Layer Thickness Analysis of Thin Metal Coatings with
micro-XRF on SEM

Bruker Nano Analytics, Berlin, Germany
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Presenters

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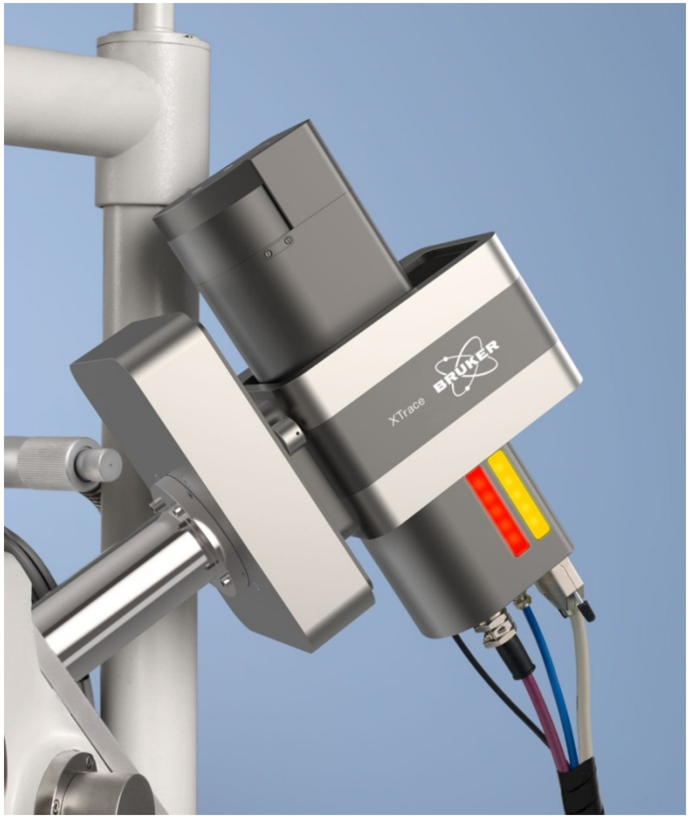
Overview

- XTrace setup and key features
- Basics: Layer thickness measurements with XRF
- Method editor
- Application examples + Live measurements
- Summary

Layer Thickness Analysis with micro-XRF/SEM

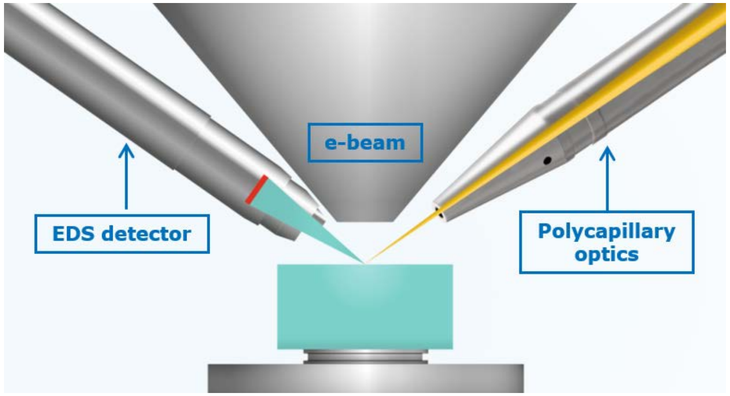
Key Features

- Micro-XRF source attachment to an SEM works in conjunction with the (existing) Bruker EDS detector
- Element range from **Na** to **U**
- Focussing polycapillary X-ray optics enables a spot size of (standard) **35 µm** (smaller optics with a spot size of 15 µm available as well)
- Integrated user interface ESPRIT 2.x for Quantax EDS/micro-XRF ...
- **Method editor** for fast layer method setup is linked to ESPRIT
- Allows the quantification of layer systems measured either in point mode or extracted from line scans or X-ray maps



Layer Thickness Analysis with micro-XRF/SEM

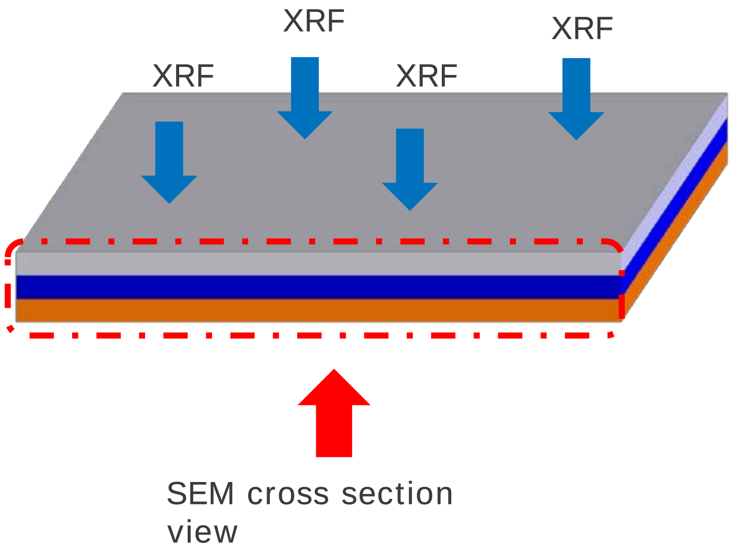
Example for instrument setup



Schematic of setup in a SEM for XRF with EDS detector

Layer Thickness Analysis

Differences in layer thickness analysis between SEM - XRF



SEM:

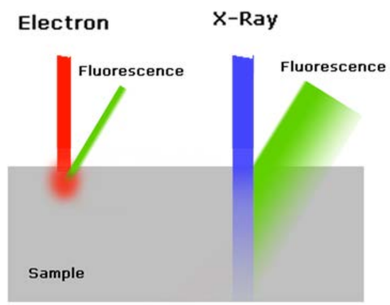
1. Sample require cross sectioned and sample preparation can be time consuming
2. Sample must be cut for cross sectioned observation and hence, it will be destroyed
3. Sufficient SEM resolution required to makes thin layer visible

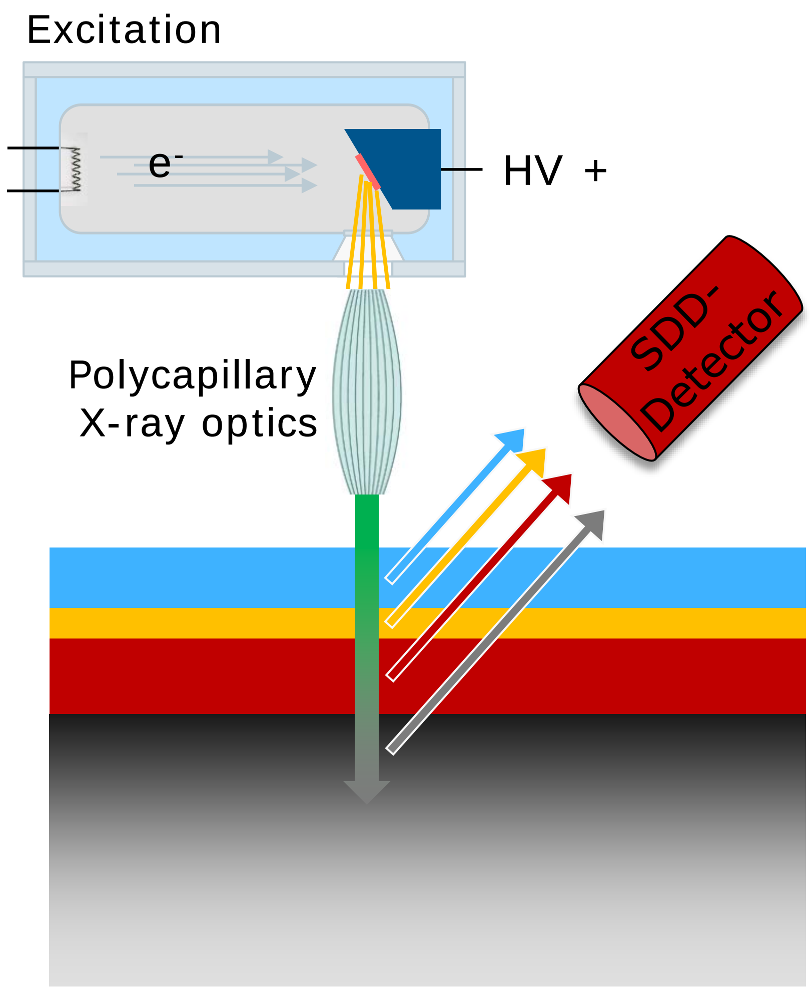
XRF:

1. Fast and non- destructive method for measuring film thickness without any sample preparation
2. Additionally, the composition of the layer can be determined at the same time
3. Large numbers of samples or areas can be measured quickly

Layer Thickness Analysis with micro-XRF/SEM

Introduction





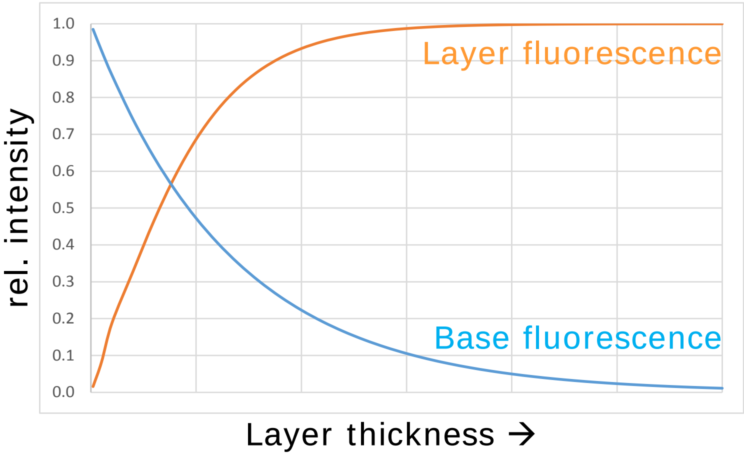
- Large information depth of X-ray excitation allows coating analysis
- Signal from base material and covered layers can be detected
- X-rays are attenuated in characteristic ways on their path through matter
- Intensity ratios of observed elemental lines were used for calculation of the respective layer thicknesses
- Generally, layers up to thickness of 40 µm can be analyzed (3- 4 layers)
- Several quantification models for layer systems available which works easily even standard-less

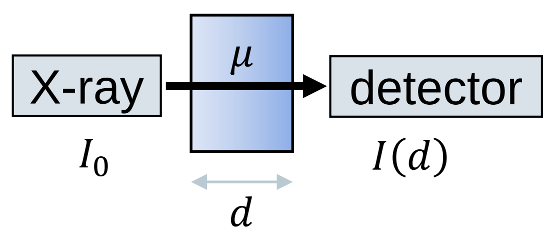
Physical Principles of Layer thickness analysis

Generation / Attenuation of XRF

For a single layer on top of a base material:

- Emission signal originating from coating increases with coating thickness up to the respective bulk intensity
- Emission from base material is attenuated stronger for thicker coatings, until it fades into the background
- Coating thickness can be calculated from absorption of base material, emission from coating, or a combination of both





Lambert-Beer-Law (absorption):

$$I(d) = I_0 \cdot e^{-\mu \cdot d}$$

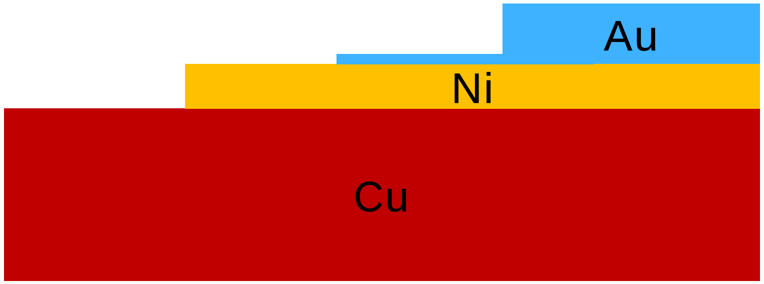
X-ray transmission image of the hand of W.C. Roentgen's wife. 22nd December 1895

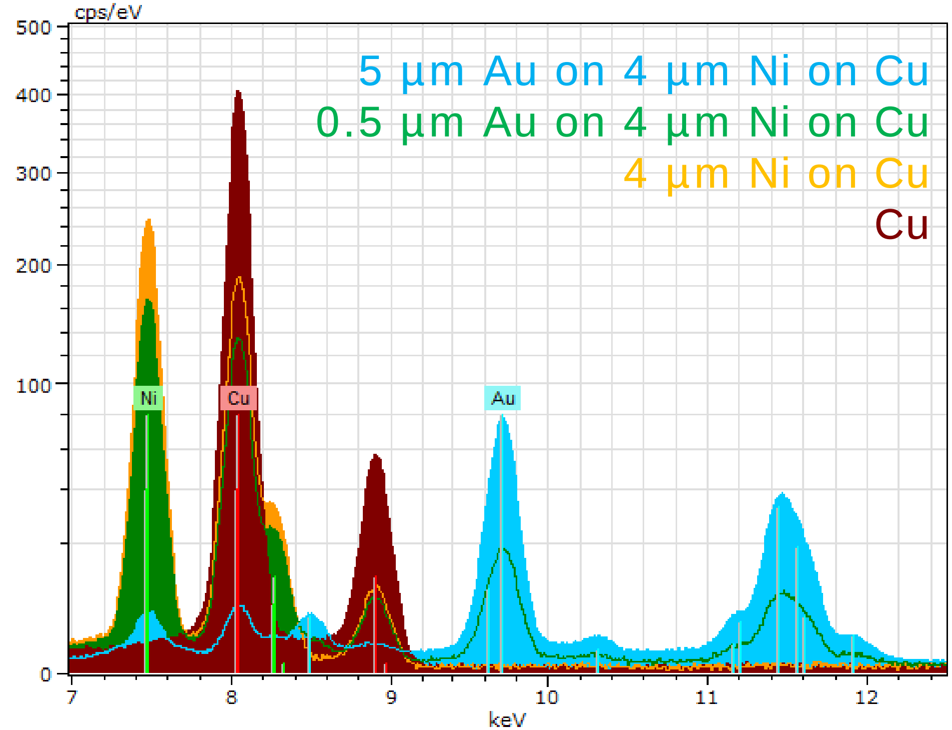
Physical Principles of Layer thickness analysis

Comparison of Layer Stacks

Comparison of stacks shows:

- Attenuation of signal from buried elements
- Increased signal strength from top layers for thicker layers
- Even though Ni reaches saturation thickness at about 25 µm, underneath 5 µm of gold the Ni intensity is reduced to about 2 %
- The overall thickness of stacked layers is limited to about 40 µm, depending on elements and matrix density

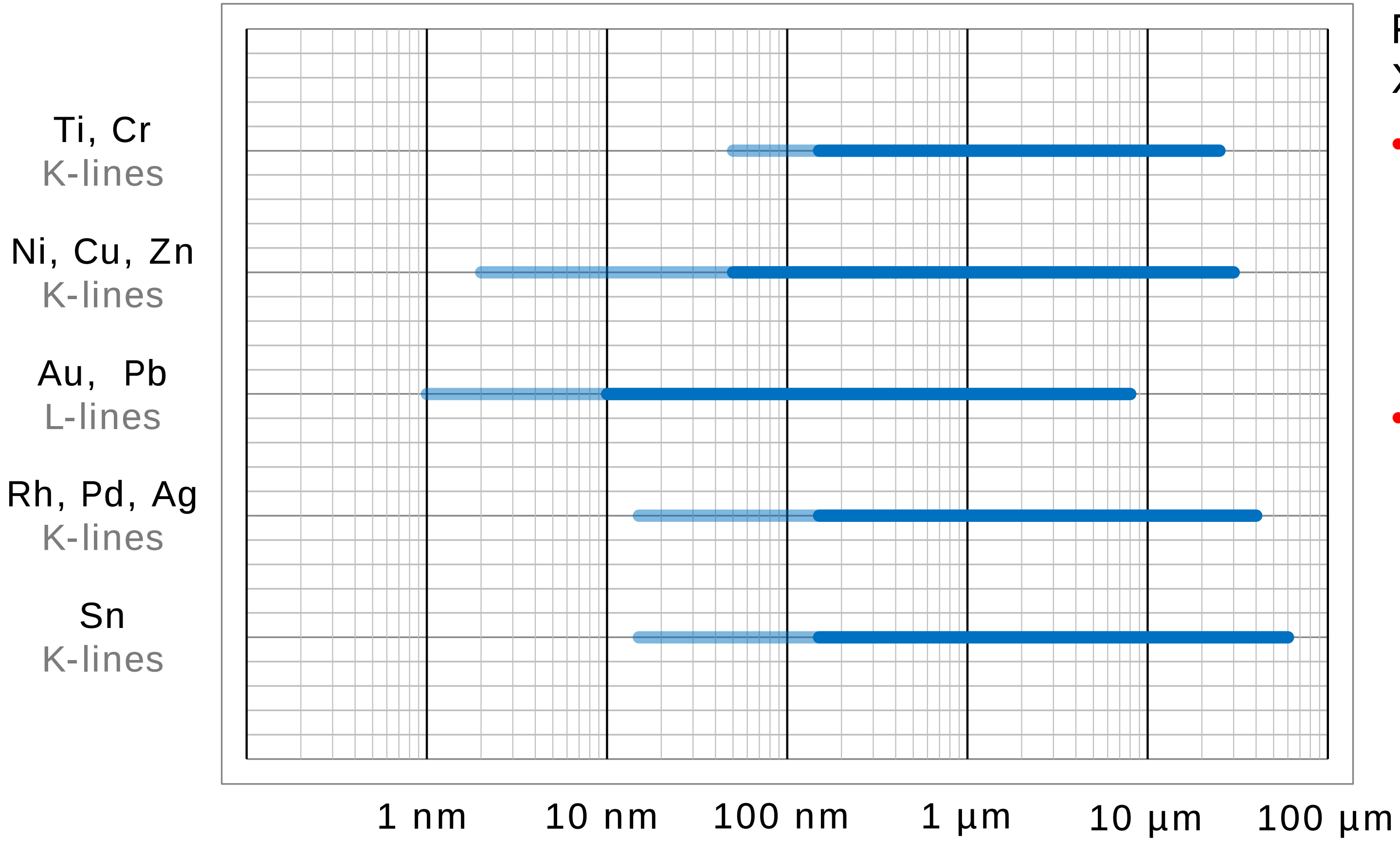




Layer Thickness Analysis with micro-XRF/SEM

Thickness Range for Element Emission

Approximate accessible thickness range for individual layers of one element



For analysis by XRF emission:

- The higher the photon energy the thicker the films that can be analyzed
- The lower the photon energy the more sensitive the method is for thinner layers

Layer Thickness Analysis with micro-XRF/SEM
Requirements

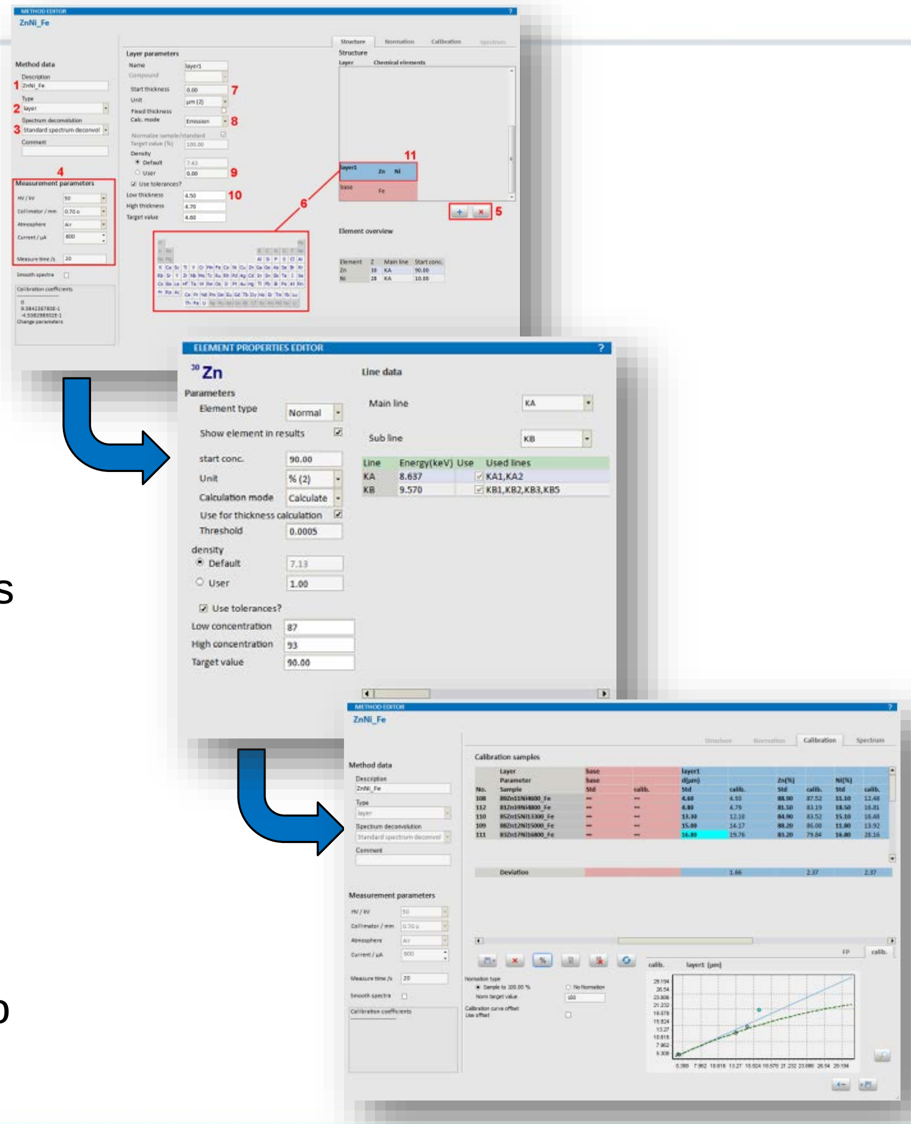
Requirements for layer analysis on the SEM:

1. Knowledge about the layer system is necessary (layer sequence)
2. Layer calculation is based on pure element spectra intensity → stable EDS + XRF conditions
3. For every layer a separate signal is required → the same element shouldn´t be in different layers (or at least different X-ray series of this element should be available for analysis
4. Tilt = 0, changing the Tilt angle will influence the TOA which isn´t considered in XMethod

Coating Thickness Analysis on SEM with X-ray fluorescence

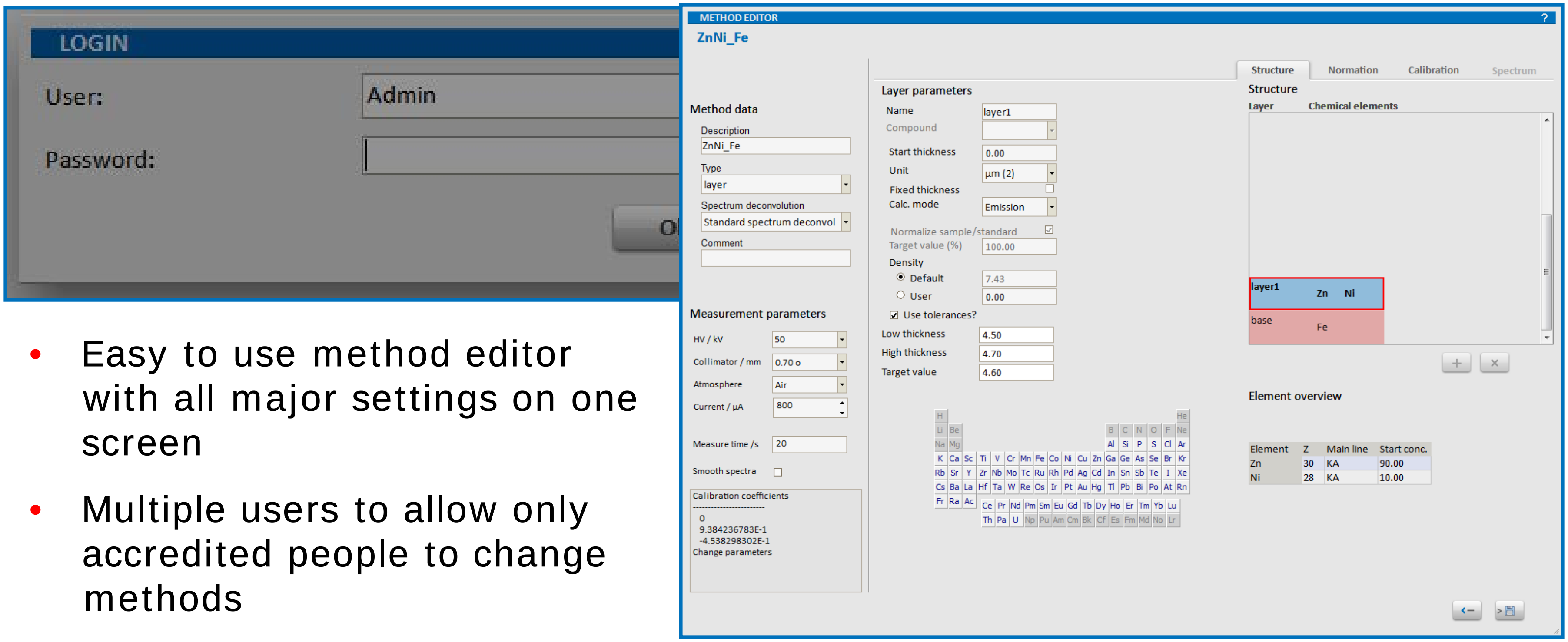
XMethod

- **Method creation**
  - For many physical different structured samples such as bulks, coatings, light matrices
- **Method optimization**
  - By editing several details on the lines to investigate or the structure of the sample in the methods
  - For bulk methods calibration ranges can be set
- **Method calibration**
  - Methods can applied based on fundamental parameter approach without any standard
  - Standards can be utilized to enhance the precision or in order to build fully empirical calibrations



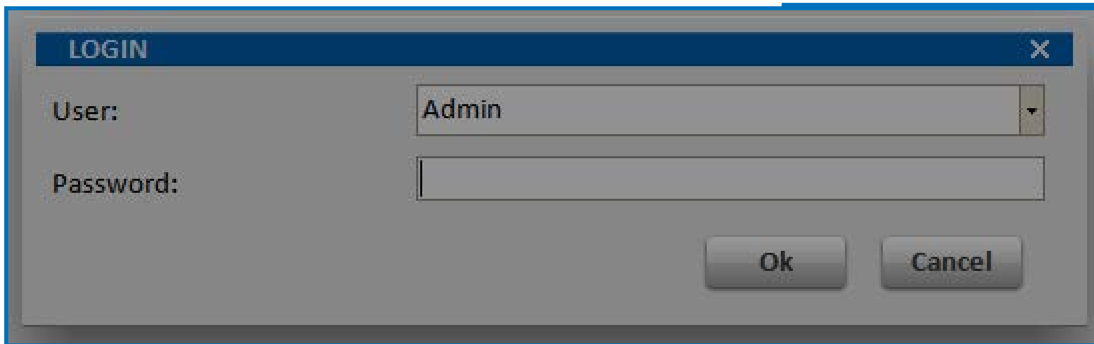
XMethod

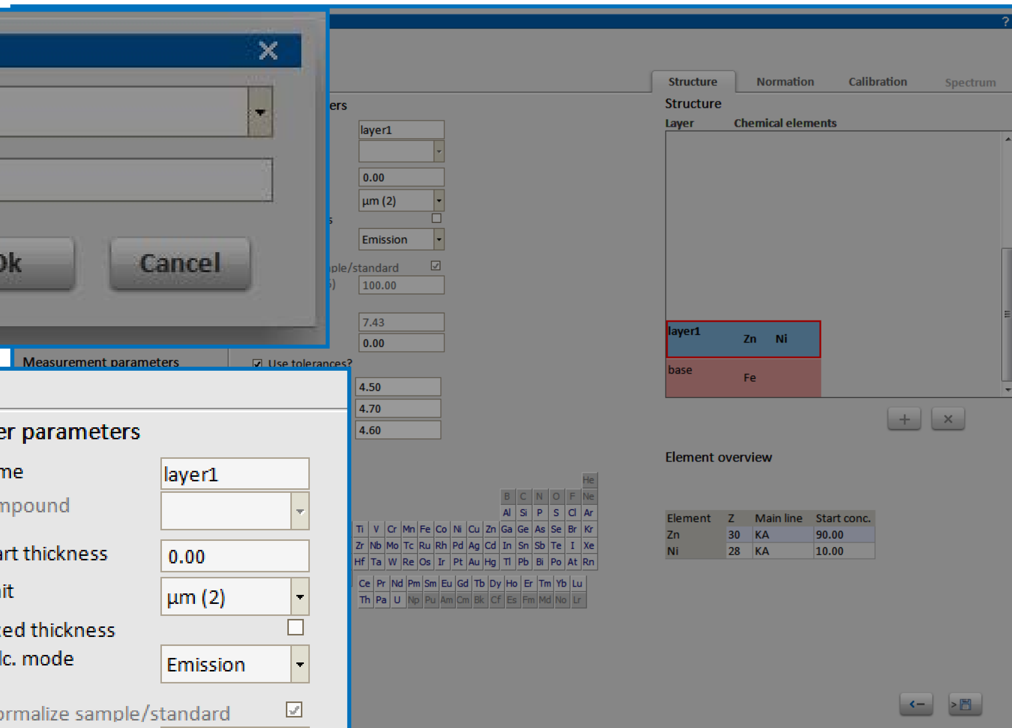
Method Setup

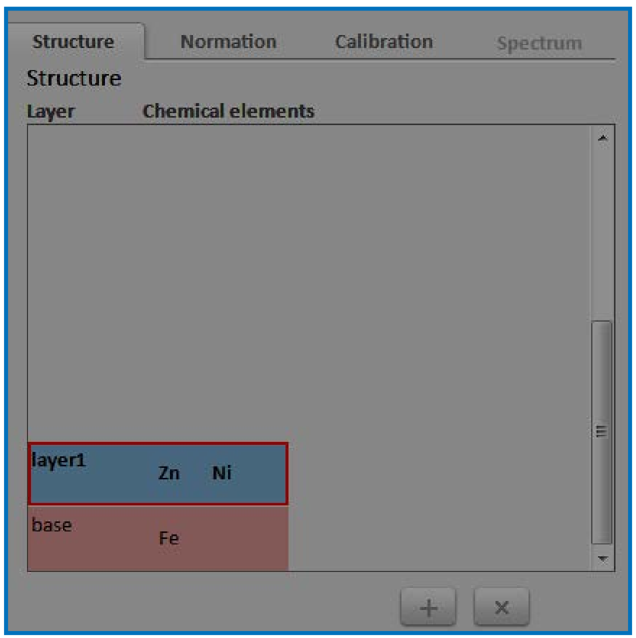


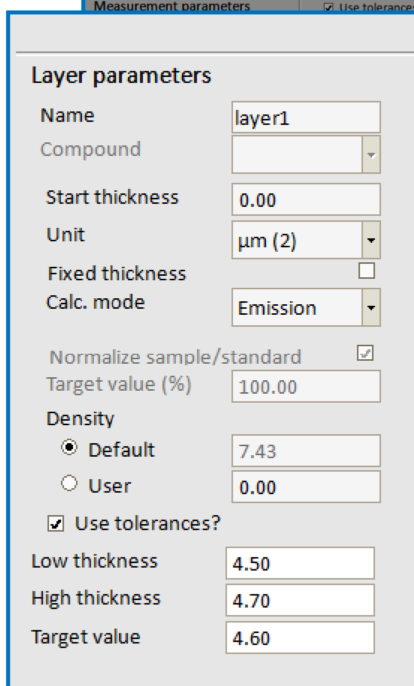
- Easy to use method editor with all major settings on one screen
- Multiple users to allow only accredited people to change methods

XMethod
Method Setup





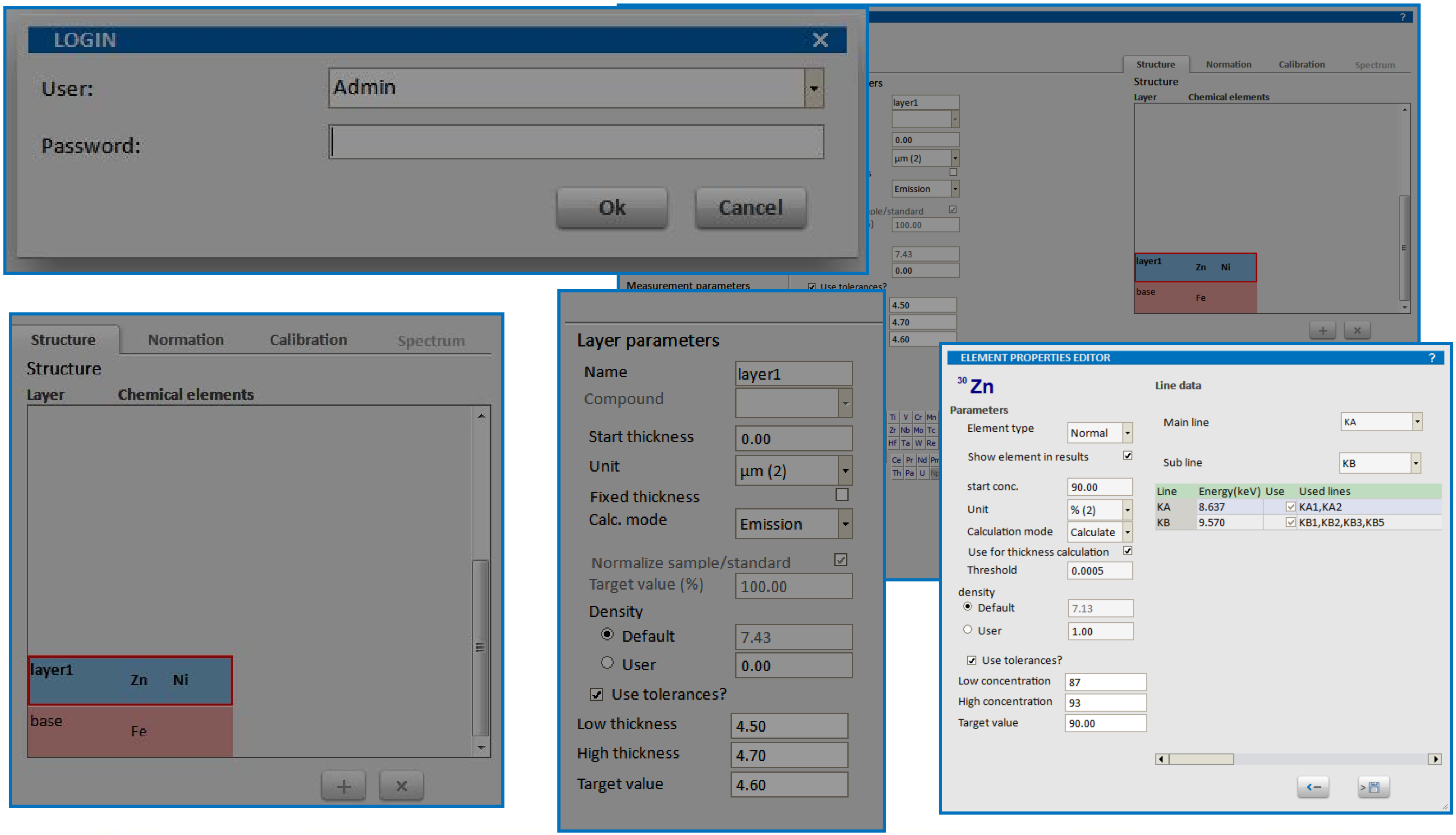




- Starting values (to accelerate computation) as well as tolerances for results can be entered

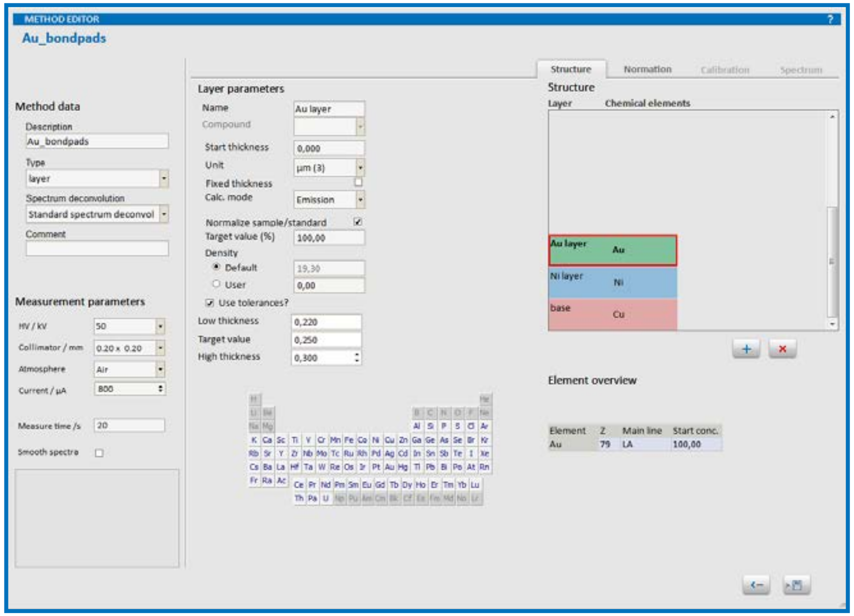
XMethod

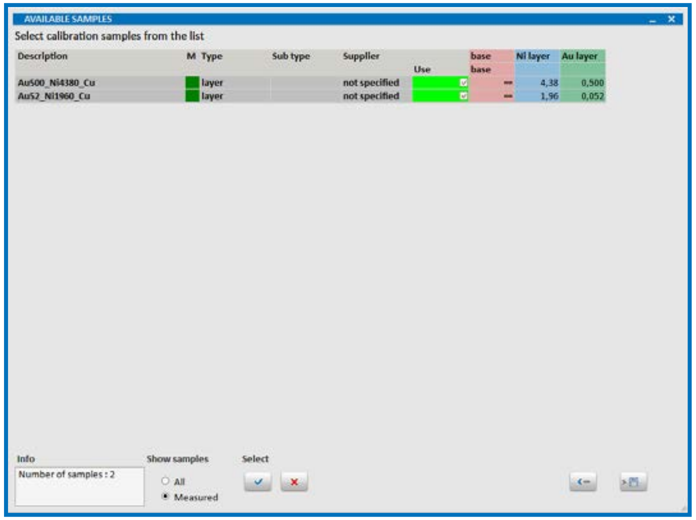
Method Setup

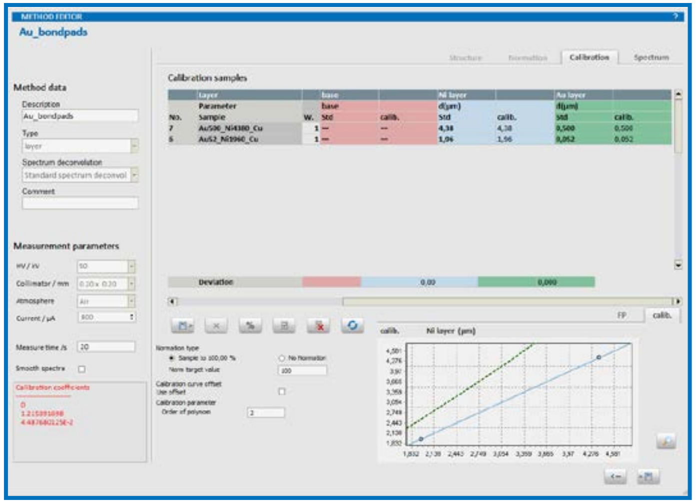


XMethod

Method Setup







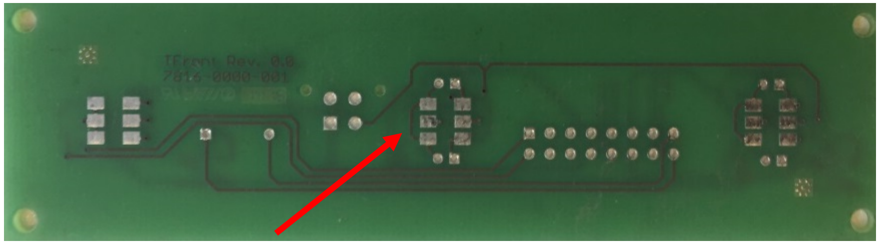
- Calibration is automated to a great extent
- Optional choice of polynomial degrees, calibration ranges, or individual parameters to be added, weighted, or excluded
- Methods available via hot keys

Application examples

Layer Thickness Analysis with micro-XRF/SEM

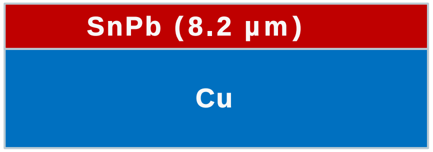
Example I: SnPb/Cu Solder bump

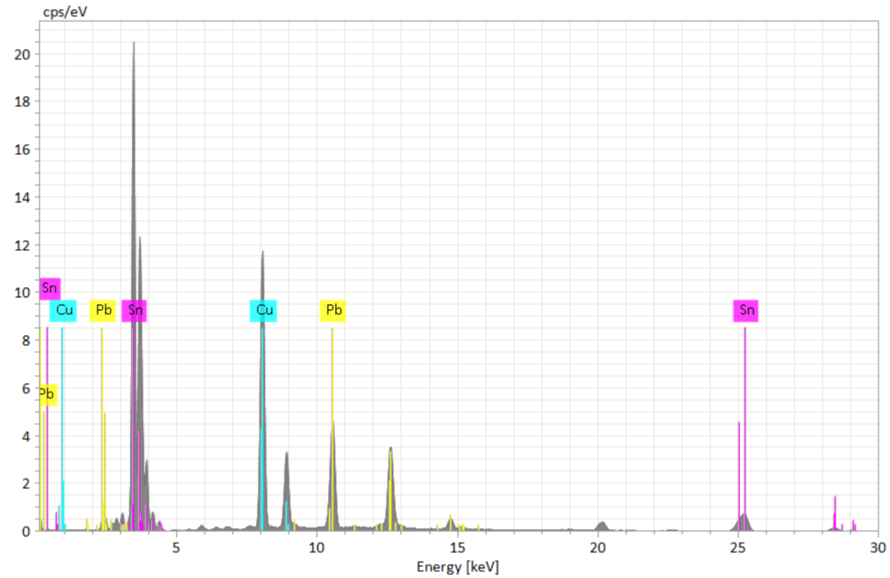
- Pb is a restricted material in consumer electronic devices
- But still used in some areas of medical (implants) or defense sector when reliability and durability are absolutely essential.



Example for solder bumps

Certified SnPb standard

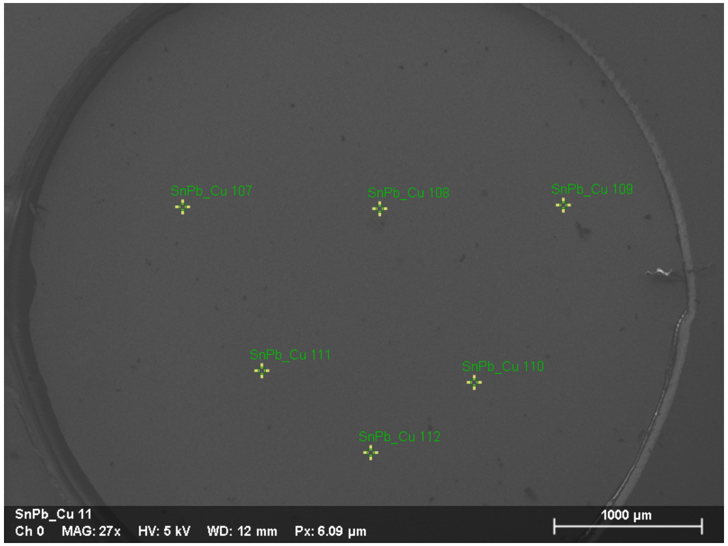




XRF spectra of the certified standard, 60 sec measurement time

Layer Thickness Analysis with micro-XRF/SEM

Example I: SnPb/Cu Solder bump



Measurement points on SnPb standard , 60 sec acquisition time (real time)

Normalized mass concentration [%]

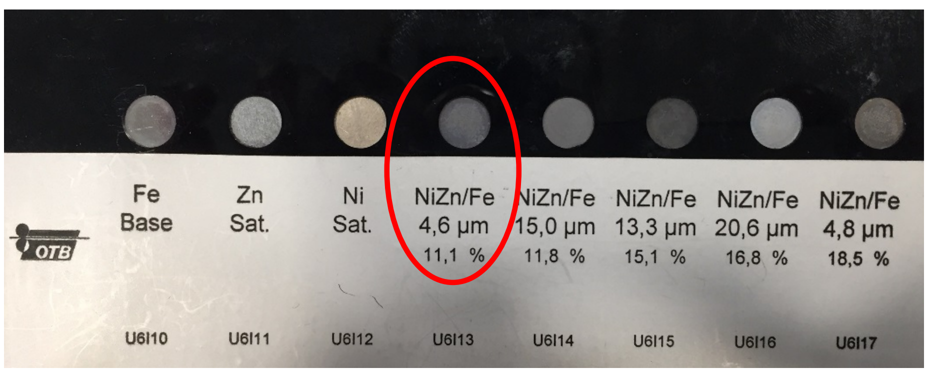
	Substrate	Layer 1		
Spectrum	Cu [%]	Thickn. [µm]	Sn [%]	Pb [%]
SnPb_Cu 107	100.00	8.78	91.48	8.52
SnPb_Cu 108	100.00	8.88	91.83	8.17
SnPb_Cu 109	100.00	8.91	91.38	8.62
SnPb_Cu 110	100.00	8.82	91.98	8.02
SnPb_Cu 111	100.00	8.71	91.88	8.12
SnPb_Cu 112	100.00	8.75	91.87	8.13
Mean value	**100.00**	**8.81**	**91.74**	**8.26**
Std dev.	**0.00**	**0.07**	**0.24**	**0.24**
Std dev. rel. [%]	**0.00**	**0.85**	**0.26**	**2.94**
Conf. interval	**0.00**	**0.03**	**0.10**	**0.10**

- Standardless quantification for the SnPb coating gives sufficient results but can be improved by using standards!

Layer Thickness Analysis with micro-XRF/SEM

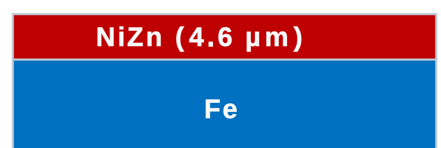
Example II: Galvanized Metal Sheet

- Consists of a layer structure of NiZn/Fe (Fe = substrate)
- Zn is used for corrosion and fire protection
- Ni protects the material against mechanical wear
- Our (unknown) sample:



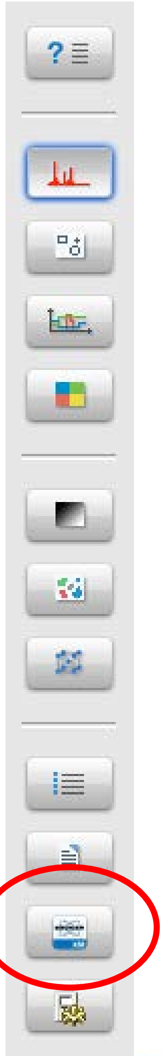
Certified NiZn/Fe standard

Examples for NiZn alloys

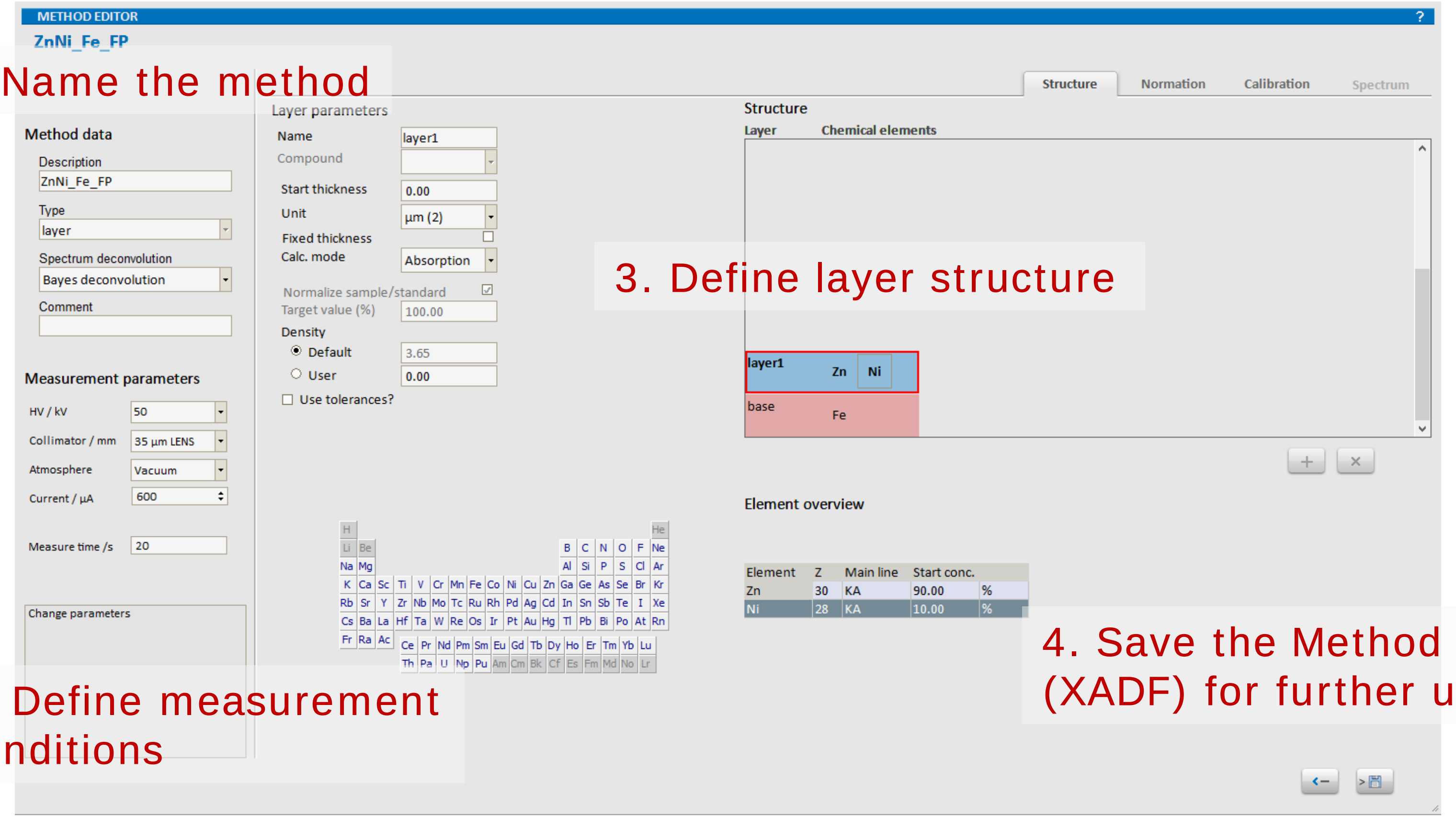


Layer Thickness Analysis with micro-XRF/SEM

Example II: Galvanized Metal Sheet



Step 1: Build a layer method in XMethod



1. Name the method

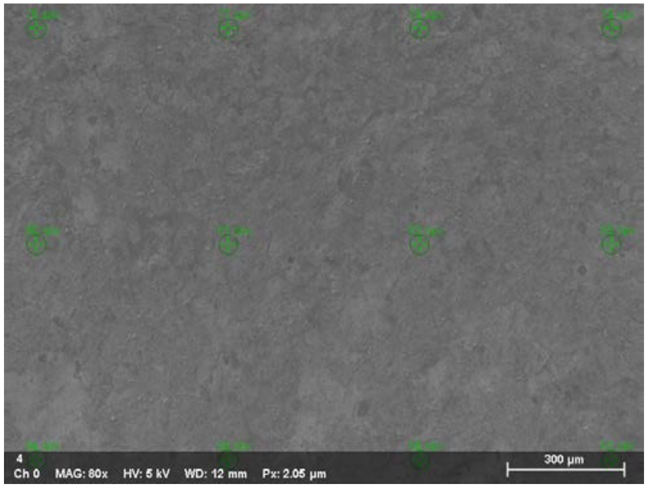
2. Define measurement conditions

3. Define layer structure

4. Save the Method (XADF) for further use

Coating Thickness Analysis
Example II: Galvanized Metal Sheet

Step 2: Acquire spectra in ESPRIT (Object mode)



Normalized mass concentration [%]

	Substrate	Layer 1		
Spectrum	Fe [%]	Thickn. [µm]	Zn [%]	Ni [%]
76.spx	100.00	3.37	85.91	14.09
77.spx	100.00	3.34	85.83	14.17
78.spx	100.00	3.23	85.79	14.21
79.spx	100.00	3.29	85.83	14.17
80.spx	100.00	3.20	85.60	14.40
81.spx	100.00	3.34	85.81	14.19
82.spx	100.00	3.36	85.92	14.08
83.spx	100.00	3.36	85.82	14.18
84.spx	100.00	3.50	85.99	14.01
85.spx	100.00	3.35	85.97	14.03
86.spx	100.00	3.31	85.88	14.12
87.spx	100.00	3.24	85.74	14.26
Mean value	**100.00**	**3.32**	**85.84**	**14.16**
Std dev.	**0.00**	**0.08**	**0.11**	**0.11**
Std dev. rel. [%]	**0.00**	**2.37**	**0.12**	**0.76**
Conf. interval	**0.00**	**0.02**	**0.03**	**0.03**

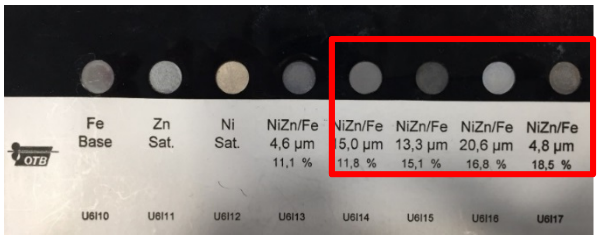
	Layer thickness	Ni %	Zn %
given	4.6 µm	11,10%	88,90%
Layer FP standard-free	3.32 µm	14,16%	85,84%

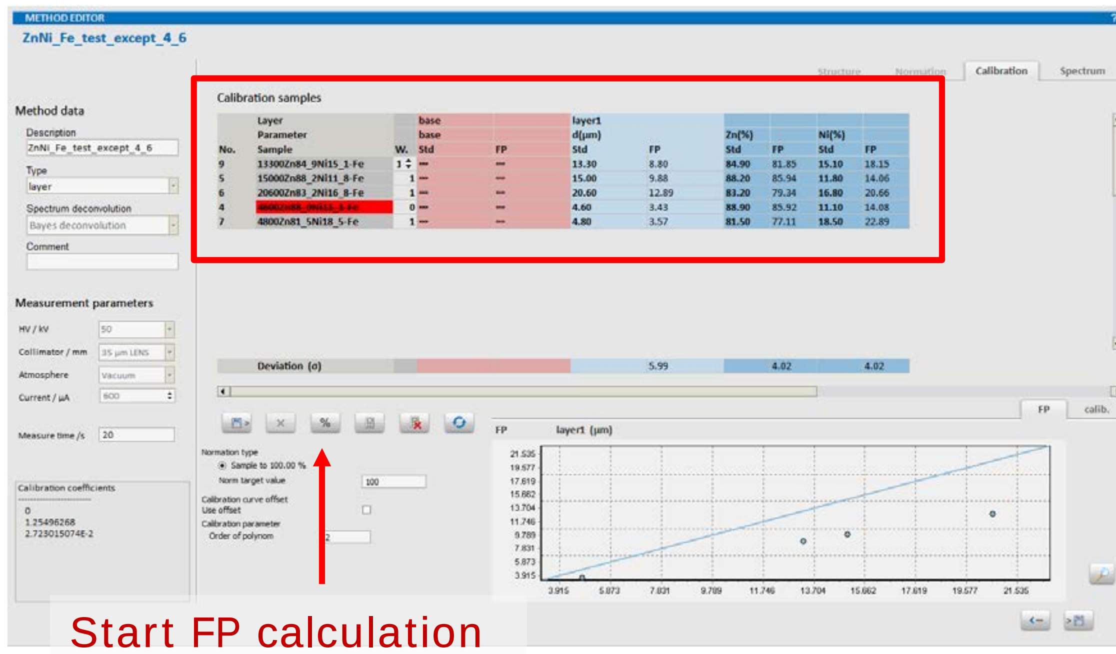
For this sample the standard- free FP is not accurate enough due to the secondary fluorescence effect (Zn excites Ni which overweight's the Ni concentration) → thickness calculation is based on the Zn intensity since Zn is the main element → **Method must be calibrated with standards!!**

Layer Thickness Analysis with micro-XRF/SEM

Example II: Galvanized Metal Sheet

Step 4: Measuring appropriated standards (with same layer structure)





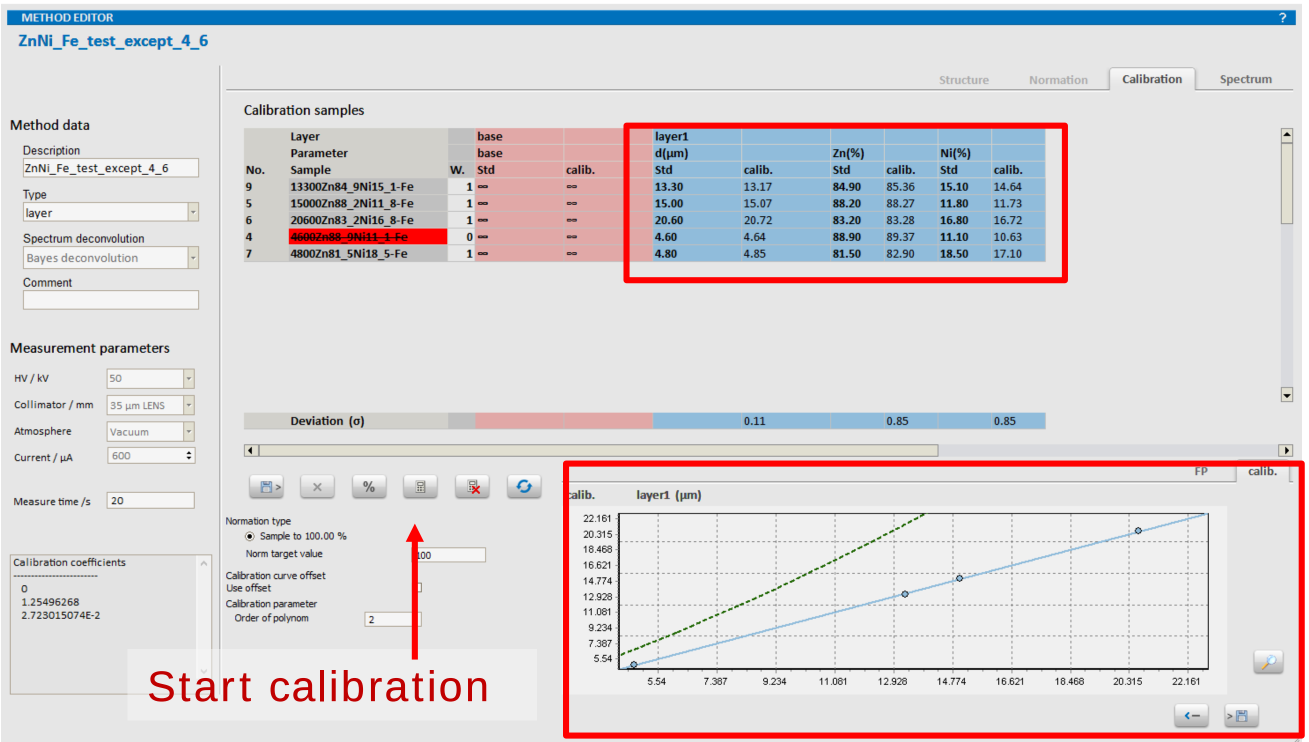
After clicking “start FP calculation” button, the chart will be updated with the FP results. The calculated FP values will be plotted against the given values of the selected standards (thickness or concentration).

Given values differs to the measured values → Calibration required!

Layer Thickness Analysis with micro-XRF/SEM

Example II: Galvanized Metal Sheet

Step 4: Calibrate the method



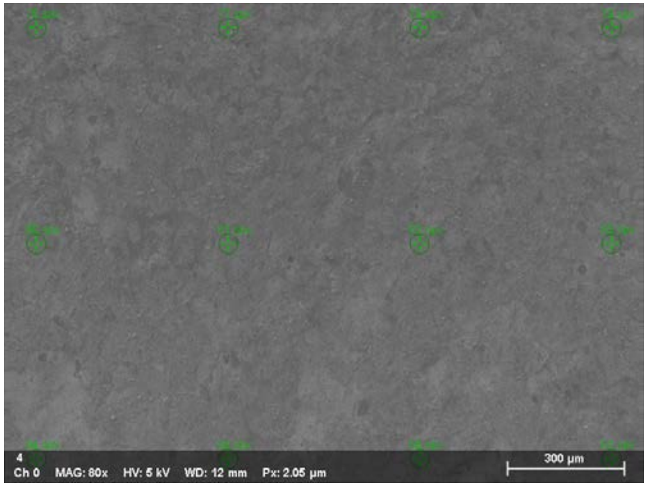
After clicking the Calibration button, the chart will be updated with the calibrated results. The results should be much closer to the blue line now. Method can be saved afterwards as standard based XADF method.

Layer Thickness Analysis with micro-XRF/SEM
Example II: Galvanized Metal Sheet

Step 5: Quantify standard-based method

Normalized mass concentration [%]

	Substrate	Layer 1		
Spectrum	Fe [%]	Thickn. [µm]	Zn [%]	Ni [%]
76.spx	100.00	4.56	89.37	10.63
77.spx	100.00	4.51	89.27	10.73
78.spx	100.00	4.36	89.22	10.78
79.spx	100.00	4.44	89.28	10.72
80.spx	100.00	4.31	89.05	10.95
81.spx	100.00	4.52	89.26	10.74
82.spx	100.00	4.54	89.36	10.64
83.spx	100.00	4.54	89.27	10.73
84.spx	100.00	4.74	89.45	10.55
85.spx	100.00	4.53	89.41	10.59
86.spx	100.00	4.47	89.32	10.68
87.spx	100.00	4.36	89.16	10.84
Mean value	**100.00**	**4.49**	**89.28**	**10.72**
Std dev.	**0.00**	**0.11**	**0.11**	**0.11**
Std dev. rel. [%]	**0.00**	**2.54**	**0.12**	**1.03**
Conf. interval	**0.00**	**0.03**	**0.03**	**0.03**

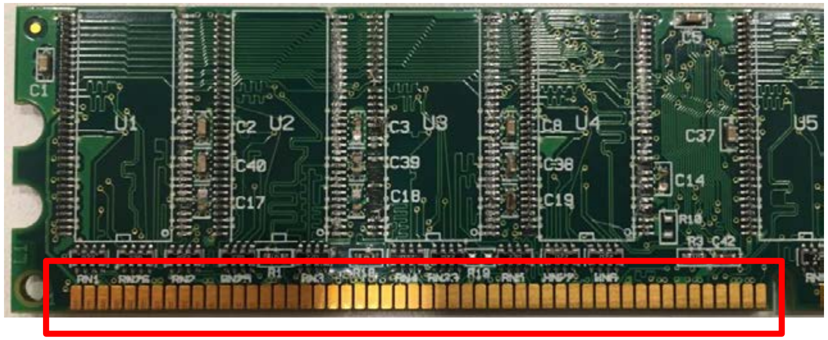


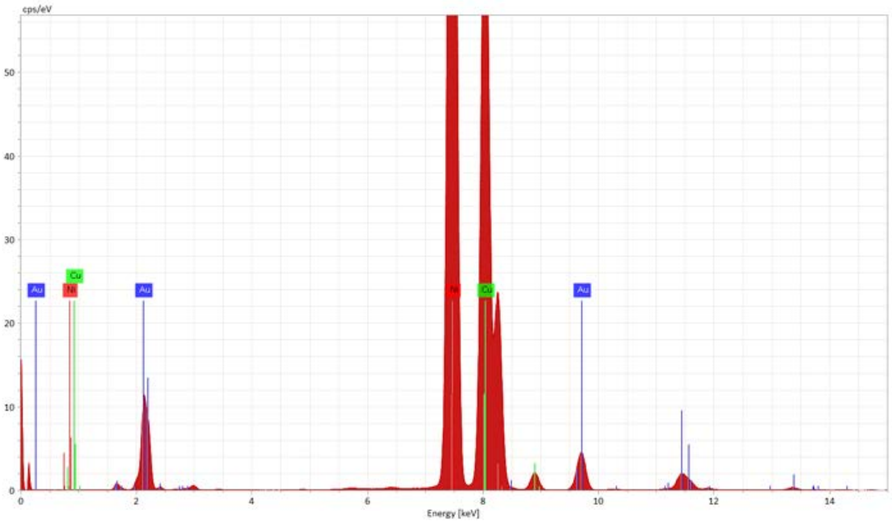
	Layer thickness	Ni %	Zn %
given	4.6 µm	11,10%	88,90%
Layer FP standard-free	3.32 µm	14,16%	85,84%
calibrated with standards	4.49 µm	10,72%	89,28%

Layer Thickness Analysis with micro-XRF/SEM

Example III: Au/Ni/Cu contact

- Popular layer system which is used for contacts in micro-electronics
- For Higher- quality contacts also Pd is embedded as separate layer
- For cost reasons the precious metal coating are very thin and Ni is used as a diffusion barrier

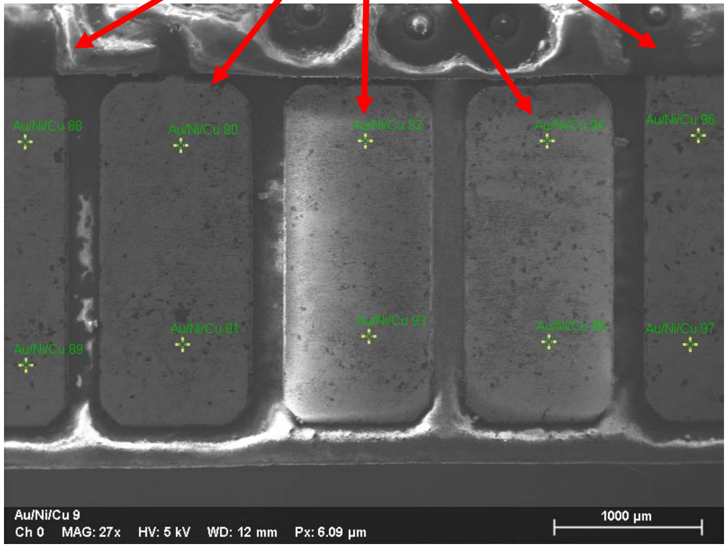




Spectra of an Au-Ni/Cu layer system, acquisition time: 60 s

Coating Thickness Analysis

Example III: Au/Ni/Cu contact



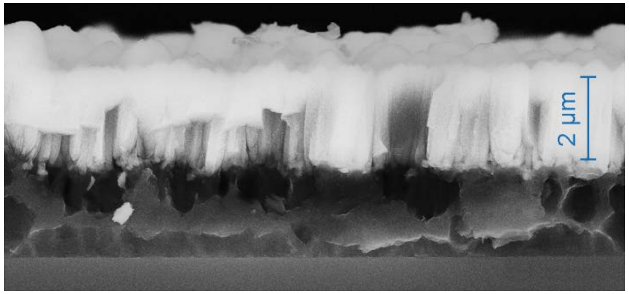
Normalized mass concentration [%]

	Substrate	Layer 1		Layer 2	
Spectrum	Cu [%]	Thickn. [µm]	Ni [%]	Thickn. [nm]	Au [%]
Au/Ni/Cu 88	100.00	3.66	100.00	112.14	100.00
Au/Ni/Cu 89	100.00	3.71	100.00	111.43	100.00
Au/Ni/Cu 90	100.00	3.66	100.00	114.56	100.00
Au/Ni/Cu 91	100.00	3.78	100.00	112.43	100.00
Au/Ni/Cu 92	100.00	3.81	100.00	110.46	100.00
Au/Ni/Cu 93	100.00	3.69	100.00	104.50	100.00
Au/Ni/Cu 94	100.00	3.80	100.00	109.37	100.00
Au/Ni/Cu 95	100.00	3.73	100.00	101.50	100.00
Au/Ni/Cu 96	100.00	3.72	100.00	113.71	100.00
Au/Ni/Cu 97	100.00	3.78	100.00	102.39	100.00
Mean value	**100.00**	**3.73**	**100.00**	**109.25**	**100.00**
Std dev.	**0.00**	**0.06**	**0.00**	**4.74**	**0.00**
Std dev. rel. [%]	**0.00**	**1.52**	**0.00**	**4.34**	**0.00**
Conf. interval	**0.00**	**0.02**	**0.00**	**1.50**	**0.00**

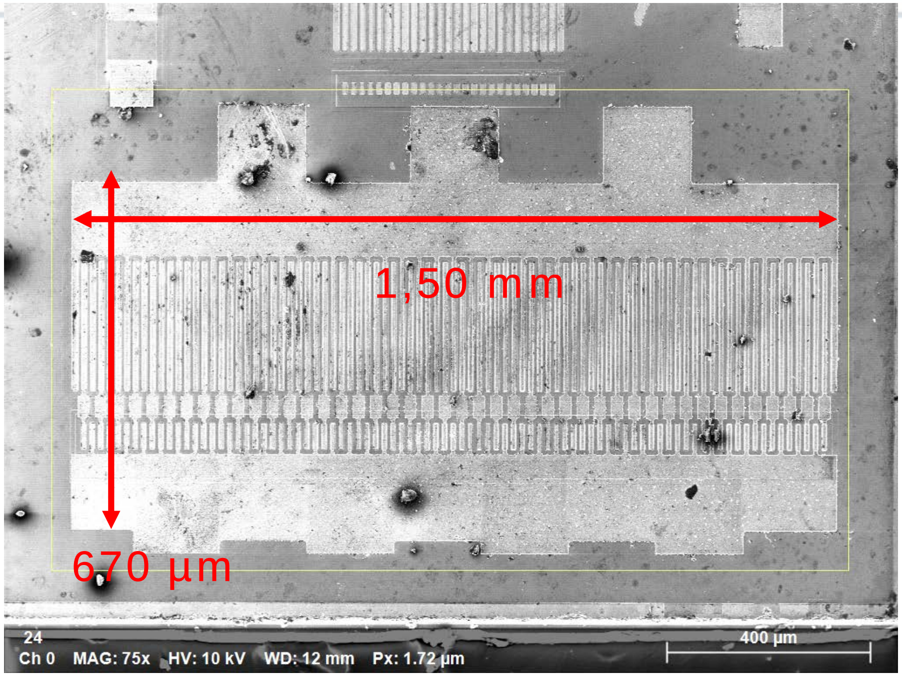
Layer Thickness Analysis with micro-XRF/SEM

Example IV: Al/Si layer

Both samples mounted on graphite sample holder



Original sample 1: SEM image of a fracture edge of layer Al (bright) and substrate Si

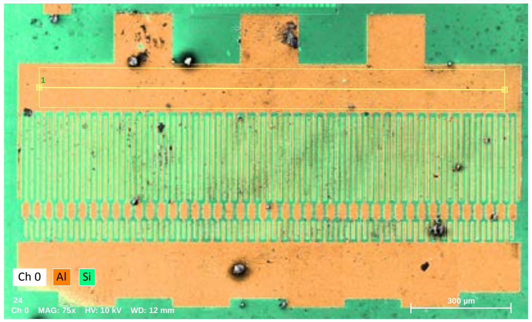


SE image of the sample 1

- Both samples were mounted on a graphite samples holder to avoid any influences coming from the sample holder due to the higher information depth of X-rays
- Both samples have the same dimensions 1.5 mm x 670 µm
- The thickness of the layer is ~ 2 µm for sample 1

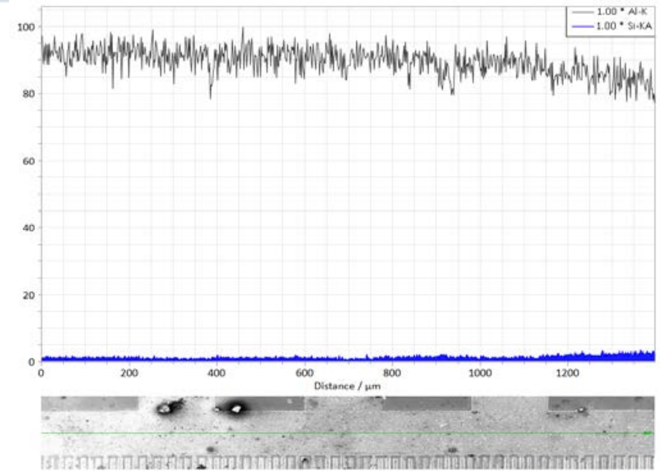
Layer Thickness Analysis with micro-XRF/SEM

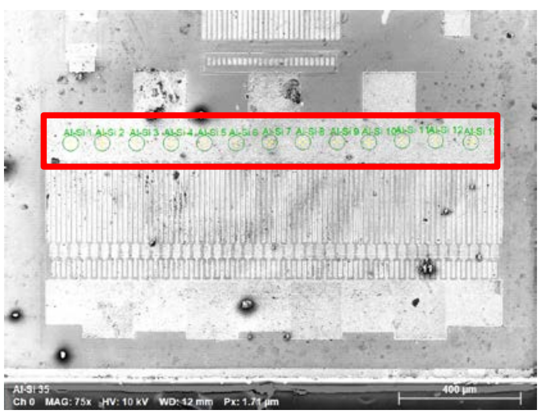
Example IV: Al/Si layer → Sample I



EDS Map of sample 1 with extracted line scan

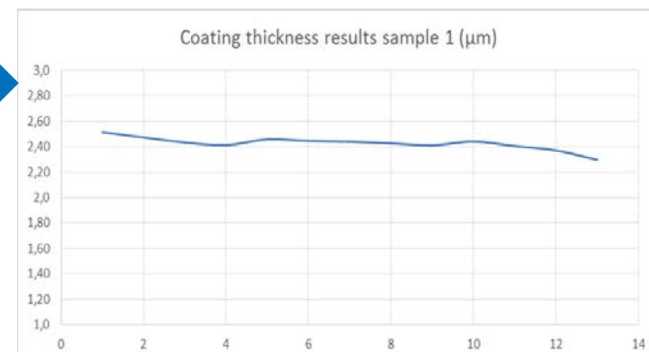
Intensity profile of the extracted EDS line scan





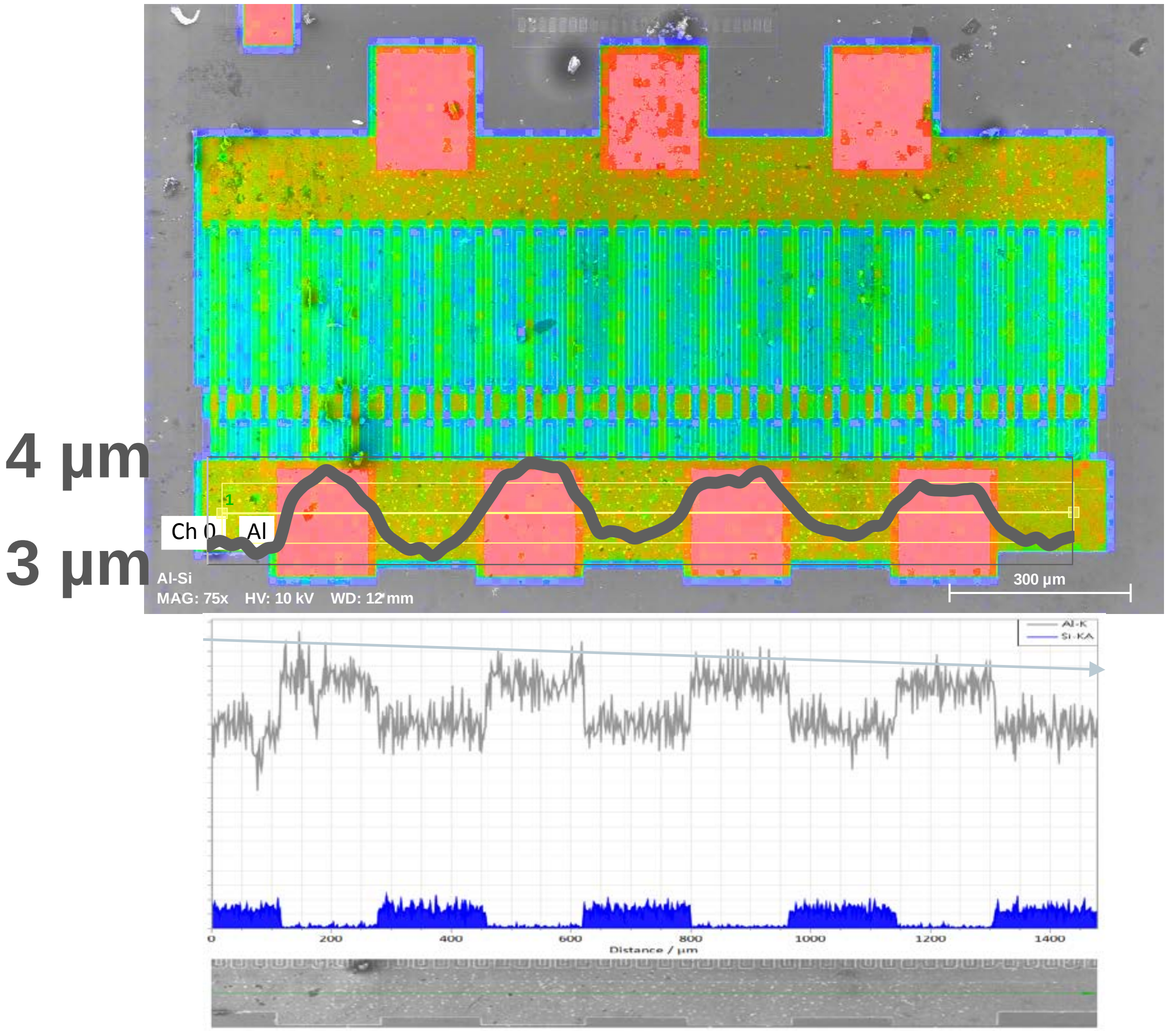
Normalized mass concentration [%]

	Substrate	Layer 1	
Spectrum	Si [%]	Thickn. [µm]	Al [%]
Al-Si 1	100.00	2.51	100.00
Al-Si 2	100.00	2.47	100.00
Al-Si 3	100.00	2.43	100.00
Al-Si 4	100.00	2.41	100.00
Al-Si 5	100.00	2.46	100.00
Al-Si 6	100.00	2.45	100.00
Al-Si 7	100.00	2.44	100.00
Al-Si 8	100.00	2.43	100.00
Al-Si 9	100.00	2.41	100.00
Al-Si 10	100.00	2.44	100.00
Al-Si 11	100.00	2.41	100.00
Al-Si 12	100.00	2.37	100.00
Al-Si 13	100.00	2.30	100.00
Mean value	**100.00**	**2.43**	**100.00**
Std dev.	**0.00**	**0.05**	**0.00**



Layer Thickness Analysis with micro-XRF/SEM

Example IV: Al/Si layer → sample 2



EDS Map of sample 2 in false color mode

XRF line-scan 75 points, Acquisition time: 30 sec / point

Example V: Analysis of solar cells by using Micro-XRF on SEM

Comparison of:

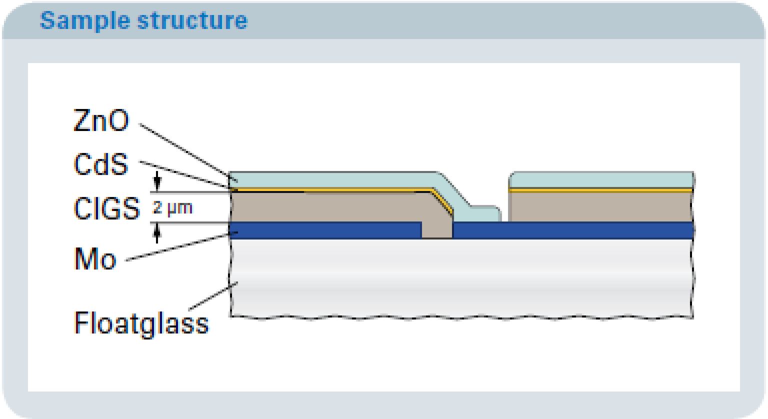
- SEM cross section – micro XRF to calculate the layer thickness
- EDS – micro XRF to calculate the layer composition

Layer Thickness Analysis with micro-XRF/SEM
CIGS- wafer

CIGS- wafer sample background:

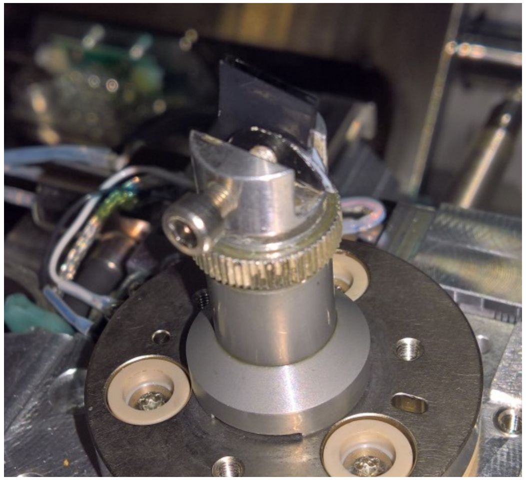
- The efficiency of solar cell is determined mainly by their chemical composition and physical structure
- Therefore the chemical composition is of particular interest for thin- film structures
- In most cases the absorber of the film cells is produced from CIGS-structures, which are Cu-In-Ga-Se or Cu-In-Ga-S compounds
- CIGS- solar cells are typically manufactured by deposition on glass substrates which are coated with a Mo- contact layer.
- For technology development and quality control during the manufacturing process it is important to check primarily composition but also thickness of these layers as well as their homogeneity
- A typical structure of a CIGS wafer is shown on the next slide

Coating Thickness Analysis
CIGS- wafer – structure and sample prep

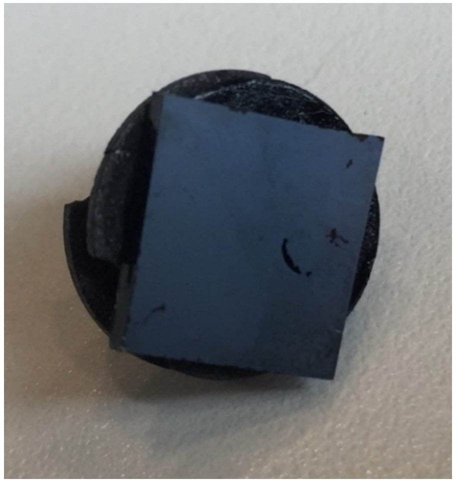


Typical structure of a CIGS solar cell

- Our sample contains of the float glass (substrate), Mo (1st layer), CIGS (2nd layer)
- No passivation layer
- Sample courtesy: PTB (Physical technical federation Berlin)

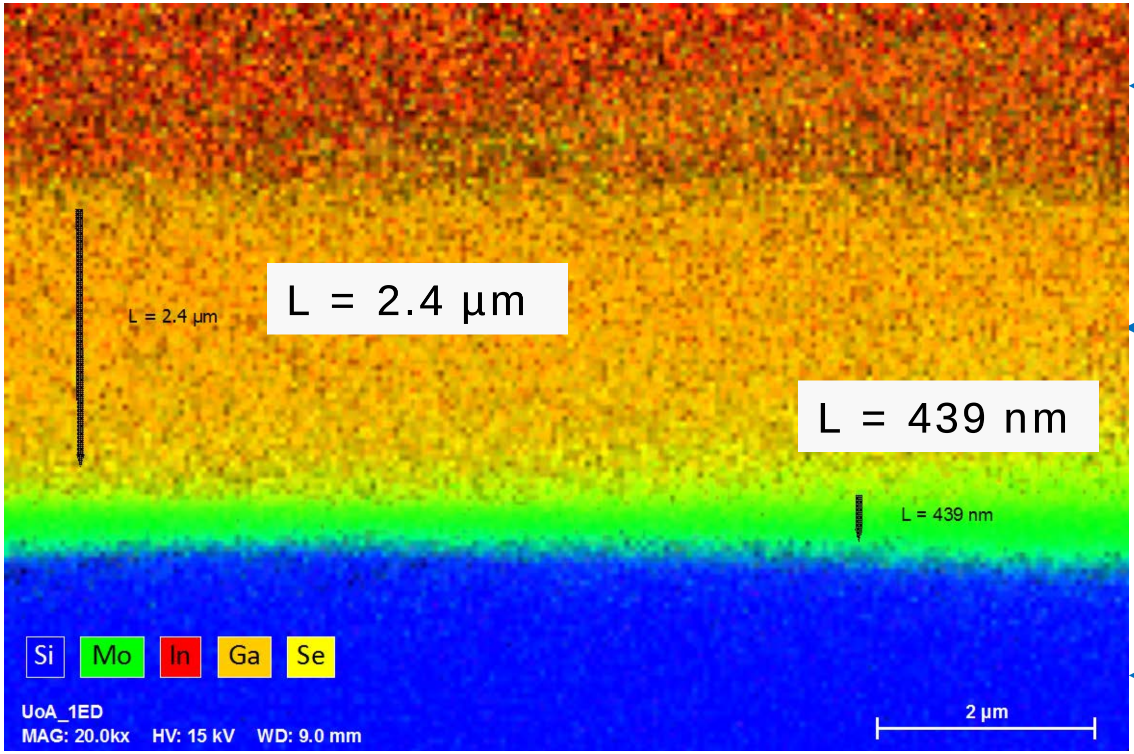


CIGS- wafer sample preparation for SEM cross section analysis in FEI NanoSEM 450



CIGS- wafer sample preparation for XRF analysis

Coating Thickness Analysis
CIGS- wafer – SEM layer observation



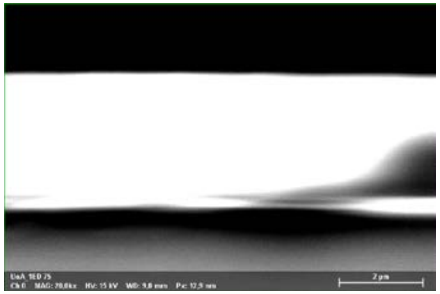
EDS map of a fracture edge of CIGS Wafer sample

Noise (edge effect, due to sample prep) → Ignore it!

CIGS Layer structure

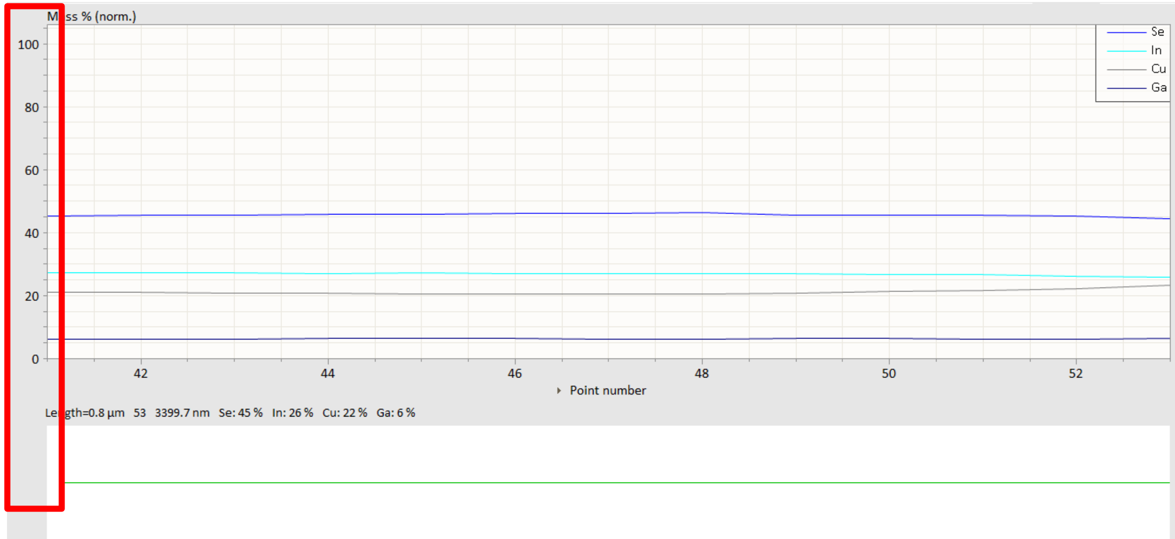
Mo – contact layer

Glass



SEM image of the map area, Backscattered image

Coating Thickness Analysis
CIGS- Wafer – EDS analysis



Extracted line scan area of the absorber (CIGS) for Cu, Ga, Se, In including concentration in wt%

Layer thickness results taken from the SEM cross section observation and quantification results of the CIGS layer taken from EDS analysis

Quantification of CIGS-layer

Method	Layer	Thickness /nm	Composition /wt.%			
			Cu	Ga	Se	In
SEM	Mo	440				
EDS	CIGS	2400	22	6	46	26

Coating Thickness Analysis

CIGS- wafer – XRF analysis

Normalized mass concentration [%]

	Substrate	Layer 1		Layer 2				
Spectrum	Si [%]	Thickn. [nm]	Mo [%]	Thickn. [µm]	Cu [%]	In [%]	Ga [%]	Se [%]
CIGS 1	100.00	422.99	100.00	2.20	20.88	26.45	5.41	47.26
CIGS 2	100.00	420.67	100.00	2.21	20.94	26.31	5.41	47.35
CIGS 3	100.00	420.73	100.00	2.21	20.93	26.24	5.37	47.45
CIGS 4	100.00	418.65	100.00	2.20	20.92	26.42	5.38	47.27
CIGS 5	100.00	423.51	100.00	2.22	20.86	26.25	5.40	47.49
CIGS 6	100.00	421.52	100.00	2.21	20.96	26.37	5.37	47.30
CIGS 7	100.00	419.95	100.00	2.20	20.97	26.32	5.33	47.37
CIGS 8	100.00	424.57	100.00	2.22	21.04	26.39	5.40	47.17
CIGS 9	100.00	425.89	100.00	2.22	20.88	26.55	5.38	47.19
CIGS 10	100.00	428.78	100.00	2.23	20.88	26.45	5.37	47.31
CIGS 11	100.00	424.12	100.00	2.22	20.98	26.37	5.40	47.25
CIGS 12	100.00	420.95	100.00	2.21	20.95	26.31	5.41	47.33
CIGS 13	100.00	420.76	100.00	2.21	21.04	26.14	5.40	47.43
CIGS 14	100.00	425.46	100.00	2.23	20.88	26.51	5.42	47.19
CIGS 15	100.00	427.83	100.00	2.22	20.96	26.38	5.37	47.29
CIGS 16	100.00	420.92	100.00	2.23	21.22	26.15	5.36	47.27
CIGS 17	100.00	429.58	100.00	2.24	20.97	26.52	5.39	47.12
CIGS 18	100.00	426.31	100.00	2.22	21.03	26.19	5.37	47.41
CIGS 19	100.00	420.22	100.00	2.22	20.93	26.29	5.34	47.43
CIGS 20	100.00	428.18	100.00	2.23	20.93	26.29	5.43	47.34
Mean value	**100.00**	**423.58**	**100.00**	**2.22**	**20.96**	**26.35**	**5.39**	**47.31**
Std dev.	**0.00**	**3.34**	**0.00**	**0.01**	**0.08**	**0.12**	**0.03**	**0.10**
Std dev. rel. [%]	**0.00**	**0.79**	**0.00**	**0.49**	**0.38**	**0.45**	**0.48**	**0.21**
Conf. interval	**0.00**	**0.75**	**0.00**	**0.00**	**0.02**	**0.03**	**0.01**	**0.02**

Quantification of CIGS-layer

Method	Layer	Thickness /nm	Composition /wt.%			
			Cu	Ga	Se	In
Micro-XRF	Mo	424				
Micro-XRF	CIGS	2220	21	5.4	47.3	26.4

Coating Thickness Analysis
Comparing XRF – SEM thickness results

Quantification of CIGS-layer

Method	Layer	Thickness /nm	Composition /wt.%			
			Cu	Ga	Se	In
SEM	Mo	**440**				
Micro-XRF	Mo	**424**				
EDS	CIGS	**2400**	**22**	**6**	**46**	**26**
Micro-XRF	CIGS	**2220**	**21**	**5.4**	**47.3**	**26.4**

Conclusion:

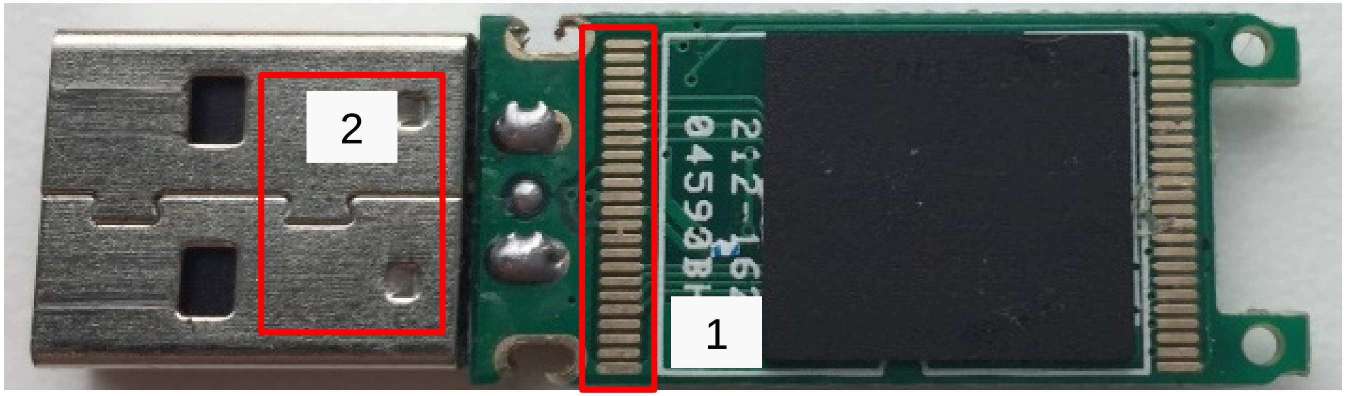
- Measurements results agree very well between SEM layer thickness observation and
- for calculating the composition of the CIGS between EDS and XRF.

Summary
Layer Thickness Analysis with micro-XRF/SEM

- XMethod software package for easy setup of analytical methods
- XRF can be utilized for coating thickness analysis of multilayer stacks
- Overall thickness of layer stack is limited (40 µm)
- Method editor for easy setup of wide range of methods, including option to choose lines to analyze
- Composition of multiple layers can be characterized
- Fundamental Parameter allows standard-less approach
- Standards can be applied in order to enhance precision

Live demonstration

Live demonstration
USB stick



Areas of interest:
1. Au/Ni/Cu contact pins
2. USB housing → Ni/Cu/Fe

Q&A

Are There Any Questions?

Please type in the questions you might have in the Q&A box and press *Send*.

More Information

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