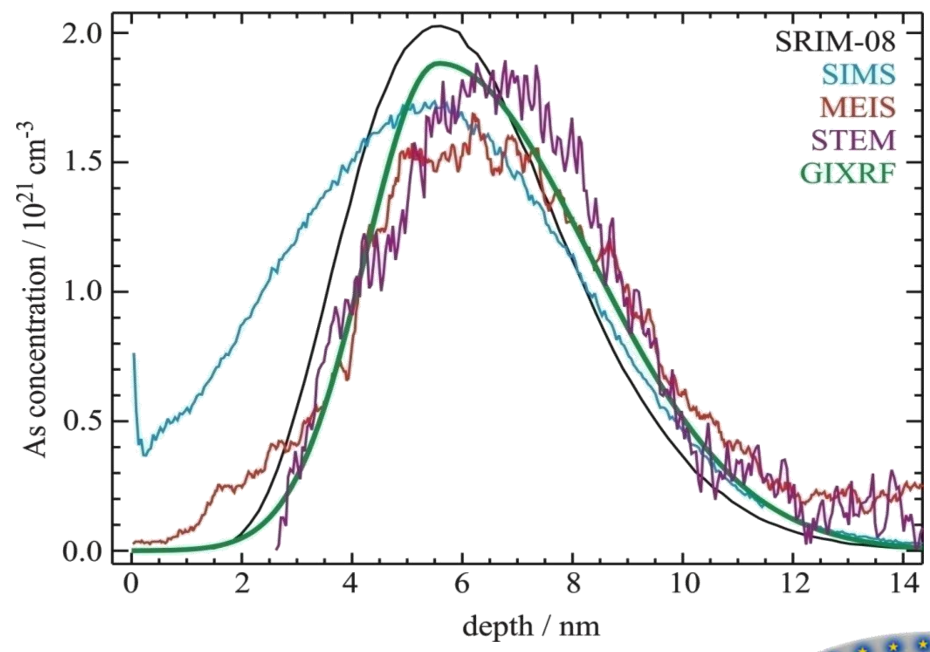
P. Hönicke

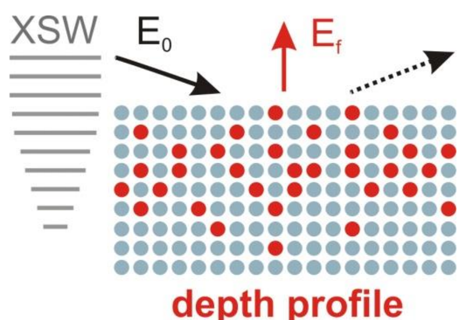
Anal. Bioanal. Chem. **396**, 2825 (2010)

GIXRF analysis of B and As implantation profiles

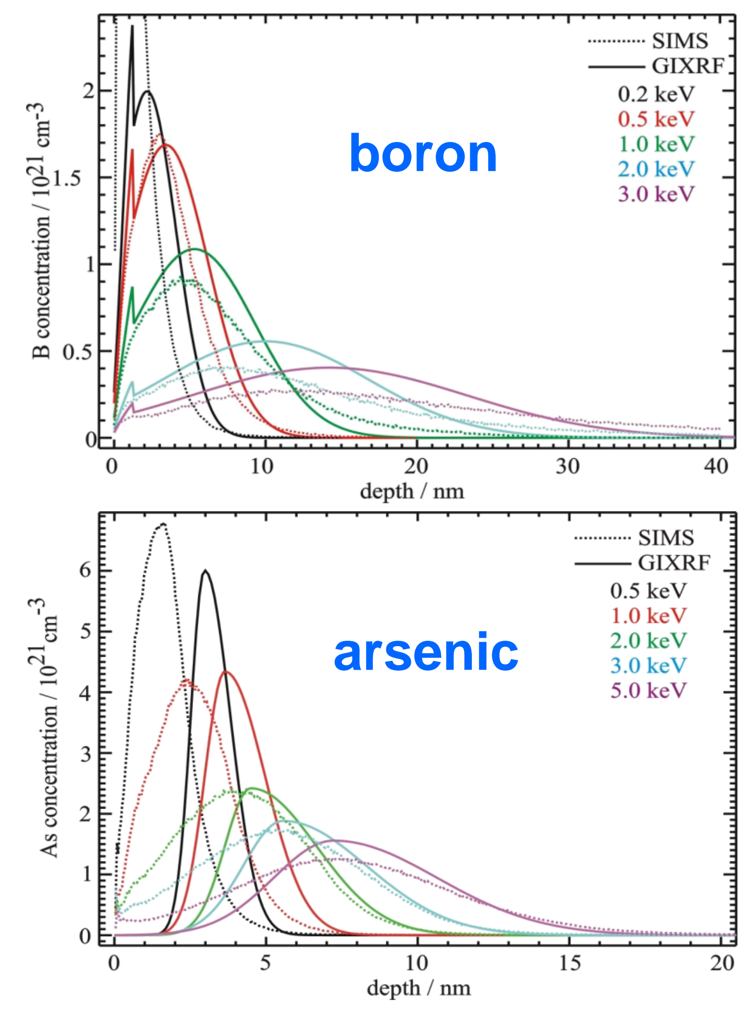
X-ray and IR spectrometry

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





Comparison of GIXRF results to SIMS



ANNA – Analytical Network for Nanotech

D. Giubertoni (FBK)

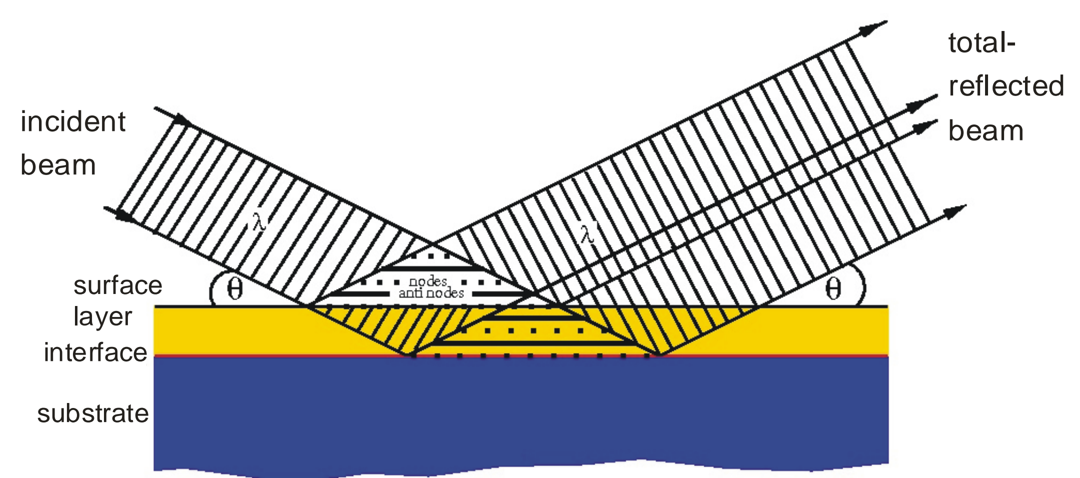
J. van den Berg (Univ. Salford)

P. Hönicke

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

Speciation of buried nanolayers by GIXRF-NEXAFS

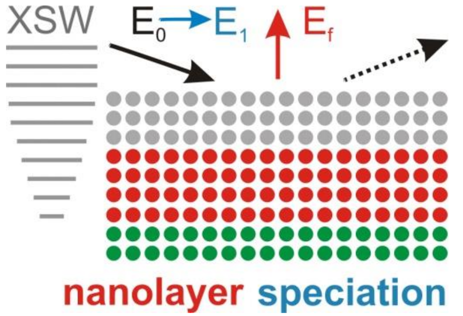
X-ray and IR spectrometry



→ **composition and speciation of buried nanolayers**

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

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

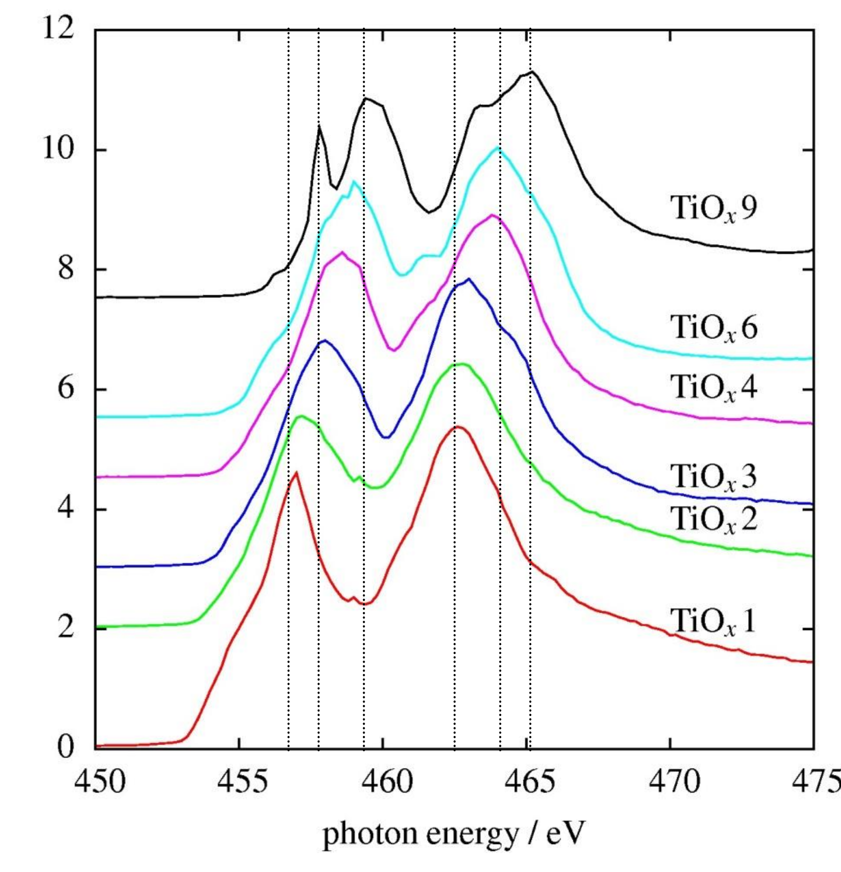


B. Pollakowski

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

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

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

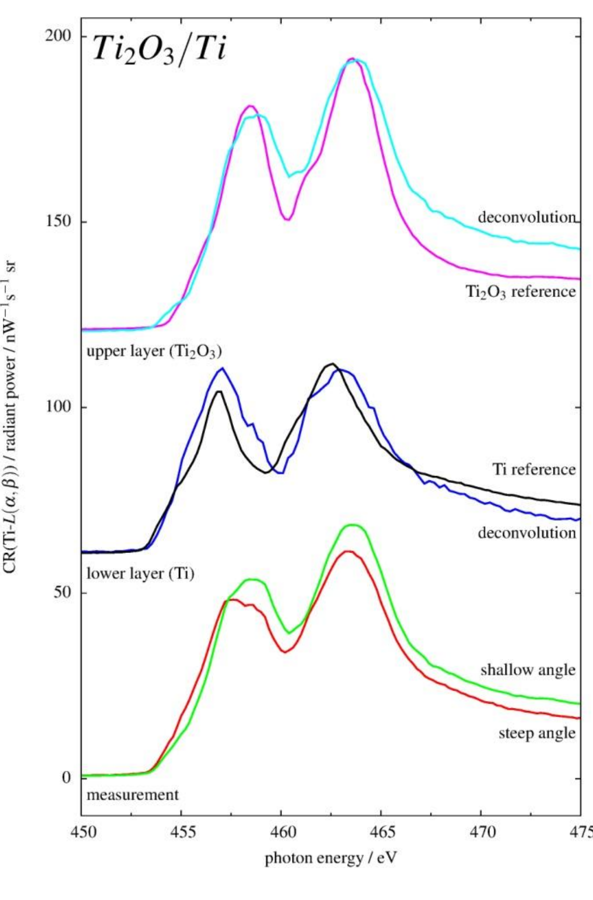


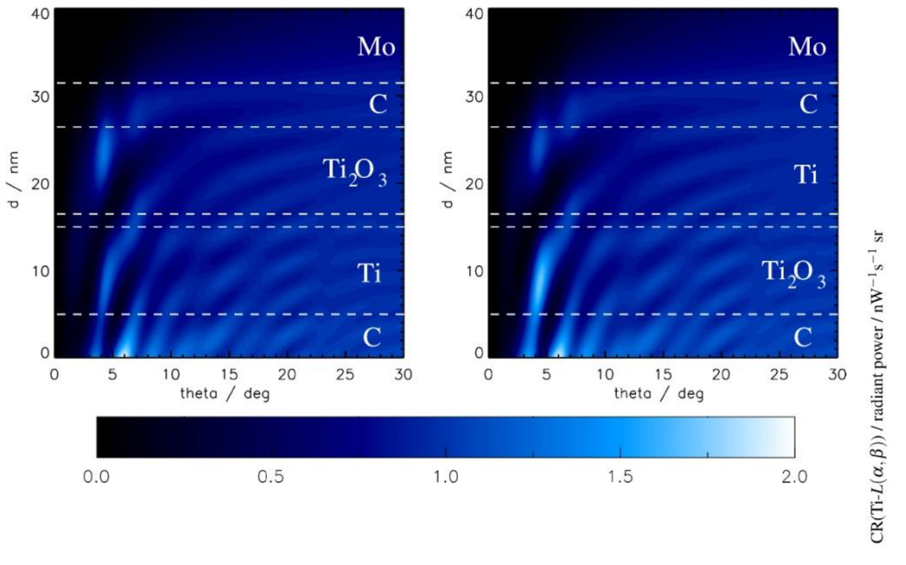
speciation of buried Ti oxide nanolayers

(the degree of oxidation scales with indices)

Speciation depth profiling by GIXRF-NEXAFS

X-ray and IR spectrometry



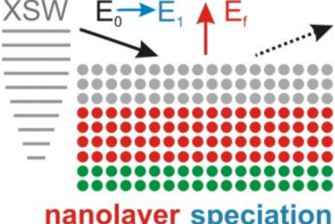


→ speciation of $Ti_{x1}O_{y1}$ /$Ti_{x2}O_{y2}$ nanolayers

→ high information depth (up to 500 nm)

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

Ti/Ti_2O_3
deconvolution
Ti reference
upper layer (Ti)
deconvolution
Ti_2O_3 reference
lower layer (Ti_2O_3)
steep angle
shallow angle
measurement
CR(Ti-L(α,β)) / radiant power / nW⁻¹s⁻¹ sr
photon energy / eV

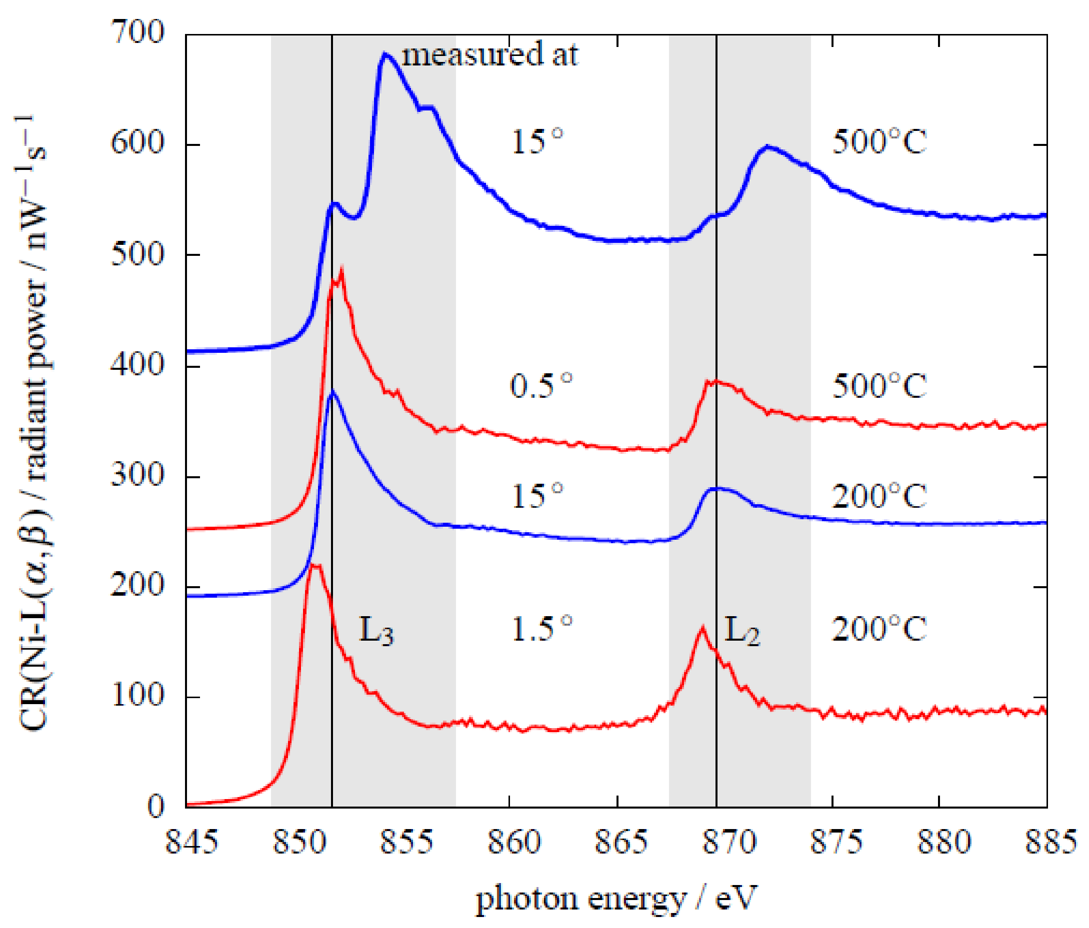


B. Pollakowski

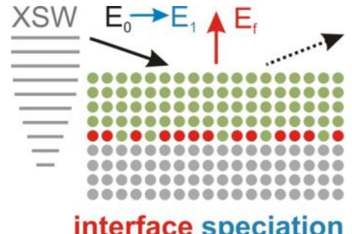
Anal. Chem. **87,** 7705 (2015)

Speciation of buried interfaces by GIXRF-NEXAFS

X-ray and IR spectrometry



- **Comparison** between a **shallow** and a **steep** angle
- Interface observable: Ni-C, Ni-N or Ni-Si bonds possible

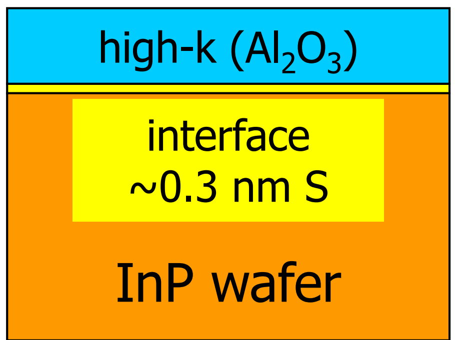


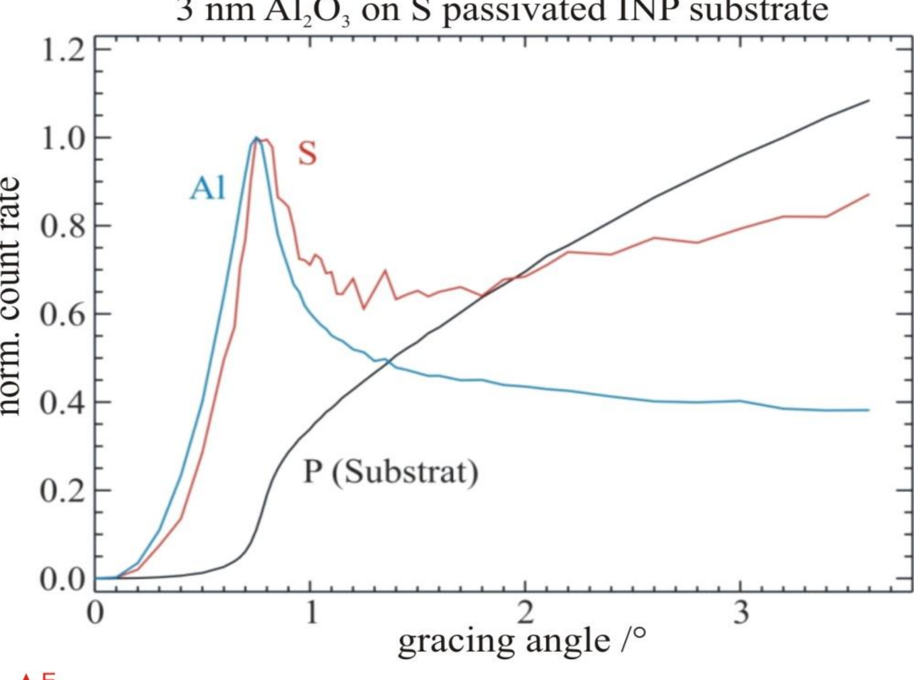
B. Pollakowski Anal. Chem. **85,** 193 (2013)

Quantitative characterization of nanoelectronics

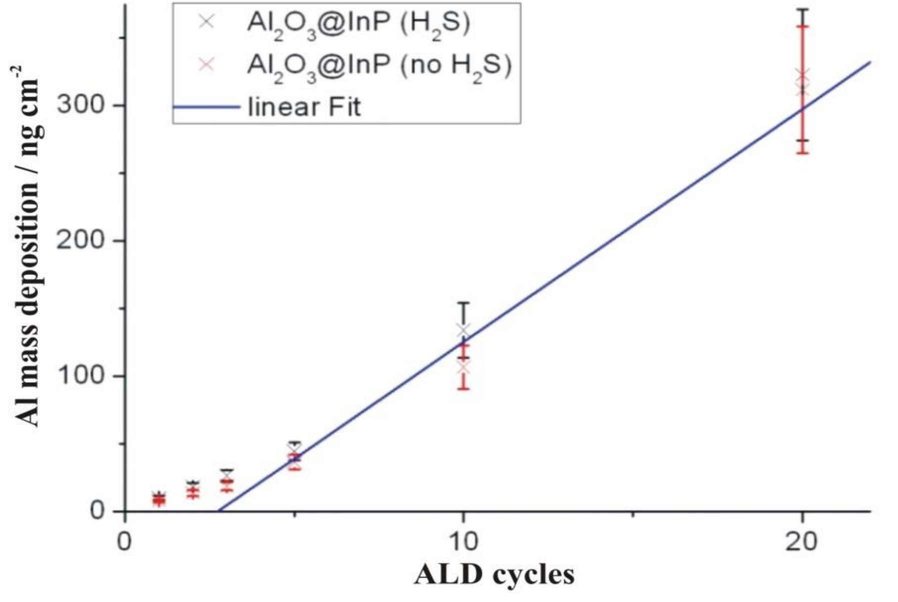
X-ray and IR spectrometry

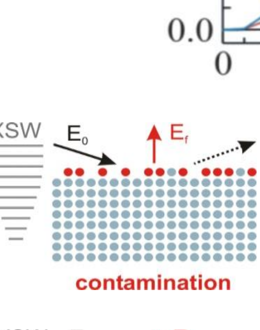
Optimization of high-k nanolayer fabrication

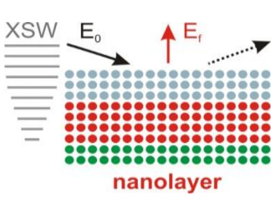




Quantification of the ALD growth rate







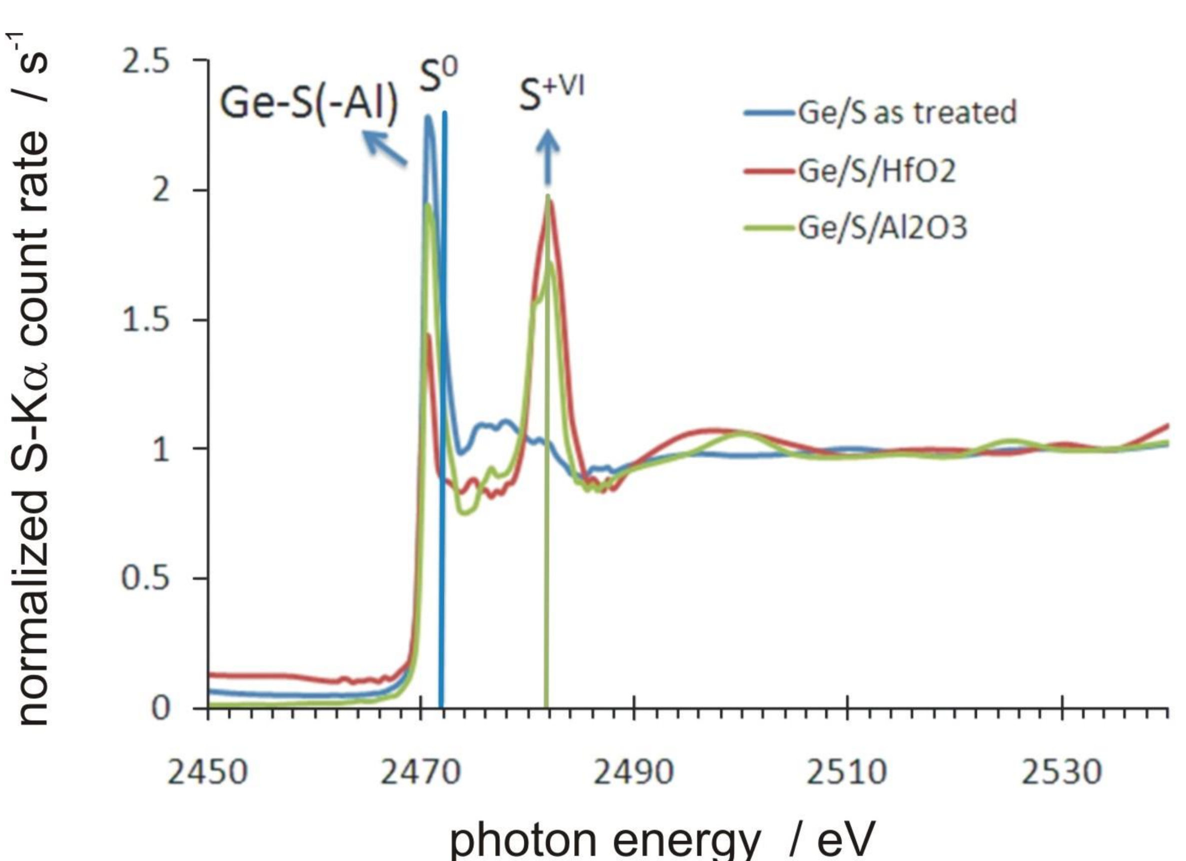
M. Müller

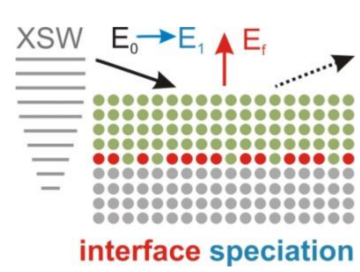
linear growth on S passivated InP substrate after the 3rd ALD cycle

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

Quantitative interface characterization and speciation

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





high-k (e.g. 5 nm HfO_2)

Ge wafer

M.Müller

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

GIXRF-NEXAFS at thin-film Si photovoltaics: probing the chemical state of buried interfaces

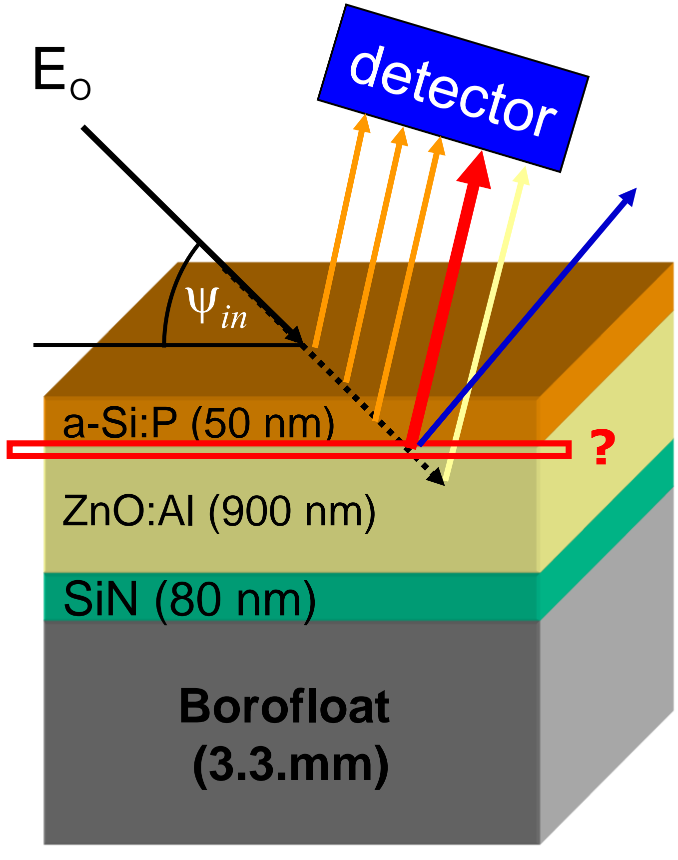
GIXRF-NEXAFS requirements:

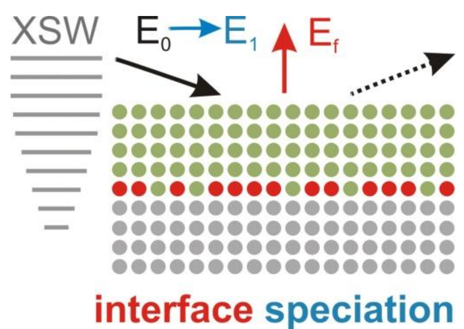
- transmission through a-Si layer
- total reflection at interface

Si:P - Si doped with 0,2 at% P

ZnO:Al - ca. 2 at.% Al

SiN - Si:N = 3:4





M. Pagels,
TUB / HZB

B. Pollakowski

NIMB **268**, 370 (2010)

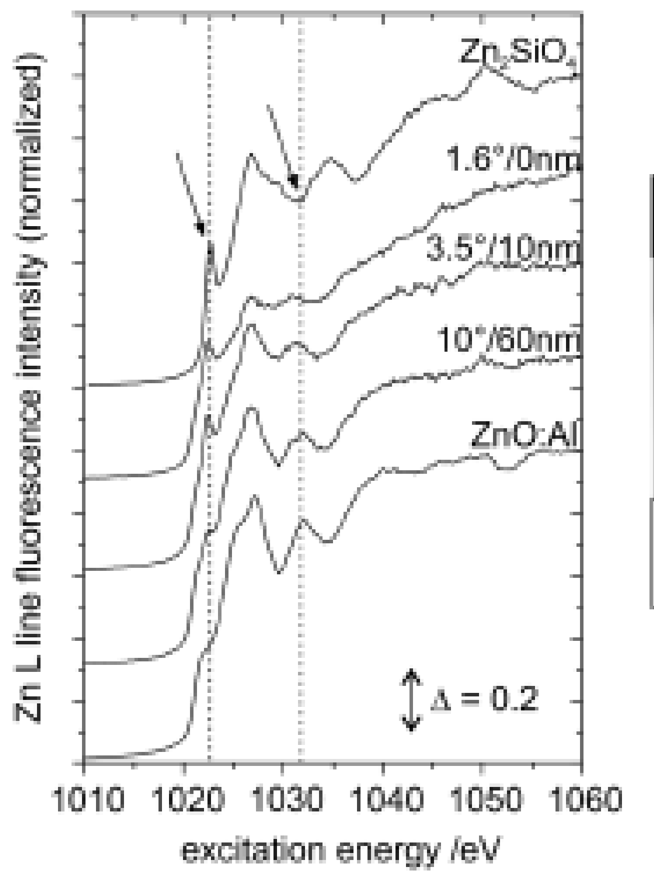
GIXRF-NEXAFS at thin-film Si photovoltaics: probing the chemical state of buried interfaces

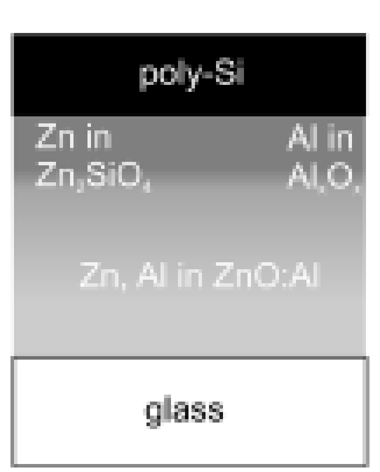
X-ray and IR spectrometry

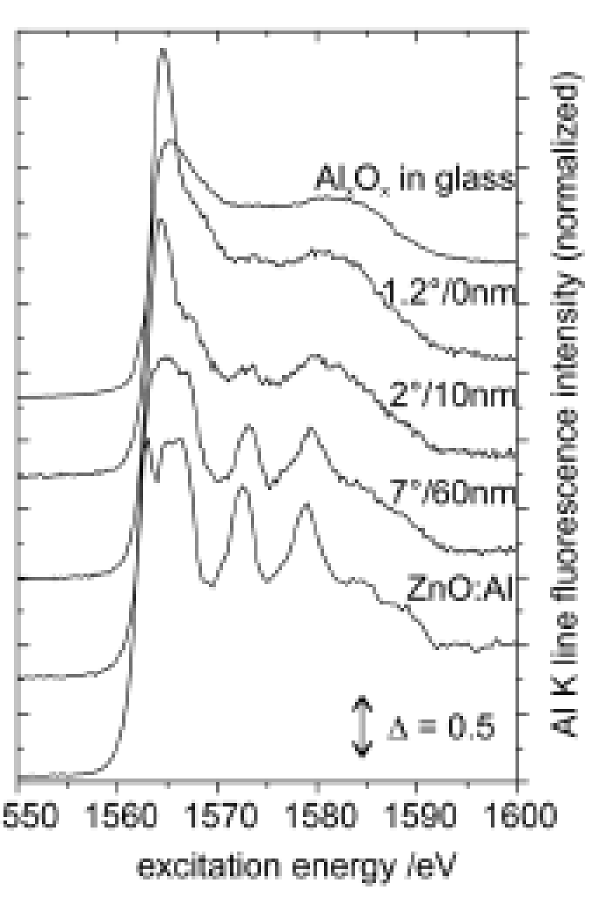
HELMHOLTZ ZENTRUM BERLIN für Materialien und Energie

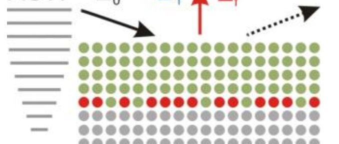
berlin

NEXAFS investigations at the Zn-$L_{iii,ii}$ and Al-K edges









M. Pagels, TUB / HZB

C. Becker, HZB

B. Pollakowski

J. Appl. Phys. **113**, 044519 (2013)

Elemental depth profiling of CIGS photovoltaics by GIXRF using calibrated instrumentation

X-ray and IR spectrometry

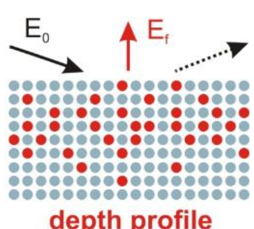
Cu(In,Ga)Se2 absorber for thin film solar cells

1µm EHT=7.00kV WD=10.0mm

Ni/Al
ZnO:Al
i-ZnO
CdS
Cu(In,Ga)Se_2
Mo
Glas

front contact
absorber
back contact
substrate

- 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

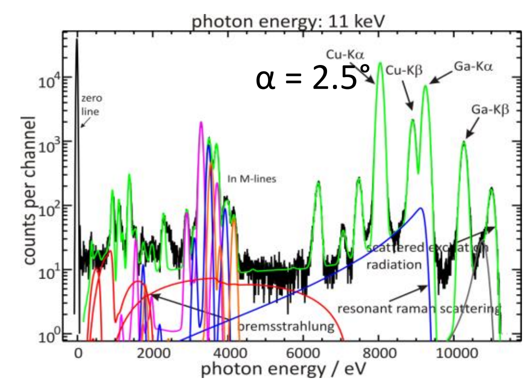
X-ray and IR spectrometry

HELMHOLTZ ZENTRUM BERLIN für Materialien und Energie

Increasing information depth with increasing incidence angle

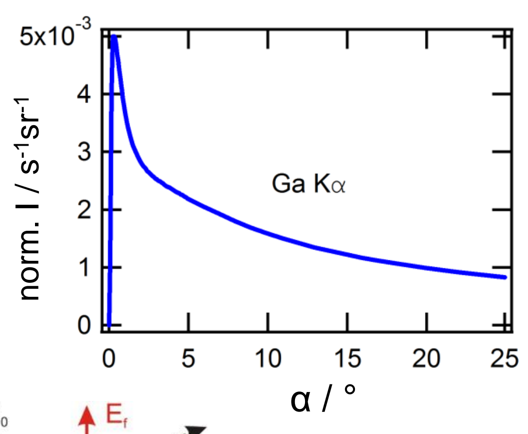
2 µm

XRF-spectrum



Fluorescence intensity in dependence of the angle of incidence

GIXRF



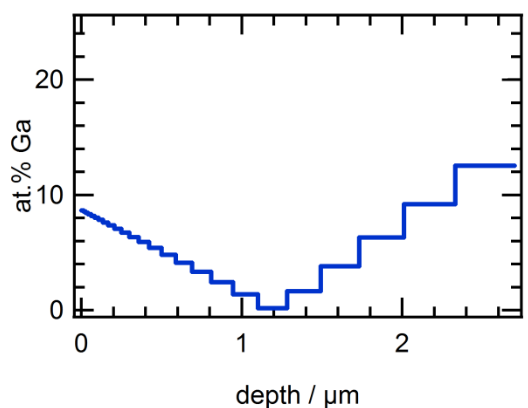
E_0 E_f

depth profile

Non-destructive access to the elemental depth profile

Fundamental parameter-based quantification

Elemental depth profile



C. Streeck

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

Elemental depth profiling of CIGS photovoltaics by GIXRF using calibrated instrumentation

X-ray and IR spectrometry

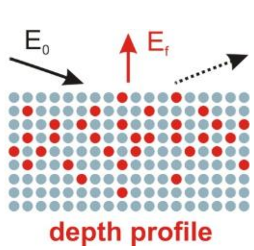
BIPM Pilot-study CCQM-P140

CCQM-P140

SURFACE ANALYSIS

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

Composition / at.%	Certified values (KRISS – Korea Research Institute of Standards and Science)	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. Suppl.), 08017 (2015)

Directed development of new energy storage materials: towards in-operando XAFS speciation of cathode films

X-ray and IR spectrometry

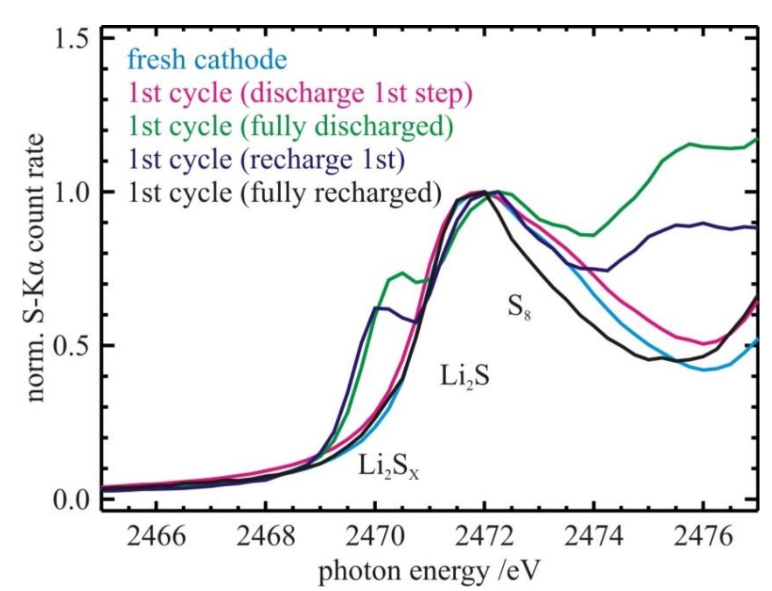
First step: No ambient air exposure

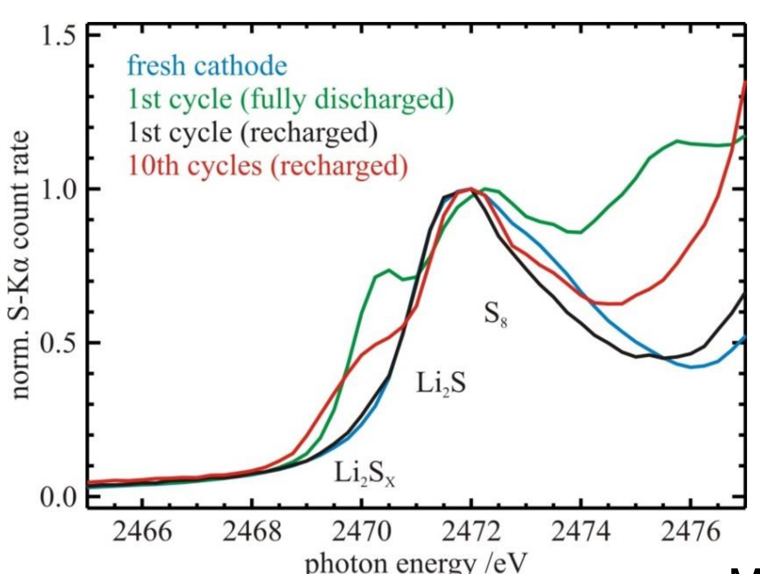
Employing a thin window argon cell for x-ray spectrometric measurements.

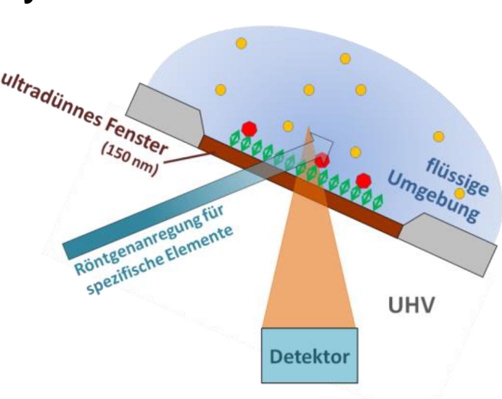
- NEXAFS measurements at different states of charge (not in-situ or operando so far)
- Formation of lithium polysulfides during discharge observed
- Polysulfides disappear during recharging
- After several recharge cycles some of the polysulfides remain

  Spectrochim. Acta B **94–95**, 22 (2014)

- **Patent application** of liquid cell (operando studies of batteries)





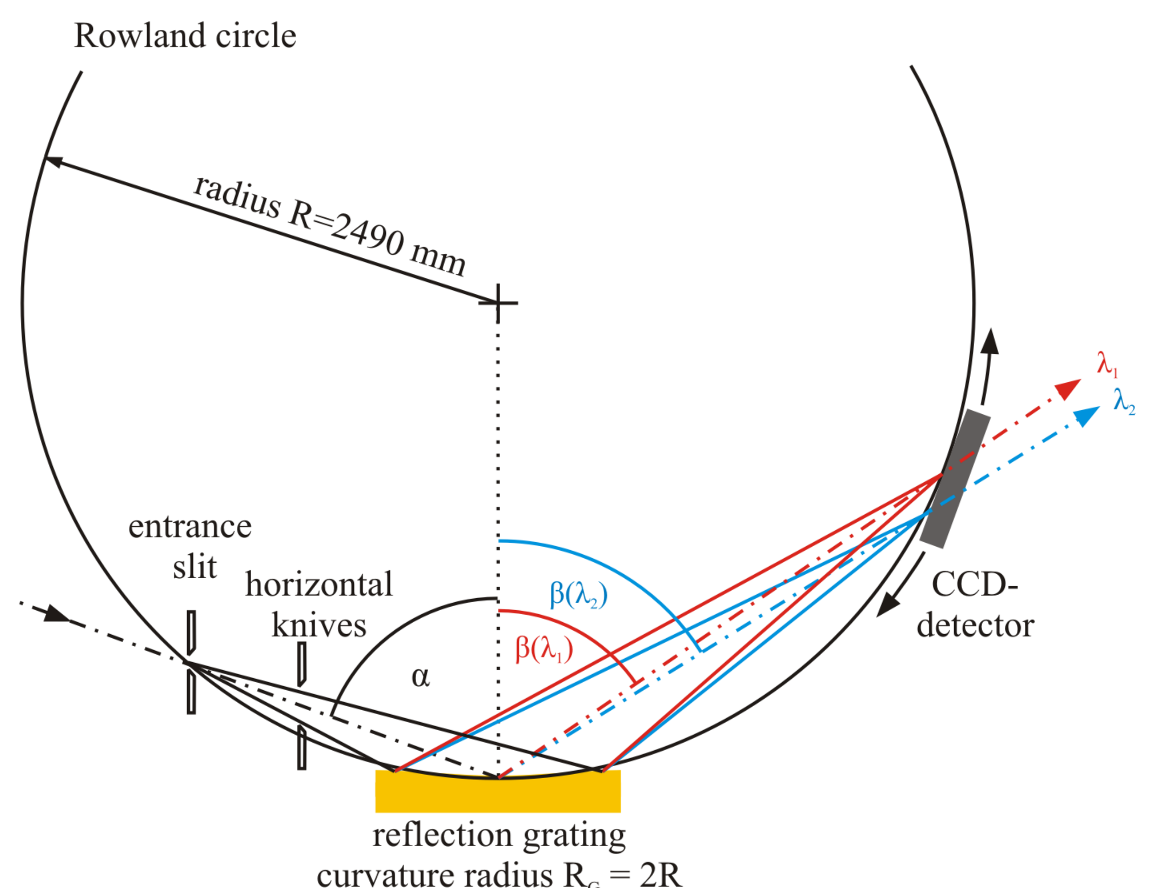


liquid-solid interfaces

M. Müller

Calibrated Wavelength-Dispersive Spectrometer (WDS)

X-ray and IR spectrometry



energy range:

75 eV to 1760 eV

energy resolution $E/\Delta E$:

150 to 400

calibration → allows for the determination of fundamental parameters

disadvantage: → low efficiency, moderate detection limit, long integration time

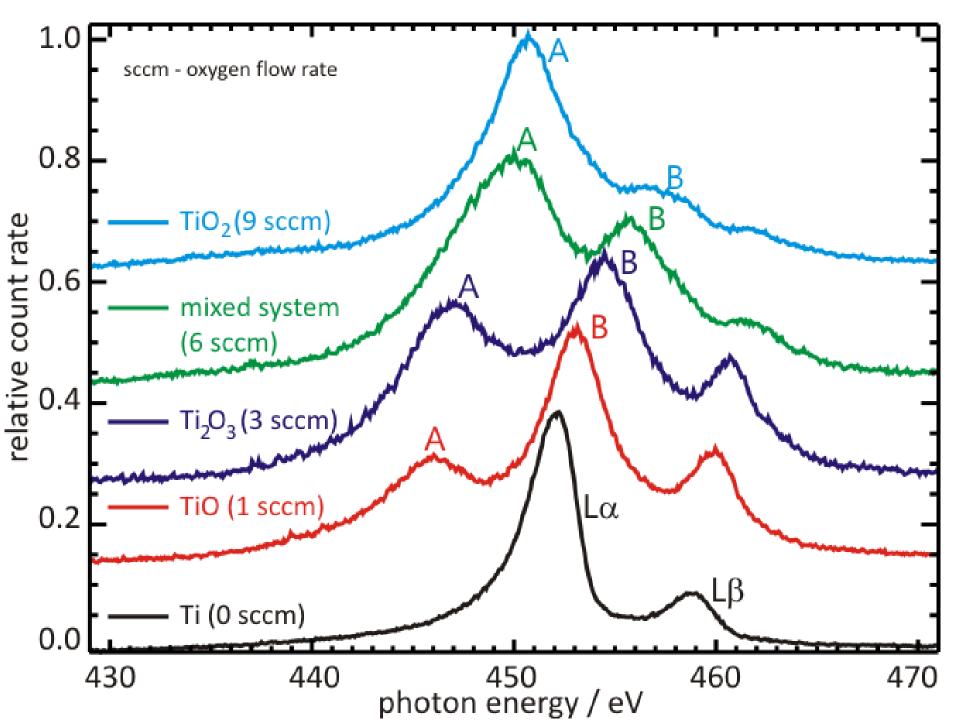
M. Müller

Phys. Rev . A **79**, 032503 (2009)

Calibrated Wavelength-Dispersive Spectrometer (WDS)

X-ray and IR spectrometry

Chemical speciation of nanoscaled materials and



fundamental parameter determination

sample	titanium Ll	uncertainties
metallic Ti	0.59	0.06
0 sccm (Ti)	0.59	0.06
1 sccm (TiO)	0.61	0.09
3 sccm (Ti_2O_3)	0.57	0.09
6 sccm (mixed system)	0.54	0.08
9 sccm (TiO_2)	0.46	0.07

Transition probabilities as a function of the oxidation state

R. Unterumsberger

Chemical speciation of titanium with a von Hamos spectrometer based on HAPG crystals

X-ray and IR spectrometry

Recorded at BESSY (undispersed bending magnet radiation)

normalized intensity

1.0
0.8
0.6
0.4
0.2
0.0

4850 4900 4950 5000 5050

photon energy / eV

$K\beta_{1,3}$

$K\beta_5$

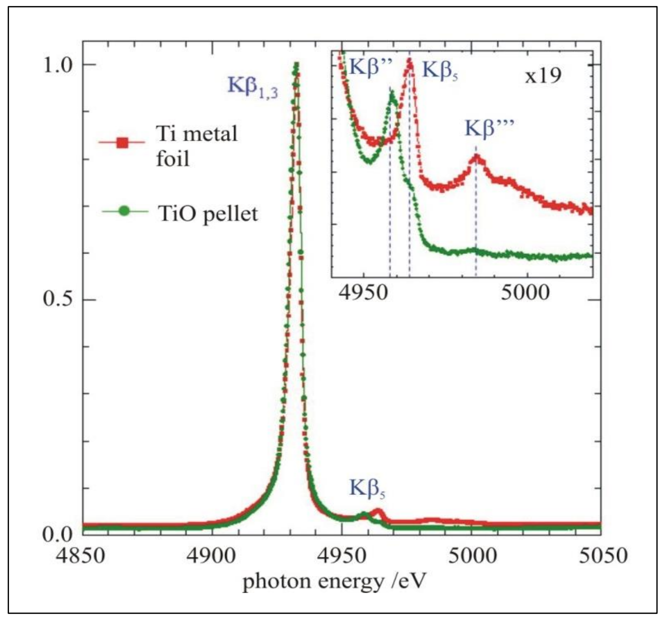
Ti foil (2µm)
TiO
Vanadium

energy resolving power $E/\Delta E = 2000$

Vanadium lines used for calibration of energy scale

J. Appl. Cryst. **48**, 1381 (2015)

Measurements at SPring-8 (Japan) with a Ge crystal spectrometer with 10 keV monochromatic radiation



Anal. Chem. **81**, 1770 (2009)

Calibratable von Hamos spectrometer for XES

X-ray and IR spectrometry

energy range:

- *2.3 keV – 10 keV (double Bragg reflection)*
- *2.3 keV – 20 keV (single Bragg reflection)*
- *10 keV – 20 keV (second order reflection)*

I. Holfelder

operation begin in Aug. 2016

Summary

X-ray and IR 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 speciation of nanoscaled materials
- New XRS instrumentation available at PTB, TUB, LNE-LNHB, IAEA/ELETTRA
- Calibrated high-resolution x-ray emission spectrometer and novel liquid cells

Further information on reported activities and instrumentation

at **EMRP IND07, ENG53** and **NEW01** at **www.EURAMET.org**

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

E-MRS Symposia ‚Analytical Techniques for Precise Characterization of Nanomaterials' 2014 / 2017

PTB laboratory at BESSY II: well-known synchrotron radiation for x-ray radiometry and x-ray spectrometry

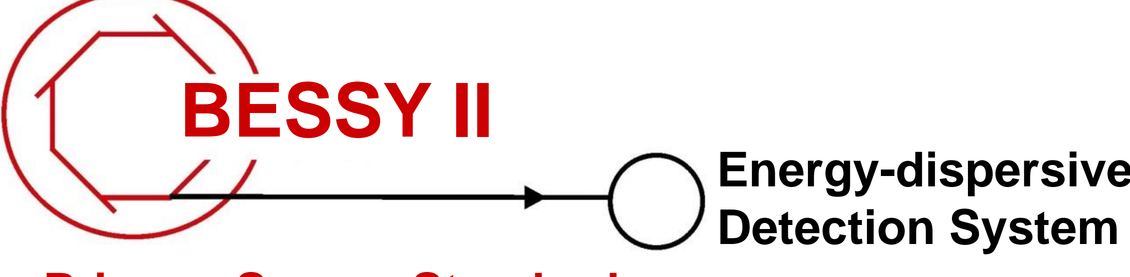
5
PTB Undulator
4c
4b
4a
3a
3b
3c
2
1
bending magnets
electrons
65 m

1	Soft X-ray radiometry beamline 30 eV to 1900 eV (EUV XRR, detect.)	**4a**	Undispersed undulator radiation
2	X-ray radiometry beamline 1.75 keV to 10 keV (XRR, **XRS, XAFS)**	**4b**	Plane grating monochromator beamline 78 eV to 1860 eV (**XRS, XAFS**)
3a	Undispersed bending magnet Radiation (detectors)	**4c**	System metrology beamline
3b	UV-VUV source characterization 3 eV to 35 eV (to be transfered to MLS)	**5**	UV-VUV radiometry beamline 3 eV to 35 eV (transfered to MLS in 2009)
3c	Irradiation testing beamline		

Phys. Stat. Sol. B **246**,1415 (2009)

PTB laboratory at BESSY II: well-known synchrotron radiation for x-ray radiometry and x-ray spectrometry

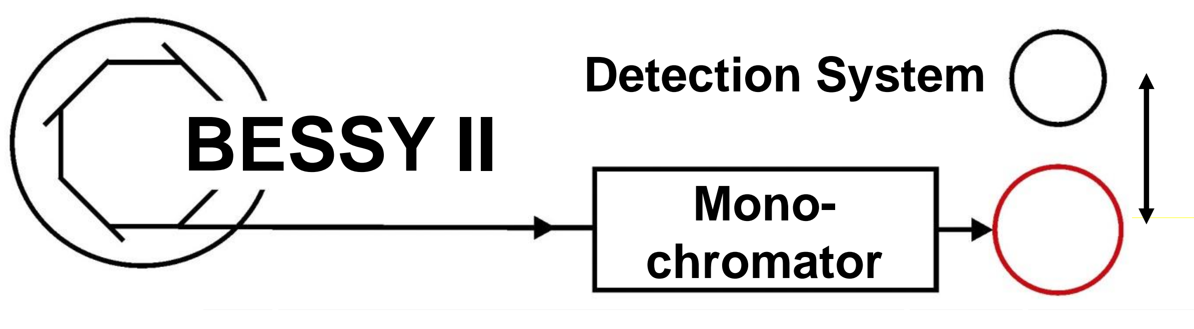
Source-based Radiometry:

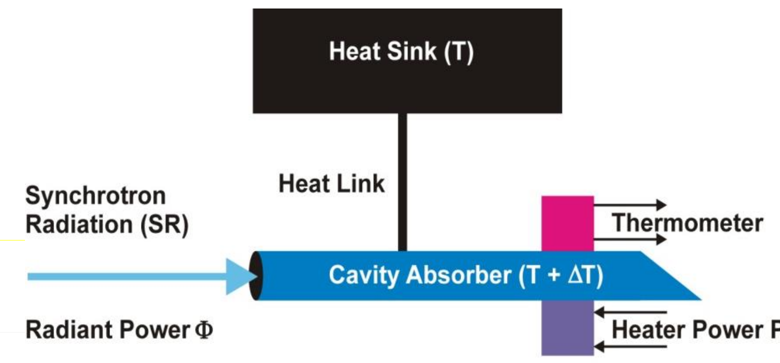


Primary Source Standard
(Relative Standard Uncertainty: u = 0.1 %)

wavelength / nm
1000 100 10 1 0,1
band width
$\Delta E/E = 10^{-2}$
spectral radiant power / W
10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5}
black body 3000 K
WLS 7 T
BESSY II
MLS
200 MeV
600 MeV
PTB special 900 MeV
1700 MeV
far IR and IR | VIS | UV | VUV / soft X ray | X ray
1 10 100 1000 10000
photon energy E / eV

Detector-based Radiometry:





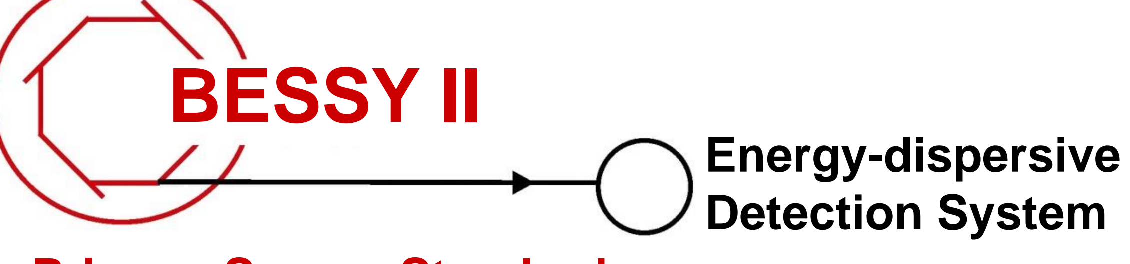
Primary Detector Standard
(Cryogenic Radiometer, Relative Standard Uncertainty: u = 0.1 %)

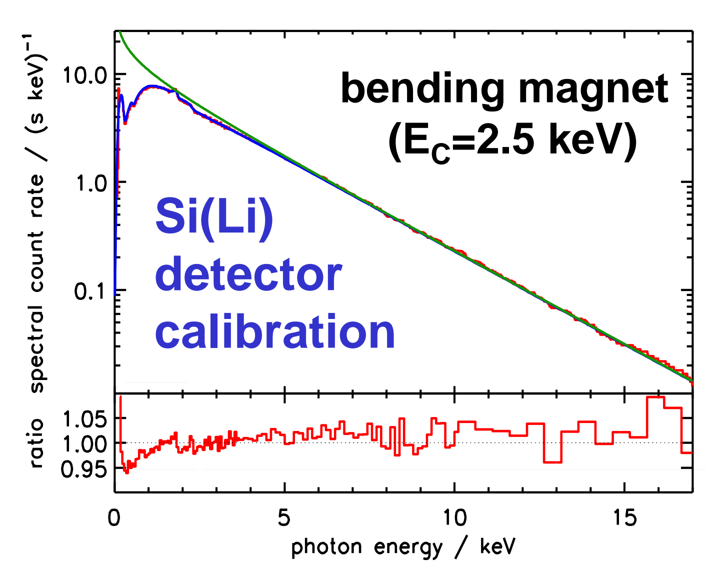
For constant absorber temperature T + ΔT:

$\Phi = P_{SR\ off} - P_{SR\ on}$ (Electrical Substitution)

PTB laboratory at BESSY II: well-known synchrotron radiation for the calibration of x-ray instrumentation

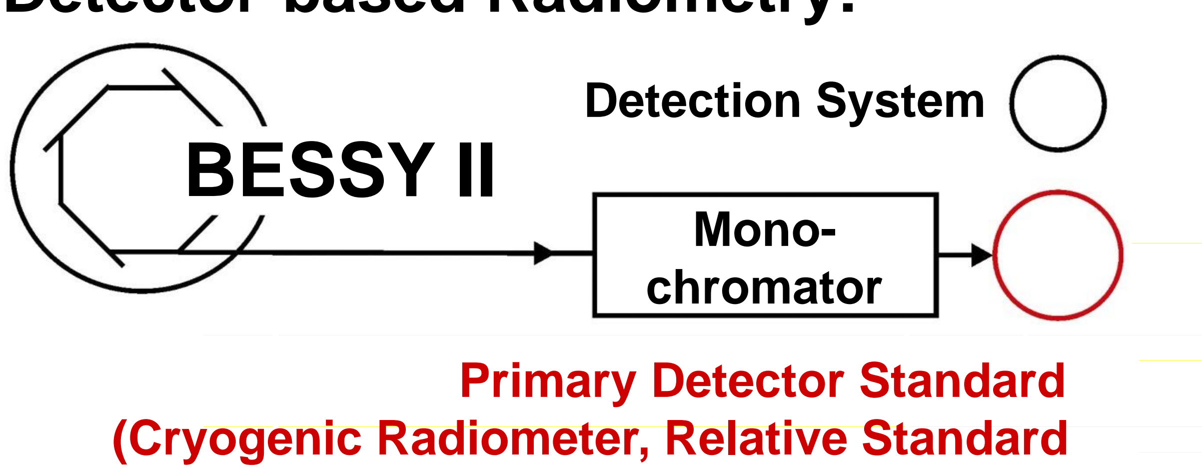
Source-based Radiometry:





Primary Source Standard
(Relative Standard Uncertainty: u = 0.1 %)

Detector-based Radiometry:

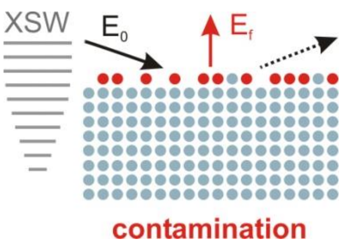


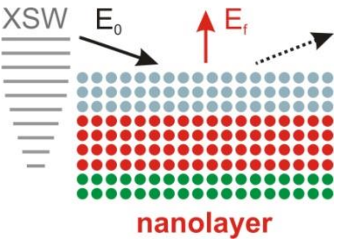
Primary Detector Standard
(Cryogenic Radiometer, Relative Standard Uncertainty: u = 0.1 %)

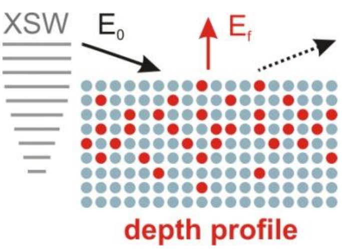
Phys. Stat. Sol. B **246**,1415 (2009)

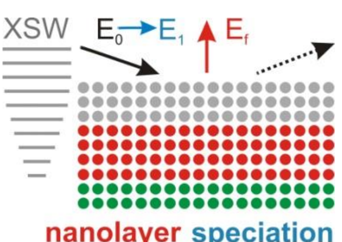
Total-reflection X-Ray Fluorescence (TXRF) facility for 200 and 300 mm Si wafers using synchrotron radiation

X-ray and IR spectrometry









mobile cleanroom class 100

PGM beamline

EFEM

Si(Li) detector

(T)XRF analysis chamber

load-lock

FOUP

PTB laboratory at BESSY II

Analytical Chemistry **79**, 7873 (2007)

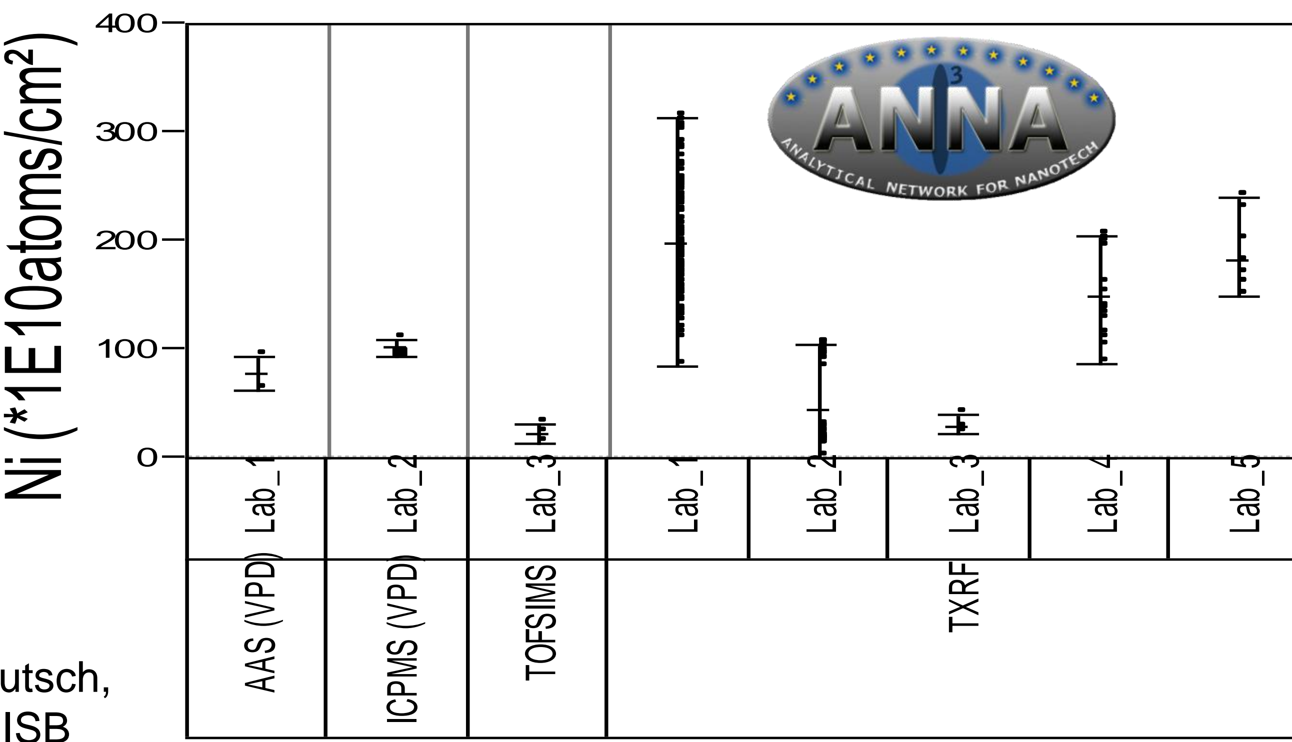
reference based TXRF - Ni surface contamination

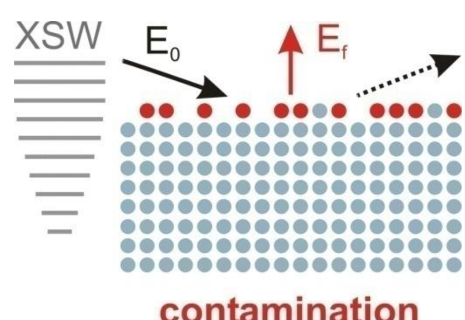
X-ray and IR spectrometry

Total-reflection X-ray Fluorescence (TXRF) analysis:

- non-consistent results from round robin tests (differences up to a factor of ten)
- reason: problems with employed calibration samples (droplet depositions)

spin coated contamination:
metals 1×10^{12} atoms/cm^2
and light elements (Na, Al)
1×10^{13} atoms/cm^2





A. Nutsch, FhG IISB

Solid State Phenomena **145-146**, 97 and 101 (2009)

Assessment of TXRF calibration samples for Ni surface contamination

X-ray and IR spectrometry

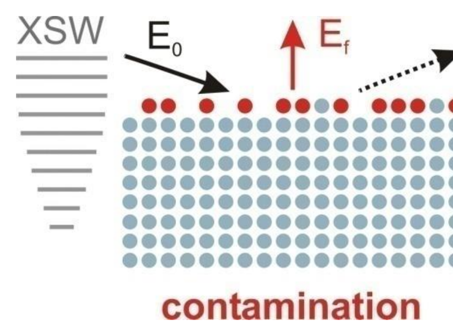
Ni droplets:
100 ng
10 ng
1 ng

mass /ng
10.000
1.000
0.100
0.010
0.001
-2 -1 0 1 2
lateral position /mm

Ni droplets:
100 ng
10 ng
1 ng

normalized count rate / Ni-L_α
0.0 0.5 1.0 1.5 2.0
1 2 3 4 5
glancing angle /°

only ‚1 ng‘ thin-layer type



Reason for deviations in contamination results: inhomogeneities and absorption saturation of TXRF calibration droplets

→ “slicing” and “angular scanning” of calibration droplets by reference-free TXRF as validation technique

M. Müller

Solid State Phenomena **187**, 291 (2012)