Traceable characterisation of thin film samples for advanced materials by reference-free X-ray fluorescence spectrometry

Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin
National Metrology Institute

Motivation

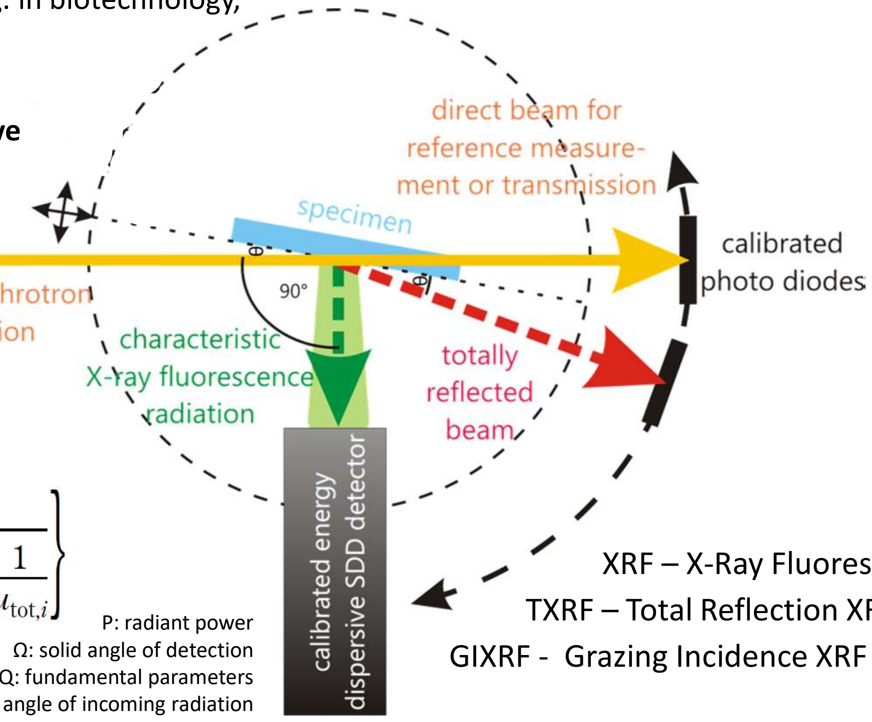
- a **growing demand on well-characterized samples** in the production and analytical processes [1]
- **increasing field of application of thin film layers**, e.g. in biotechnology, semi-conductor industry, or in the field of energy conversion and storage
- physically traceable method enabling **the quantitative analysis of the mass deposition or mole fraction** of the elements in a sample

Reference-free X-ray Spectrometry

- based on **well-known synchrotron radiation** and **radiometrically calibrated instrumentation** as well as on the **knowledge of the atomic fundamental parameters [2]**

PTB capabilities:

- characterized synchrotron radiation beamlines (well-known spectral distribution, radiant power)
- calibrated photodiodes and calibrated diaphragms
- calibrated detectors with known absolute detection efficiency and response functions
- fundamental atomic parameters determination and databases



Mass deposition of an element determined by the radiant power of characteristic fluorescence line:

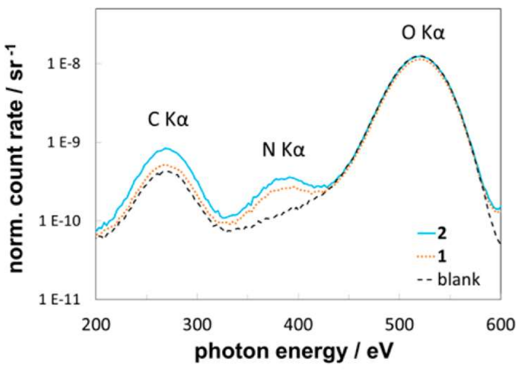
$$\frac{m_i}{F_I} = \frac{-1}{\mu_{tot,i}} \ln\left\{1 - \frac{P_i}{P_{0,Wsurf}\,\tau_{i,E_0}\, Q\, \frac{\Omega_{det}}{4\pi}\, \frac{1}{\sin\psi_{in}}\, \frac{1}{\mu_{tot,i}}}\right\}$$

P: radiant power
Ω: solid angle of detection
μ, τ, Q: fundamental parameters
ψ: Incident angle of incoming radiation

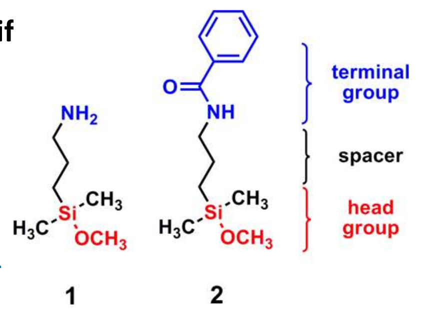
XRF – X-Ray Fluorescence Analysis
TXRF – Total Reflection XRF
GIXRF - Grazing Incidence XRF

Traceable Quantification of Silane Molecules [5]

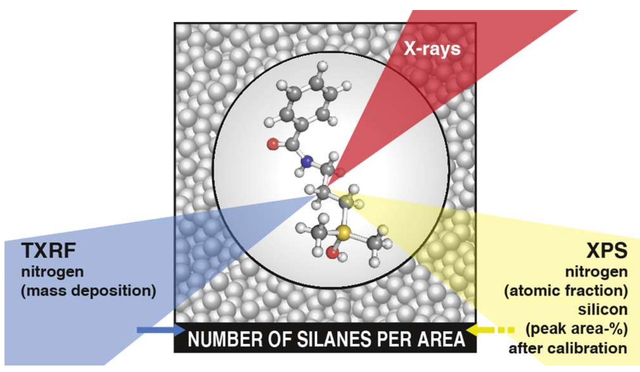
- traceable and absolute determination of the **molecular area density of organic mono-layer of silane molecules** by reference-free TXRF
- silanes routinely used **to functionalize** various support materials to **modif surface properties**
- hardly reliable **quantitative information about surface functional group densities** after layer formation available



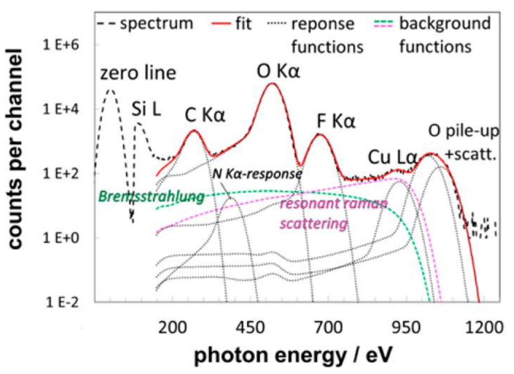
TXRF spectra of silane layers 1, 2 and the SiO2/Si wafer (blank)



Amino- (1) and Benzamidosilane (2) used for monolayer formation on silicon wafers



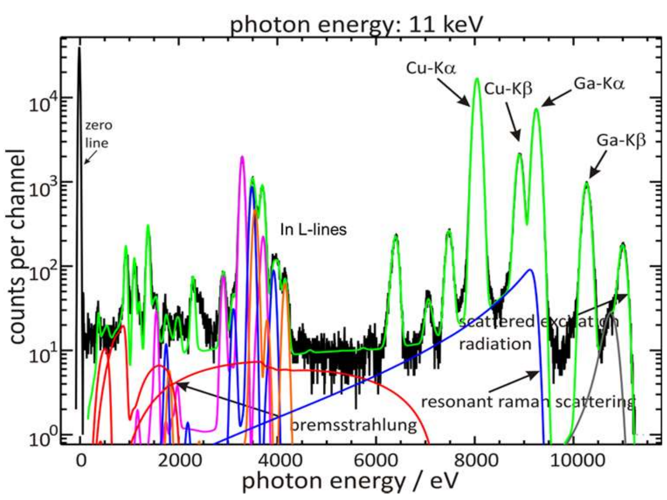
- **areic density** of 2–4 silane molecules per nm^2
- **determined from the nitrogen mass deposition obtained by reference-free TXRF**
- **traceable calibration of X-Ray Photoelectron Spectroscopy**: same result by using component intensity of the silane's silicon atom



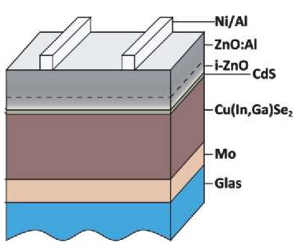
spectral deconvolution based on detector response functions and physical background modeling.

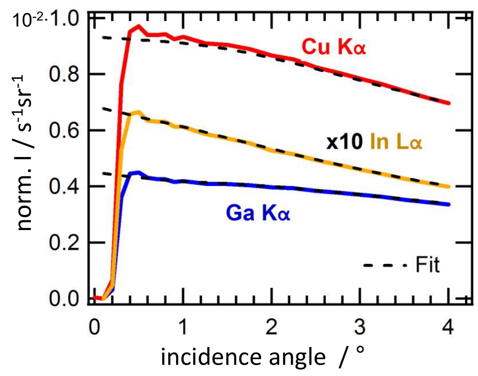
Reference-free quantification of in-depth matrix gradients in CIGS solar cell absorbers [3]

- development of **highly efficient thin film solar cells** of $Cu(In,Ga)Se_2$ (**CIGS**) involves band gap engineering by tuning the elemental in-depth composition
- reference-free GIXRF analysis for a non-destructive analysis of compositional depth profiles in the thin films

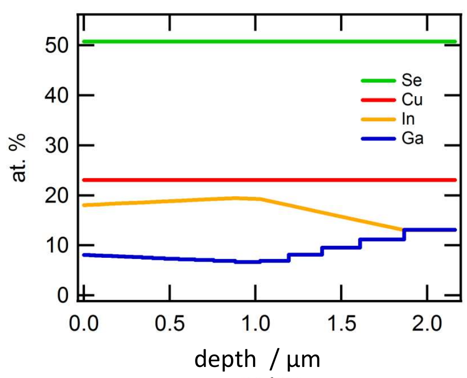


De-convolution with detector response functions, partially in multiplets ,and with modeled background contributions





Measured and fitted intensities.



Elemental depth gradient.

- the **variation of the incident angle** provides quantitative access to the in-depth distribution
- double Ga gradients can be revealed
- reference-free XRF under conventional 45° conditions had been used for the **CCQM-SAWG key comparison K-129** on the measurement of mole fractions of Cu, In, Ga and Se in CIGS [4]

	Cu / at.%	In / at.%	Ga / at.%	Se / at.%	d, x_M / µm
Average	23.1 ± 1.4	17.9 ± 1.9	8.3 ± 0.4	50.7 ± 2.8	2.16 ± 0.08
Gradient		18; 19.3; 13 ± 2.0;2.1;2.3	8.2; 6.9; 13.2 ± 0.9;1.0;1.3		1.0 ± 0.2

References

[1] Streeck, et al. Spectroscopy Europe, Vol. 30 No. 1, (2018).
[2] Beckhoff, JAAS **23**, 845 (2008)
[3] Streeck et al., Appl. Phys. Lett. **103**, 113904 (2013)
[4] Kim, et al. Metrologia, Vol. 53(1A), 08011 (2016).
[5] Dietrich et al., Anal. Chem. **87**, 10117 (2015)

Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin

Dr. Cornelia Streeck
Dr. Burkhard Beckhoff
X-ray Spectrometry

Abbestr. 2-12
10587 Berlin, Germany
Telefon: +49 (0)30 3481 7157
Fax: +49 (0)30 3481 7102
Email: cornelia.streeck@ptb.de
www.ptb.de