

EDS Of Semiconductor Lamellae in SEM (T-SEM) and STEM October 8th, 2020



Max Patzschke, Meiken Falke and Purvesh Soni



EDS Of Semiconductor Lamellae in SEM (T-SEM) and STEM; Quantitative Element Mapping and More



Max Patzschke

Application Scientist,
Bruker Nano Analytics

Host



Dr. Meiken Falke

Global Product Manager EDS/TEM,
Bruker Nano Analytics

Speaker

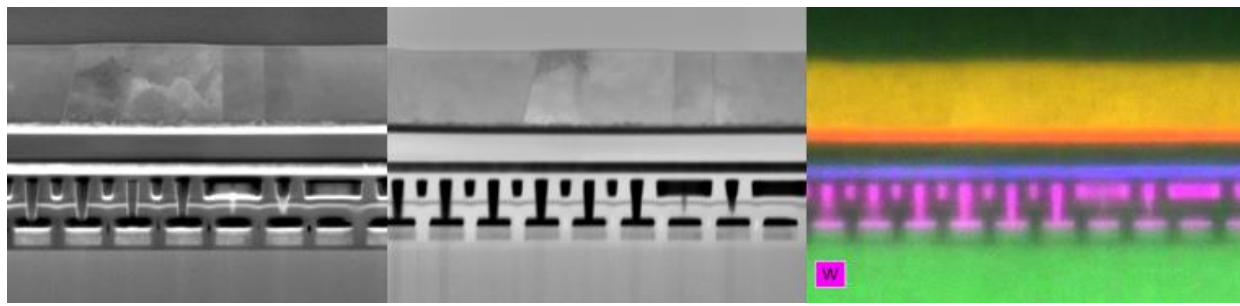


Purvesh Soni

Application Scientist,
Bruker Nano Analytics

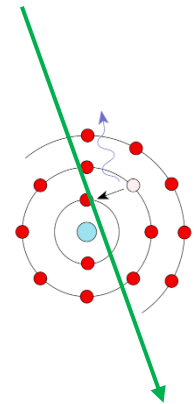
Speaker

Overview

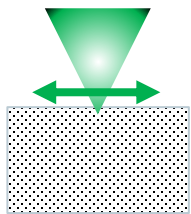


- Intro: Microscopy of bulk and e-transparent specimens
 - Quantitative EDS for lamellae in SEM (FIB) > "T-SEM" and TEM/STEM
- Specimen preparation
- Optimum specimen-detector geometries in SEM

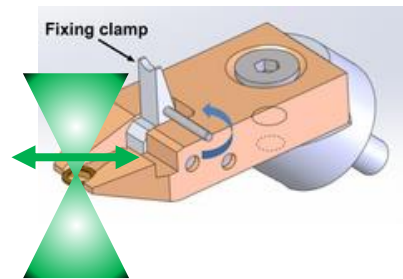
- Examples of quantitative EDS analysis of semiconductor lamellae
 - in SEM (T-SEM)
 - and STEM and
 - in relation to available complementary analysis methods



SEM
Scanning EM

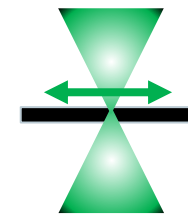


SEM: „T-SEM“

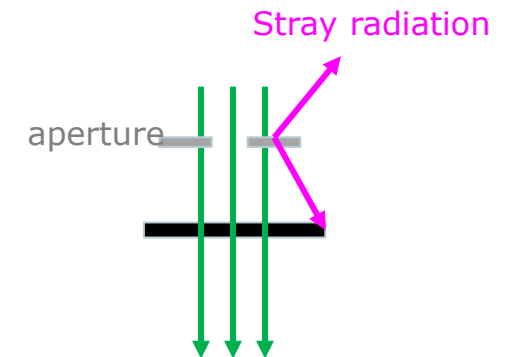


- TKD holder, patented
- Commercial STEM holders and detectors
- Home made versions

STEM
Scanning TEM



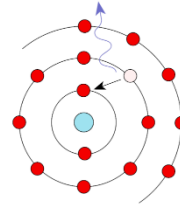
TEM
Parallel illumination



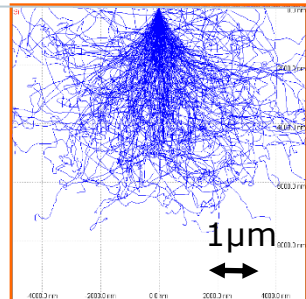
Spatial Resolution for Bulk and Electron Transparent Specimens



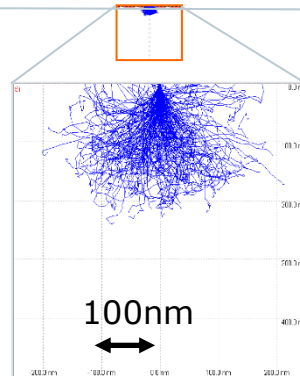
SEM: bulk



High voltage
30kV



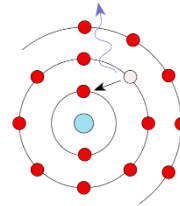
Lower voltage
4kV



Spatial Resolution for Bulk and Electron Transparent Specimens



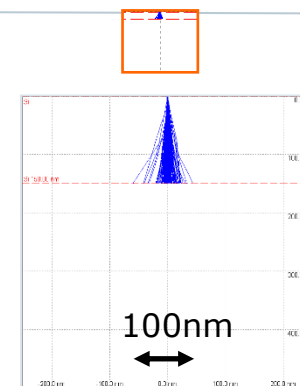
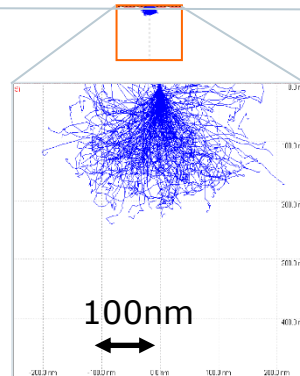
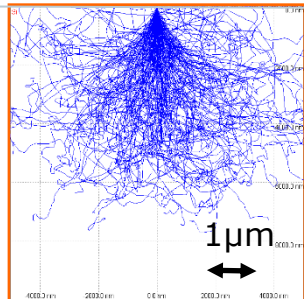
SEM: bulk



S/TEM, T-SEM (**trajectories for 30kV**):
thin specimen, small probe

High voltage
30kV

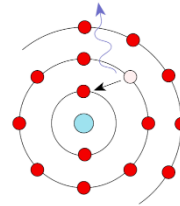
Lower voltage
4kV



Spatial Resolution for Bulk and Electron Transparent Specimens

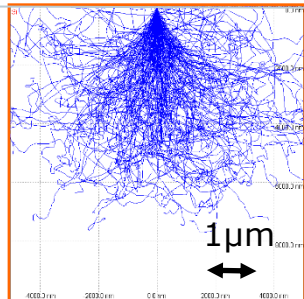


SEM: bulk

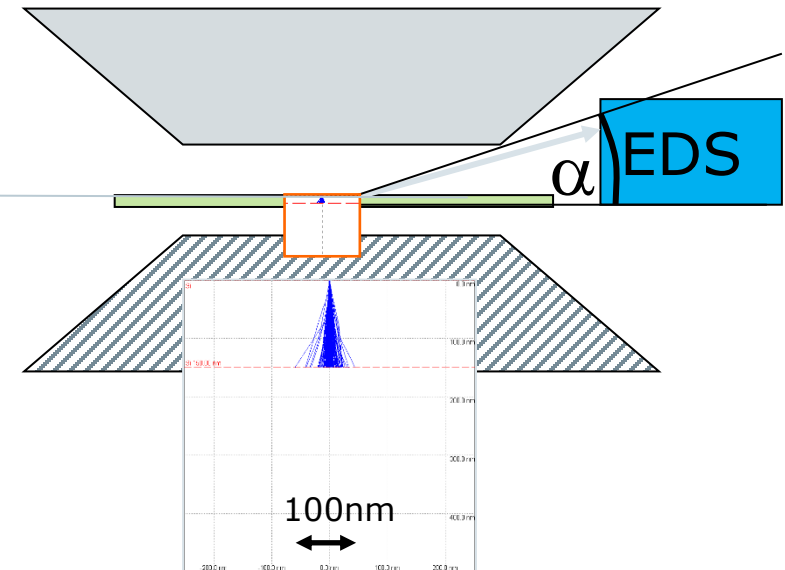
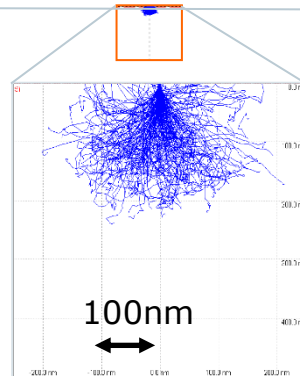


S/TEM, T-SEM (trajectories for 30kV):
thin specimen, small probe

High voltage
30kV



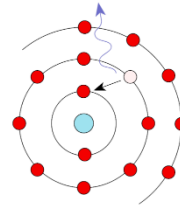
Lower voltage
4kV



Spatial Resolution for Bulk and Electron Transparent Specimens

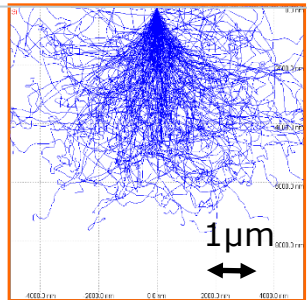


SEM: bulk

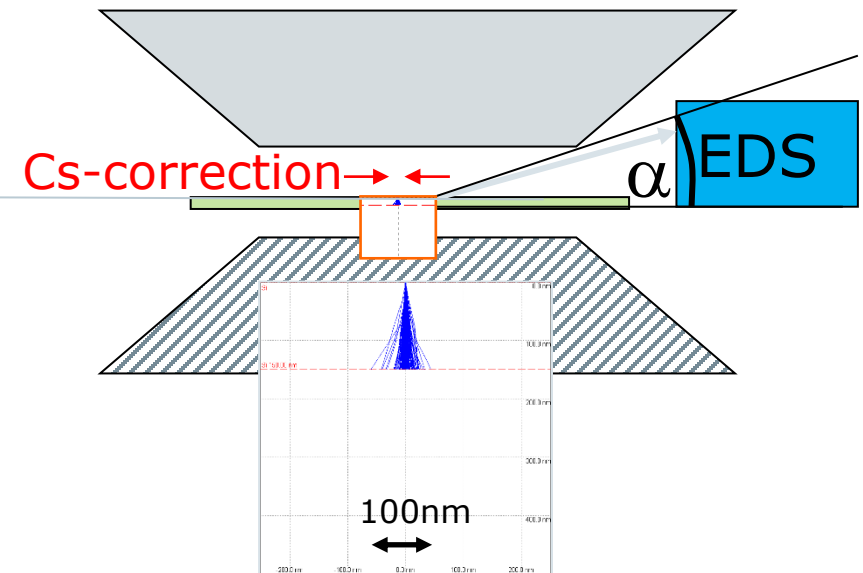
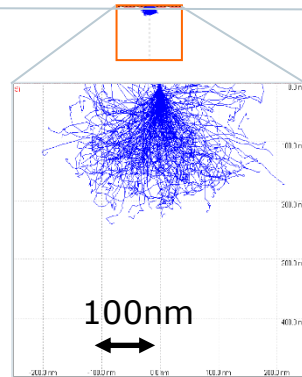


S/TEM, T-SEM (trajectories for 30kV):
thin specimen, small probe

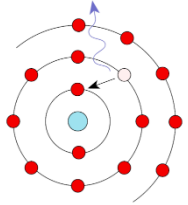
High voltage
30kV



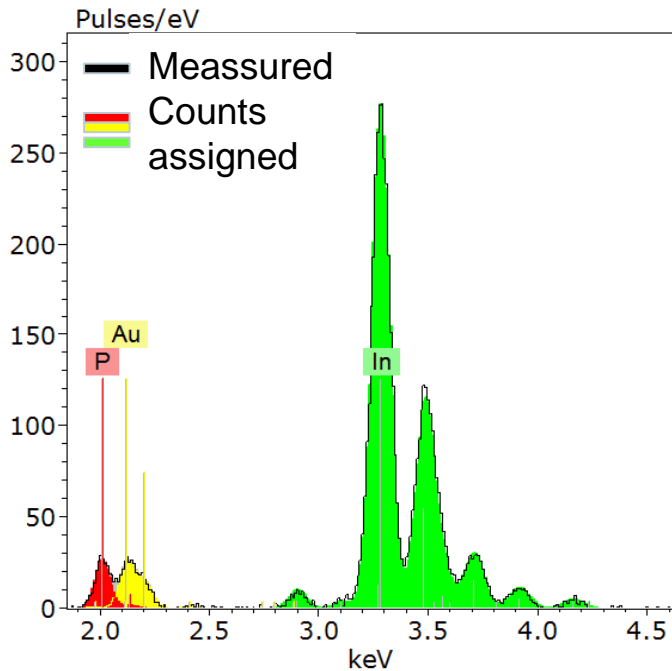
Lower voltage
4kV



(TEM) EDS Quantification; R. Egerton 1994,
line intensity for a particular element line / transition:

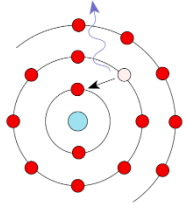


$$I_x = N_A \sigma_A \omega_A (\Omega/4\pi) \varepsilon N_e = n_A t \sigma_A \omega_A (\Omega/4\pi) \varepsilon N_e$$



- I_x number of X-ray photons in a characteristic peak of species A
- N number of atoms per unit volume
- $n t$ density times thickness
- σ ionization cross section (Casnati et al., 1982, Bote et al., 2009)
- ω fluorescence yield (Hubbell et al., 1994, Krause, 1979)
- $\Omega/4\pi$ solid angle / geometrical collection efficiency
- ε detection quantum efficiency (window: SLEW or no window or other)
- N_e number of incident electrons
- + absorption, fluorescence, other effects...

(TEM) EDS Quantification; The Cliff-Lorimer Method



Cliff and
Lorimer:

$$I_x = N_A \sigma_A \omega_A (\Omega/4\pi) \varepsilon N_e = n_A t \sigma_A \omega_A (\Omega/4\pi) \varepsilon N_e$$

$$\frac{I_A}{I_B} = \frac{C_A}{k_{AB} C_B} ; k_{AB} \text{ can be determined experimentally or } \textbf{theoretically}$$

- I_x number of X-ray photons in a characteristic peak of species A
- N number of atoms per unit volume
- $n t$ density times thickness
- σ ionization cross section (Casnati et al., 1982, Bote et al., 2009)
- ω fluorescence yield (Hubbell et al., 1994, Krause, 1979)
- $\Omega/4\pi$ solid angle / geometrical collection efficiency
- ε detection quantum efficiency (window: SLEW or no window or other)
- N_e number of incident electrons
- + absorption, fluorescence, other effects...

(TEM) EDS Quantification; The Zeta-Factor Method ... and EELS



Bulk, thick samples:
Zeta-Factor Method,
needs Standard!

$$I_x = N_A \sigma_A \omega_A (\Omega/4\pi) \varepsilon N_e = n_A t \sigma_A \omega_A (\Omega/4\pi) \varepsilon N_e$$

G. Kothleitner, Micr. Microanal. 2014

M. Watanabe, J. of Micr. 2005:

For a **standard with known density ρ**
and known thickness t ζ can be determined:
 D_e (total electron dose) must be known for
all measurements.

Then, for a sample C_A, C_B, \dots and pt are unknown
with:

$$C_A + C_B = 1$$

$$(C_1 + C_2 + \dots = 1)$$

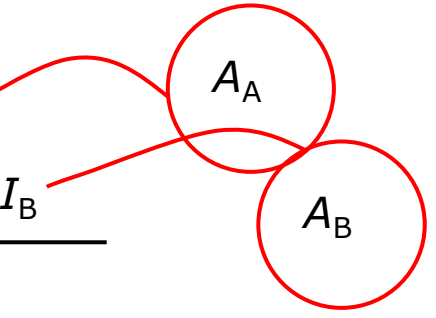
$$\rho t = \frac{\zeta_A I_A + \zeta_B I_B}{D_e}$$

$$C_A = \frac{\zeta_A I_A}{\zeta_A I_A + \zeta_B I_B}$$

$$C_B = \dots$$

EELS: $t/\lambda = \log_e (I^{E_{total}} / I^{E_0})$

$$\rho t = \zeta_A \frac{I_A A_A}{C_A D_e} \dots = \frac{I^{E_{core}} \text{AtWeight}}{I^{E_{0_low}} \sigma N_{Avog}}$$



absorption coefficients

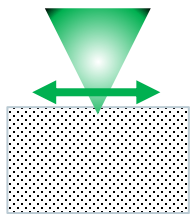
With a few ζ data points
all ζx can be calculated
from existing k -factors

by just one click in the
Esprit SW !!!

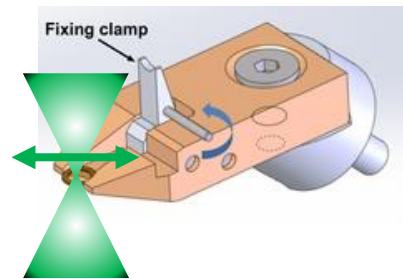
Electron Microscopy



SEM
Scanning EM

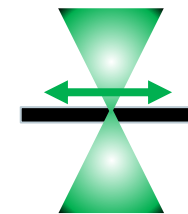


SEM: „T-SEM“

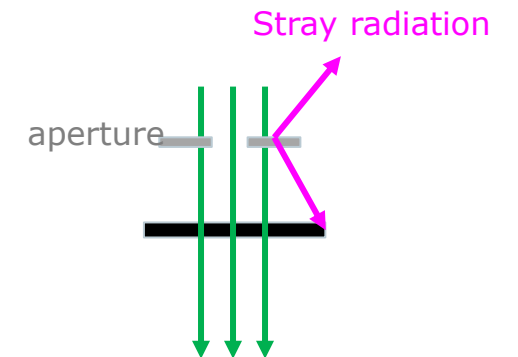


- TKD holder, patented
- Commercial STEM holders
- Home made versions

STEM
Scanning TEM



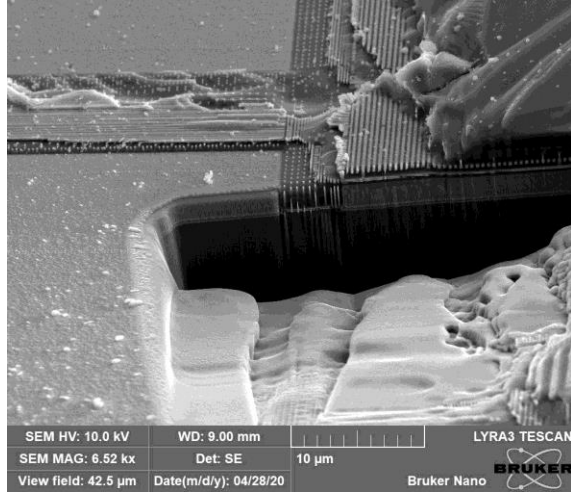
TEM
Parallel illumination



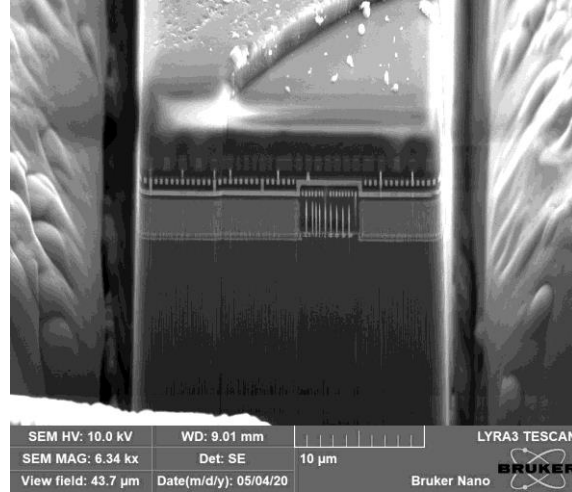
Application examples: FIB/TEM lamellae
Lift out from a bulk sample

Application examples: FIB/TEM lamellae

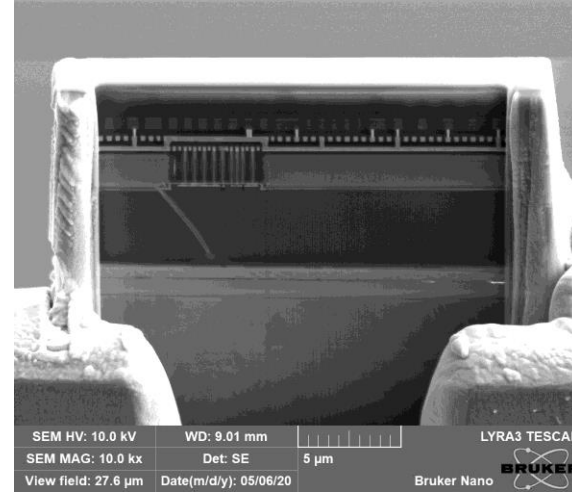
Lift out and thinning



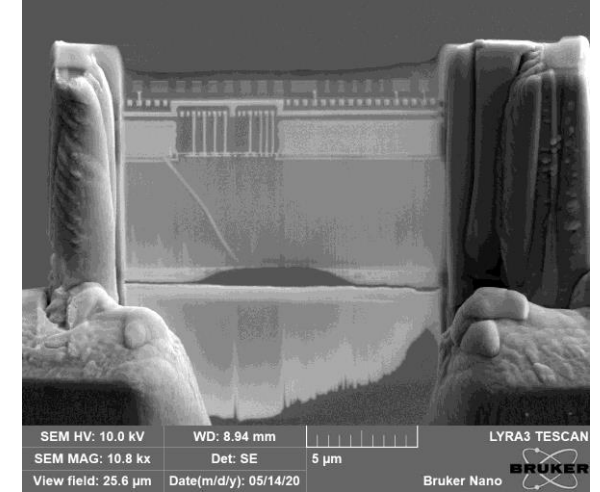
Locating ROI



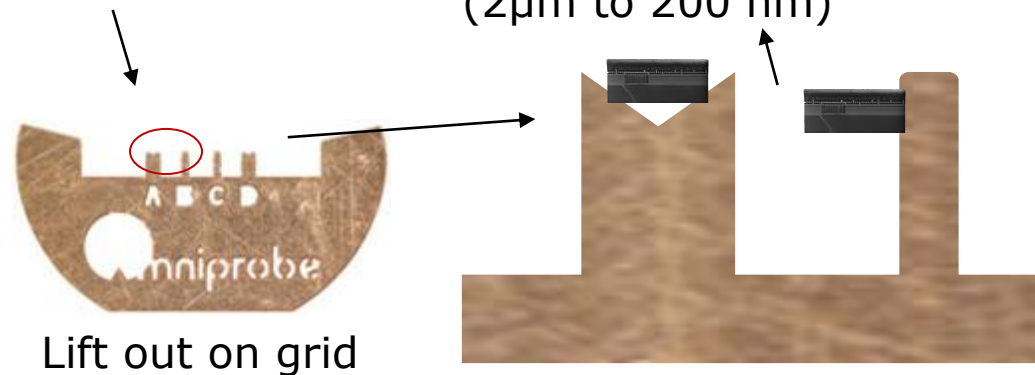
Trenches milling



Coarse thinning
(2 μ m to 200 nm)

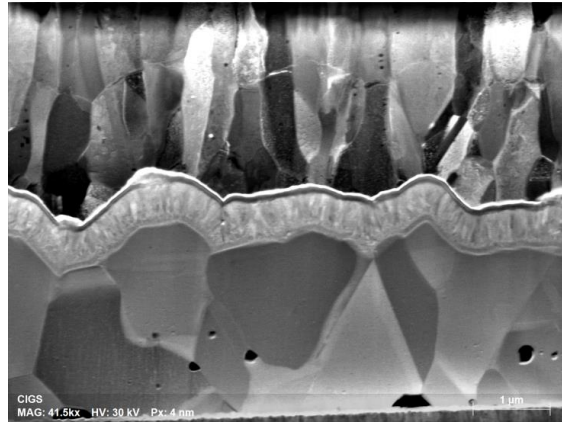


Final thinning /
Low kV milling
(50 nm)

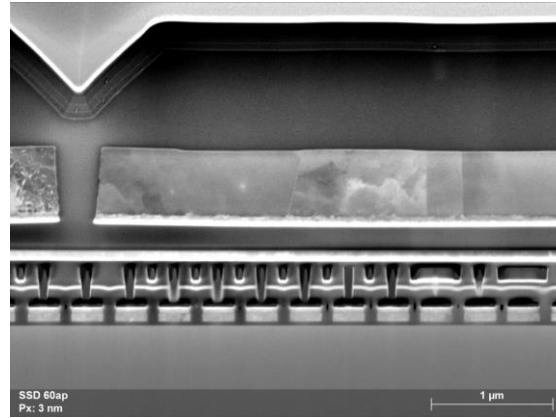


Application examples overview

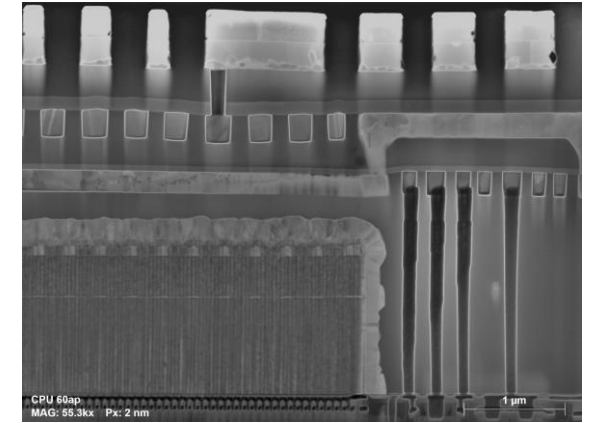
STEM images



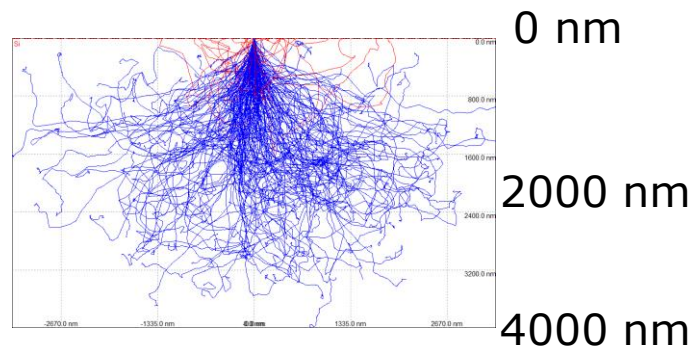
CIGS solar cell



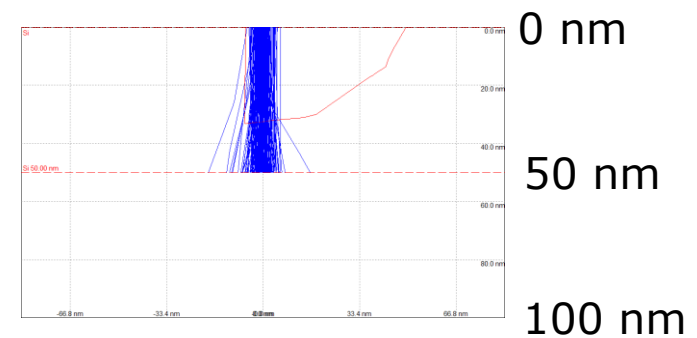
Solid state drive



Microprocessor



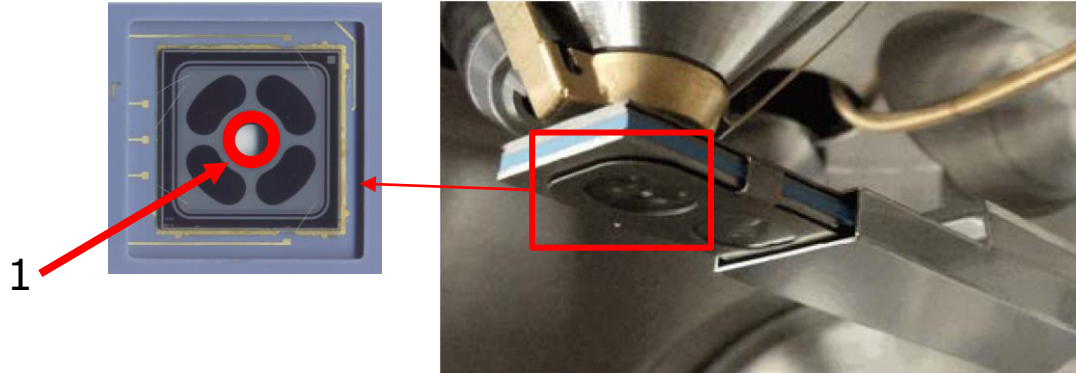
Bulk specimen



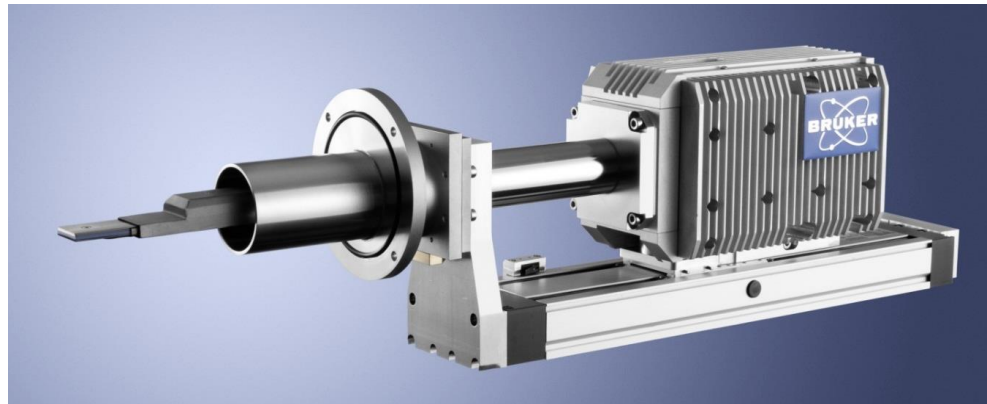
FIB/TEM lamellae

XFlash[®] FlatQUAD

Features



- Side entry, energy dispersive x-ray spectra detector
- Annular design; Central aperture for primary beam¹
- 4 × SDD modules (total area 60 mm²)

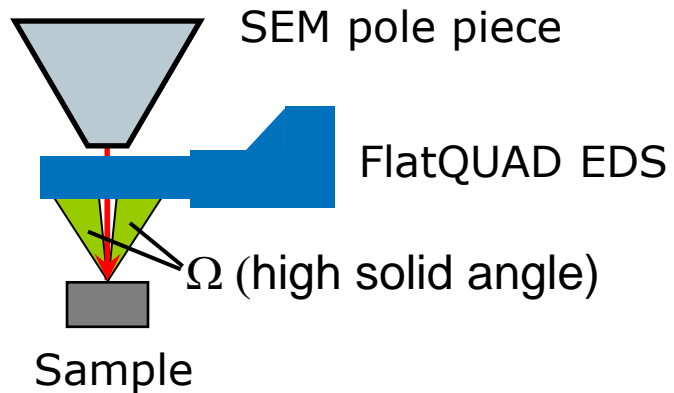
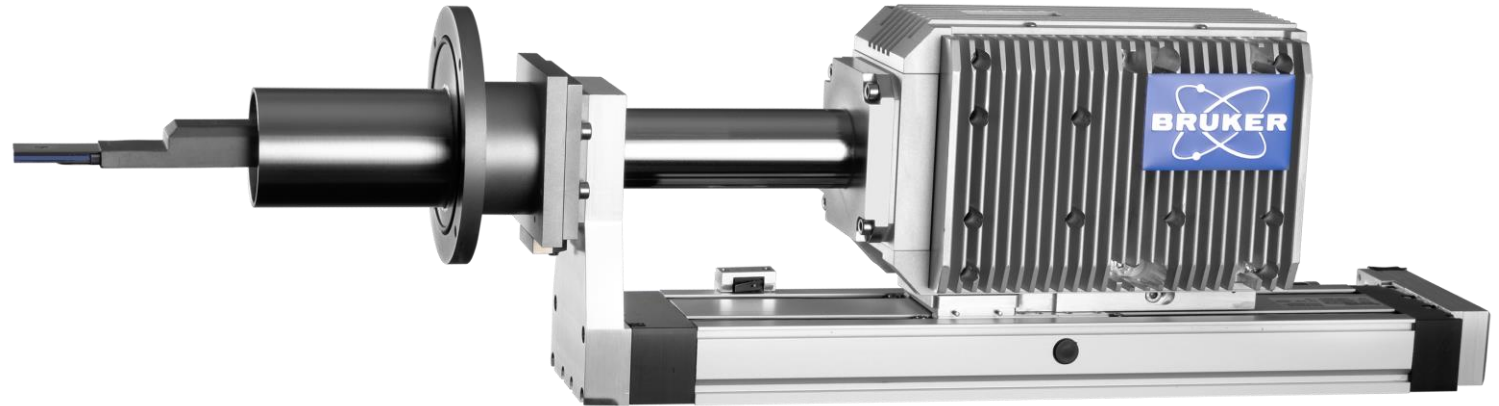


Advantages:

- Optimum signal collection geometry
- High sensitivity, high signal – low noise
- Large solid angle (up to 1.1 sr)
- Shadowing minimized for topographic samples
- High count rate at low beam currents

XFlash[®] FlatQUAD

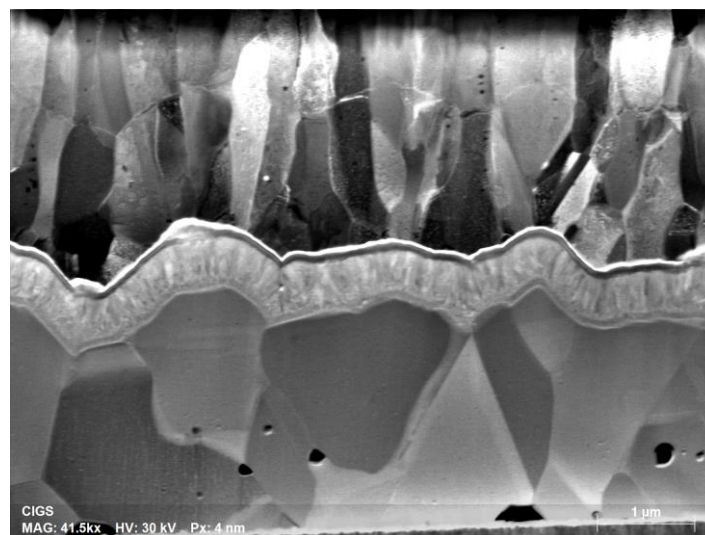
Features and Advantages



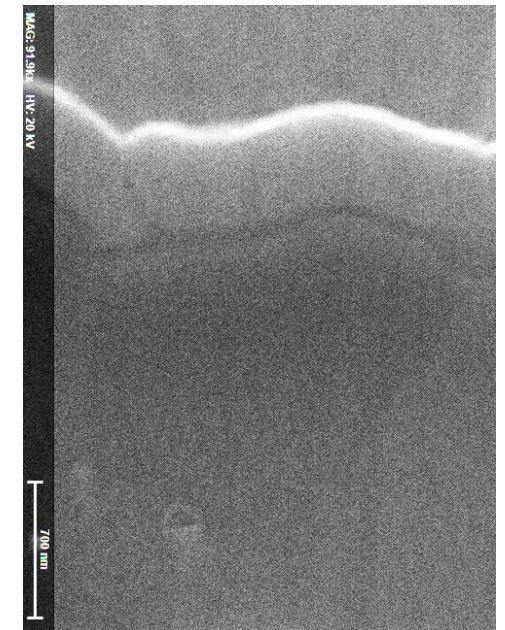
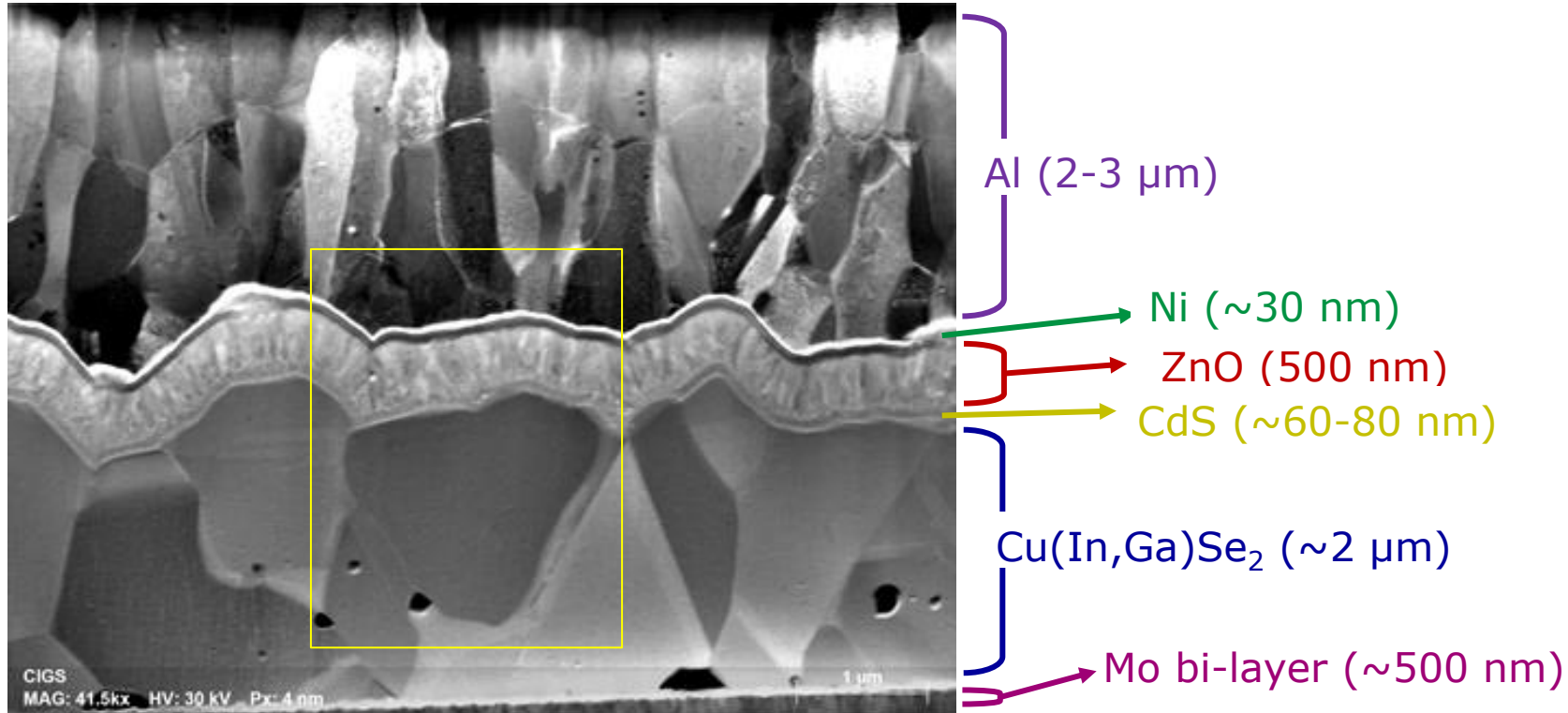
Ideal for samples with low x-ray/EDS yield:

- TEM/FIB lamellae
- Thin films
- Nanoparticles
- low Z (light elements)
- Ultra-sensitive for bulk samples

Application example: CIGS



Application example: Cu(In,Ga)Se₂ solar cell STEM DF – Layered structure (FIB-Lamella)



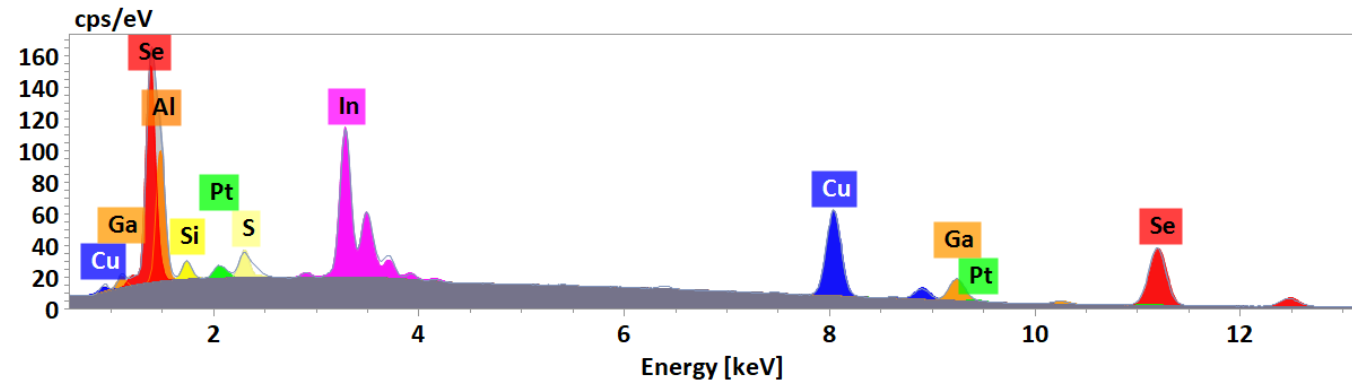
EDS mapping region

Lamella thickness ~ 70 nm

Sample courtesy: M. Raghuwansi, RWTH Aachen University, Aachen, Germany

Application example: Cu(In,Ga)Se₂ solar cell

Hypermap and Quantification results



Cliff-Lorimer quantification

Element	Atomic No.	Line series	Net counts	Atom abs. [%]	Error (1-sigma %)
Copper	29	K	8.91E+05	21.71	0.51
Indium	49	L	1.72E+06	22.52	3.2
Gallium	31	K	2.39E+05	6.39	0.17
Selenium	34	K	7.04E+05	44.75	0.18
Sulfur	16	K	1.81E+05	4.63	0.06
Sum				100	

Cliff Lorimer Quantification method for e-transparent samples

MAPPING

BRUKER

Sample
 Coating: None
 Company: DemoCo Ltd.
 Batch: AF-10/45
 Sample: 12

Standards
 No of standards: 0
 Calib. date: 01/10/2020
 Calib. time: 12:54:16 PM
 HV: 20.0 kV
 Geometry: wrong

Microscope
 WD: 13.900 mm
 Magn: 91900.0 x
 Stage X: 0.000 mm
 Stage Y: 0.000 mm
 Stage Z: 0.000 mm
 HV: 20.0 kV

X-ray source
 60°C
 30°C
 0°C
 Current: 0 µA
 Filter: Empty
 Status: OK

Scan
 Dwell time: 8 µs
 Frame time: 8 s
 Drift qual: --- %
 Drift range: --- %
 Size: 800 px

1
 Range: 20 keV
 Max. throughput: 60 kcps
 Temperature: 20.4 °C
 Real time: --- s
 Live time: --- s
 ICR: 60 kcps

2
 Range: 20 keV
 Max. throughput: 0 kcps
 Temperature: -20.0 °C
 Real time: --- s
 Live time: --- s
 ICR: 0 cps

WDS
 State: Not initialized
 Crystal: ---
 Optic H: 0.0000 mm
 Optic V: 0.0000 mm
 Optic L: 0.0000 mm

EBSD
 MP: 0 mm
 Tilt: 0.0 °
 Board temp: --- °
 Camera temp: --- °
 Frame rate: --- fps
 Size: 80 px

Preview Capture Acquire QMap EDS Default XRF XRF d: C:\Users\purvesh.soni\Data\FlatQUAD\CIGS\CIGS-Zeiss-FQ\2ab_20kV_92kx_5nm_25m.bcf

SE Map Phases Map Phases Charts Line scan Spectrum

MAG: 91.9kx HV: 20 kV WD: 13.9 mm
 Loaded image: 656 x 491 3.3 x 2.5 µm
 0.5 µm

Cu Ga In Al S Se Ni Pt Fe Cr
 CIGS 157
 MAG: 91.9kx HV: 20 kV WD: 13.9 mm
 0.5 µm

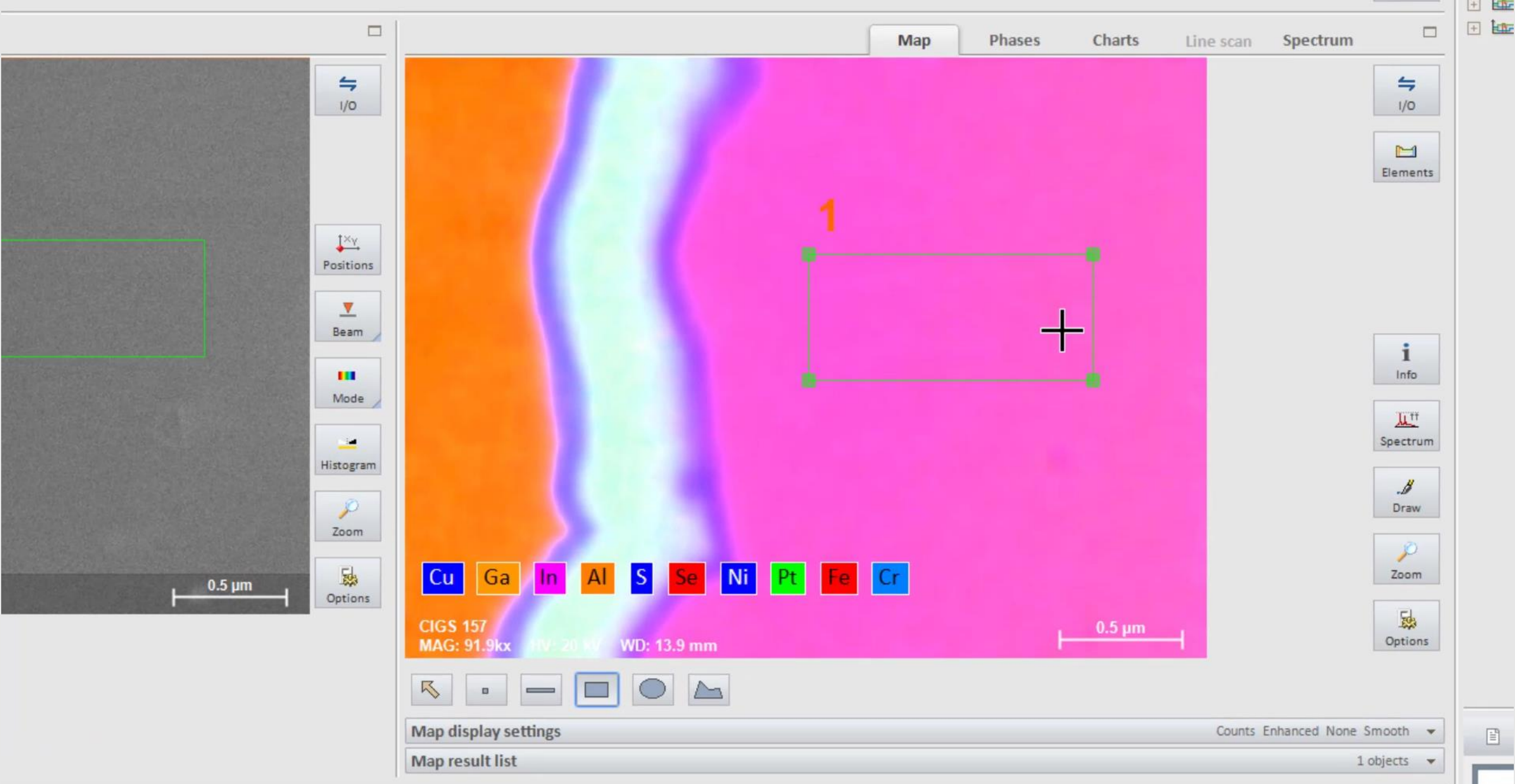
Map display settings Counts Enhanced None Smooth
 Map result list no objects

Ch 1 1.23 + Cu-Kα 1.00 + Ga-Kα
 1.00 + Cr-Kα 1.00 +

Project (mod.) 18/09/2020
 1 25/09/2020 8:5
 1 25/09/2020 9:5

Report preview Page 1

To calibrate the cliff lorimer factors, first select a region with known concentration.



This region is selected since the concentration of CIGS layer is known

The screenshot displays the Bruker software interface with various panels and data. At the top, there are several configuration panels: Sample (None), Standards (CIGS-2a(m)), Microscope (20.0 kV), X-ray source (0.0 kV), Scan (800 px), and two WDS channels. The main area is split into a left panel with a grayscale image and a right panel with an EDS spectrum. The spectrum shows peaks for S, Cr, Pt, Ni, Al, Si, Fe, Ga, Cu, In, and Se. A 'Quantify' button is highlighted with a red box, and the 'Spectrum' tab is also highlighted. Below the spectrum, there is a table with two rows of data.

		cps/eV	Factor	Results [Atom-%]	Sort: Element
<input type="checkbox"/>	All				
<input type="checkbox"/>	EDS Map	3.04	1.000	No quant results available.	
<input checked="" type="checkbox"/>	EDS CIGS	3.36	1.000	No quant results available.	

Go to spectrum tab, select the spectrum from below, and click Quantify. You can also save it with the name "spectrum.spx" from the I/O button under the spectrum tab.

Element overview list

Standards

Background settings

SEM
 TEM
 Math

Auto

	Start [keV]	End [keV]	
1	4.498	5.118	+ Add
2	13.767	17.947	
3			- Delete

Deconvolution settings Series fit

Quantification model

P/B - ZAF
 Phi(Rho,Z)
 Use standards
 P/B film

Zeta factor method
 Cliff-Lorimer

Layer density [g/cm³]
 Layer thicken. [μm]
 Substrate (mean. AN)

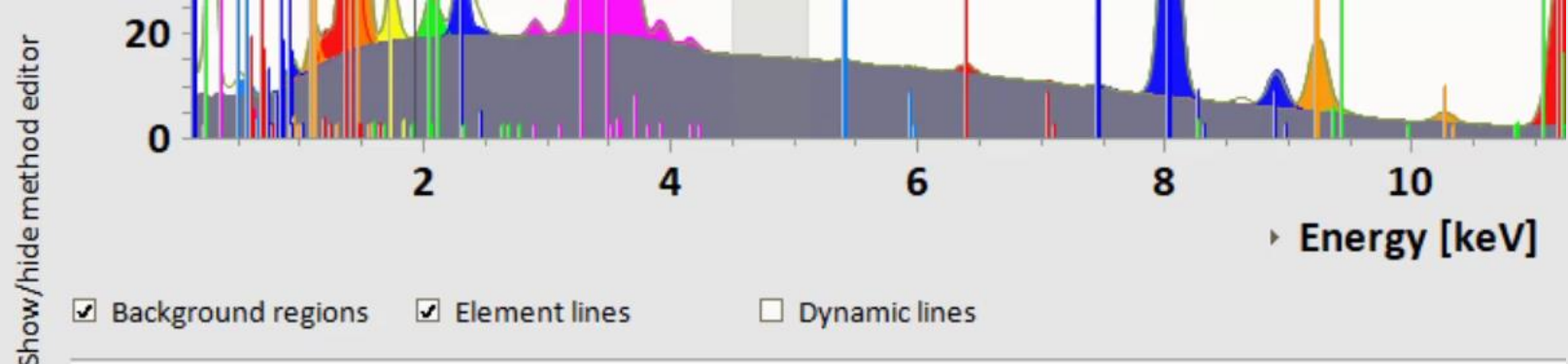
Additional settings 20.0 keV, 0°

High voltage [kV] A
 Sample tilt angle [°] A
 Fast quantification

Description

Automatic element identification, quantification with P/B-ZAF

Load Save To project Apply



Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Copper	29	1180987	13.58	13.58	13.19	0.41	3.02
Gallium	31	333730	5.23	5.23	4.63		
Indium	49	2236535	26.07	26.07	14.01		
Silicon	14	153674	1.46	1.46	3.20		
Aluminium	13	961157	14.21	14.21	32.51		
Sulfur	16	258137	1.70	1.70	3.28		
Selenium	34	918873	35.99	35.99	28.13		
Nickel	28	18795	0.20	0.20	0.21		
Platinum	78	34831	1.14	1.14	0.36		
Iron	26	37642	0.33	0.33	0.37		
Chromium	24	10822	0.08	0.08	0.10		
		Sum	100.00	100.00	100.00		

Continue with Cliff-Lorimer Quant only, if you have already (1) calculated the theoretical Cliff-Lorimer factors using the voltage and angle settings of the measurement, or additionally to this (2) calibrated some Cliff-Lorimer factors experimentally, using data from a representative standard spectrum out of the HyperMap. See later in this pdf or the manual for details on this. There will be a warning from the SW – do not continue without (!). → See next slide for details

Density: 4.92 g/cm³

now select Cliff-Lorimer as the quantification model and Mathematical background (the mathematical bg is for samples which are neither bulk nor really thin, so that the physical SEM or TEM Background don't work perfectly).

Sample: None, DemoCo Ltd., AF-10/45, 12
 Standa...: 2, Uncalibrated, Uncalibrated, 20.0 kV, OK
 Mi...: 11.100 mm, 200000.0 x, 0.000 mm, 0.000 mm, 0.000 mm
 X...: 60°C, 0 µA, Empty, OK
 Sc...: Dwell time 8 µs, Frame time 8 s, Drift qual. --- %, Drift range --- %
 1: 20 keV, 60 kcps, 20.4 °C
 2: 20 keV, 0 kcps, -20.4 °C
 W...: 10 k, Not initialized, 0.0000 mm, 0.0000 mm, 0.0000 mm
 EB...: 0 mm, 0.0 °, --- °, --- °, --- °, --- fps
 Test sampl: CIGS-2a (1)
 HV 20.0 kV
 0.0 kV
 800 px
 ICR 60 kcps
 ICR 0 cps
 --- eV
 Size 160 px

ADMINISTRATION OF STANDARD LIBRARY

CIGS-2a(mod.)

Date: 29/09/2020 Elevation angle: 48.0° WDS elevation angle: 0.0°
 High voltage: 20.0 keV Azimuth angle: 45.0° WDS azimuth angle: 0.0°
 Calibration: Copper reference Tilt angle: 0.0°
 Standards: 2 Beam entrance angle: 42.0°

Bulk Electron transp.

Cliff-Lorimer factors Zeta factors

Legend: 0.000 - Undefined data
 1.234 - Calculated data from theory
 1.234 - Calibrated data

AN	El.	K	L	M
30	Zn	1.667	22.798	0.000
31	Ga	1.781	14.414	0.000
32	Ge	2.383	8.386	0.000
33	As	2.849	5.823	0.000

Samarium

Se.	Ref.	Standard
K		
L		
M		

NEW STANDARDS LIBRARY

Name: FIB Lamella #4B

Energy [keV]: 20.00 (3)
 Elevation angle [°]: 48.0
 Azimuth angle [°]: 45.0
 Tilt angle [°]: 0.0
 Beam entrance angle [°]: 42.0
 Take off angle: 48.0°
 WDS elevation angle [°]: 0.0
 WDS azimuth angle [°]: 0.0
 WDS takeoff angle [°]: 0.0°
 Reference sample: Copper reference
 Main element: Cu

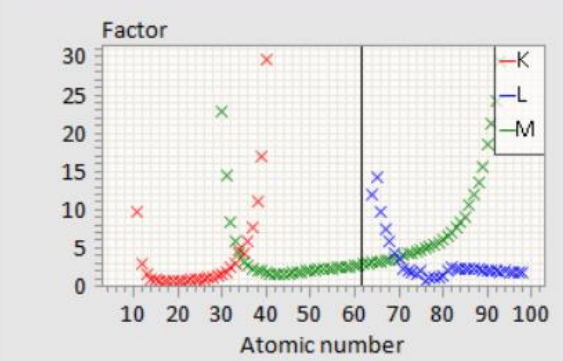
Load OK Cancel

Enter the values manually

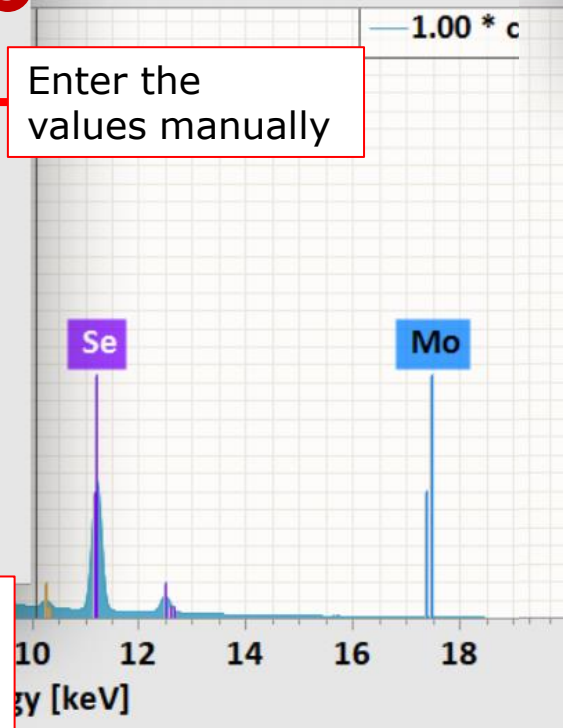
Standards library

Add to project

New (2)
 Load
 Save (4)
 Remove



OR "load" a corresponding spectrum.spx file – this will load the values automatically



QUANTIFICATION - CIGS

Settings

Elements

Element finder

Element overview

Standards

Background settings

Deconvolution settings

Quantification model

Additional settings

Results

cps/eV

Energy [keV]

Dynamic lines

	Count	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Gallium	31 333730	5.23	5.23 4.63
Indium	49 2236535	26.07	26.07 14.01
Silicon	14 153674	1.46	1.46 3.20
Aluminium	13 961157	14.21	14.21 32.51
Sulfur	16 258137	1.70	1.70 3.28
Selenium	34 918873	35.99	35.99 28.13
Nickel	28 18795	0.20	0.20 0.21
Platinum	78 34831	1.14	1.14 0.36
Iron	26 37642	0.33	0.33 0.37
Chromium	24 10822	0.08	0.08 0.10
Sum	100.00	100.00	100.00

Cr Chromium

Available series

- EDS
 - Automatic
 - K series 5.412 keV
 - L series 0.572 keV
 - M series
- WDS

Fixed concentration

Use fixed concentration

Deconvolution only

Quantify per difference

Quantification model

- P/B - ZAF
- Phi(Rho,Z)
- P/B film
- Zeta factor method
- Cliff-Lorimer

Use standards

Layer density [g/cm³]

Layer thicken. [μm]

Substrate (mean. AN)

High voltage [kV]

Sample tilt angle [°]

Fast quantification

Description

Automatic element

Load

Cancel

With an e-transparent sample, the signal from the sample holder and the SEM stage (e.g. from Alu and Steel) are present in the spectrum. To exclude these elements from calibration of Cliff-Lorimer factors and from quantification and correct peak separation in case of overlaps, change all these elements to "Deconvolution only".

Settings

Elements

H	He
Li Be	B C N O F Ne
Na Mg	Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr	
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe	
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn	
Fr Ra Ac	
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu	
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr	

Clear all Auto ID

Element finder

Y	LA1	1.922	LA2	1.921
Os	MA1	1.907	MA2	1.904 MB 1.978
Ir	MA1	1.980	MA2	1.976
Kr	LG2	1.907	LG3	1.907
Sr	LB3	1.946	LB4	1.936 LB6 1.901 LG5
Nb	LL	1.902		
Tm	M2N	1.910		

Element overview list

Standards

Background settings

SEM
 TEM
 Math

	Start [keV]	End [keV]
1	4.498	5.118
2	13.767	17.947
3		

Auto

Deconvolution settings

Quantification model

P/B - ZAF Zeta factor method
 Phi(Rho,Z) Cliff-Lorimer

Use standard

P/B film

Layer density [g/cm³] 0
 Layer thckn. [µm] 0.07
 Substrate (mean. AN) 0

Additional settings

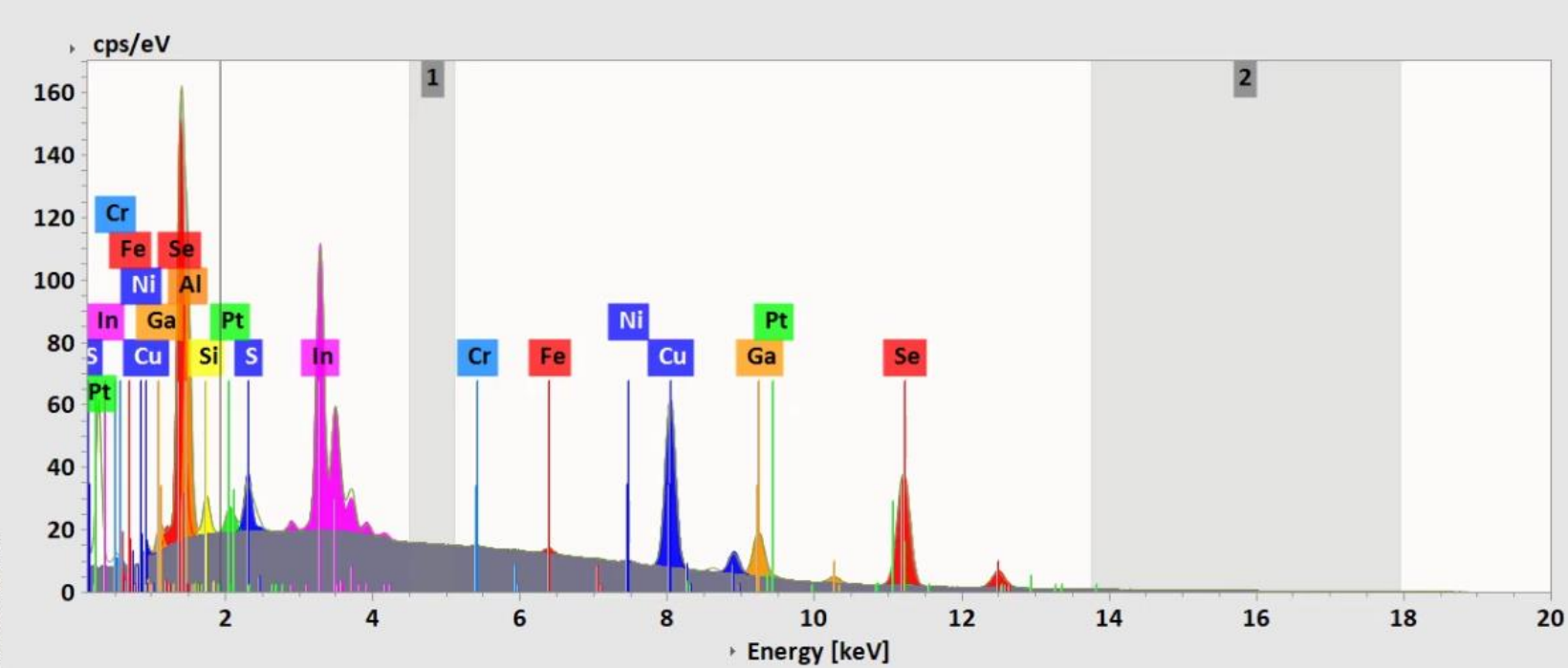
High voltage [kV] 20.0
 Sample tilt angle [°] 0
 Fast quantification

Description

Automatic element identification, quantification with P/B-ZAF

Load Save To project Apply

Results



- Background regions Element lines Dynamic lines

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Copper	29	1180934	16.08	16.08	20.58	0.48	3.02
Gallium	31	333481	5.77	5.77	6.73	0.17	3.03
Indium	49	2225760	33.41	33.41	23.67	0.07	0.20
Silicon	14	153564	0.00	0.00	0.00	0.00	0.00
Aluminium	13	966695	0.00	0.00	0.00	0.00	0.00
Sulfur	16	257683	1.11	1.93	4.90	0.06	3.03
Selenium	34	918777	42.81	42.81	44.11	1.30	3.03
Nickel	28	18748	0.00	0.00	0.00	0.00	0.00
Platinum	78	34461	0.00	0.00	0.00	0.00	0.00
Iron	26						
Chromium	24						

Density: 5.81 g/cm³

If known, the layer thickness can also be added, here it is 70 nm. The layer density value is calculated theoretically from the spectrum elements, unless changed. Now select "Add to standards" to calibrate Cliff-Lorimer factors experimentally.

All Fact

Orig. 1.00

Bkg. 1.00

Cu 1.00

Ga 1.00

In 1.00

Si 1.00

Al 1.00

S 1.00

Se 1.00

Ni 1.00

Pt 1.00

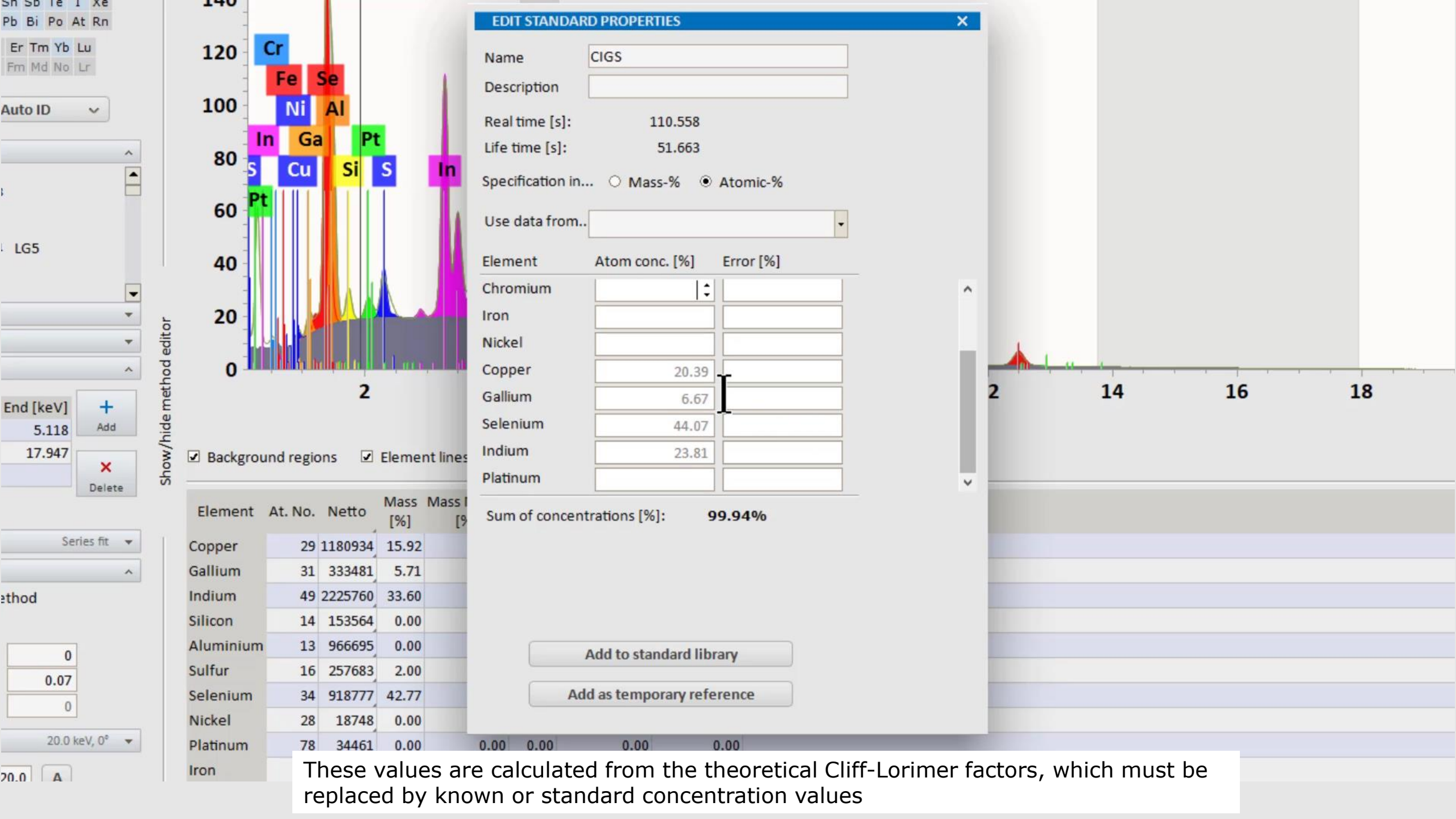
Fe 1.00

Cr 1.00

Deconv. 1.00

Add to standards

OK Cancel

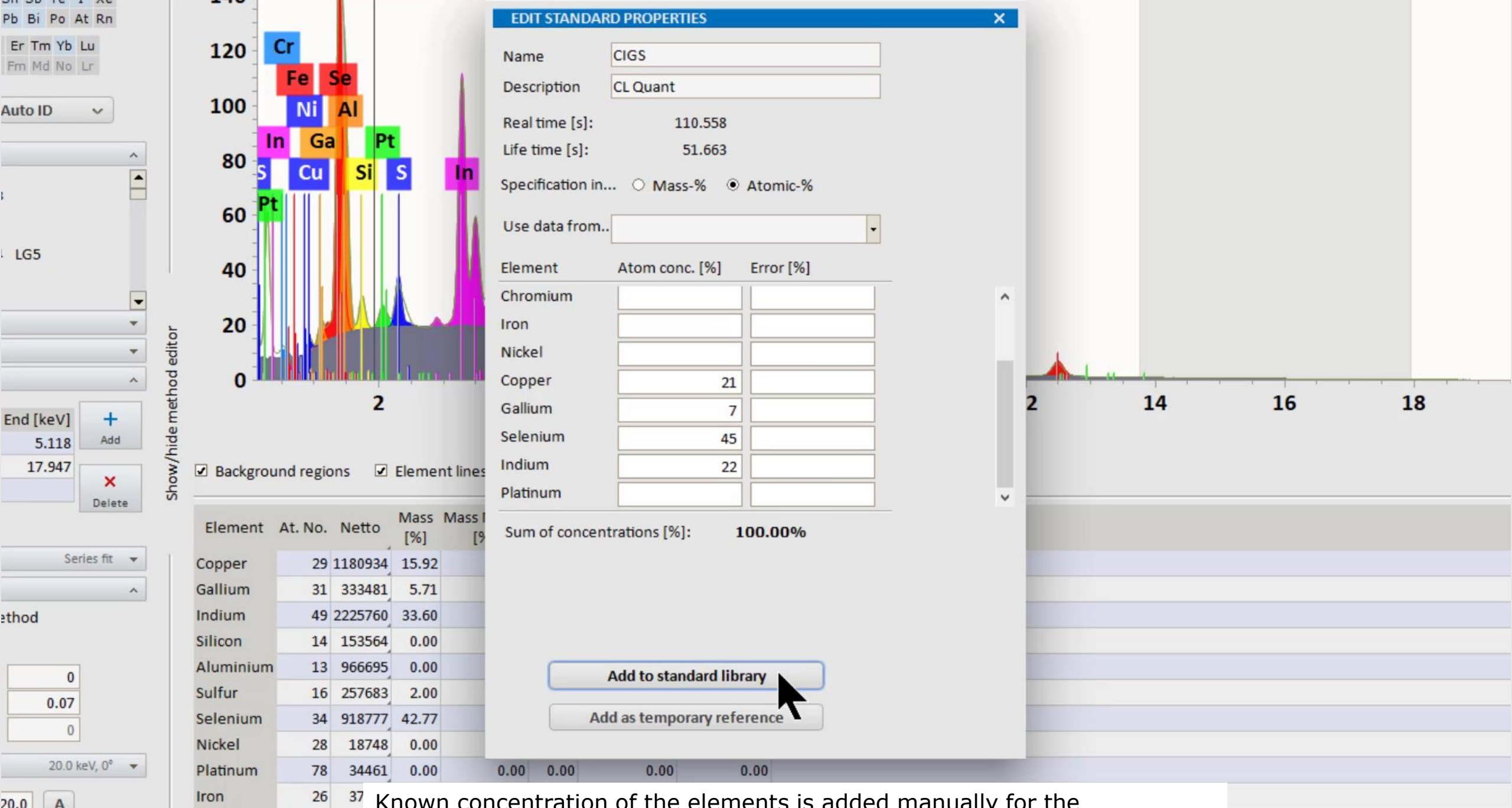


EDIT STANDARD PROPERTIES

Name: CIGS
 Description:
 Real time [s]: 110.558
 Life time [s]: 51.663
 Specification in... Mass-% Atomic-%
 Use data from..
 Element Atom conc. [%] Error [%]
 Chromium
 Iron
 Nickel
 Copper 20.39
 Gallium 6.67
 Selenium 44.07
 Indium 23.81
 Platinum
 Sum of concentrations [%]: 99.94%

Element	At. No.	Netto	Mass [%]	Mass I [%]
Copper	29	1180934	15.92	
Gallium	31	333481	5.71	
Indium	49	2225760	33.60	
Silicon	14	153564	0.00	
Aluminium	13	966695	0.00	
Sulfur	16	257683	2.00	
Selenium	34	918777	42.77	
Nickel	28	18748	0.00	
Platinum	78	34461	0.00	0.00
Iron			0.00	0.00

These values are calculated from the theoretical Cliff-Lorimer factors, which must be replaced by known or standard concentration values

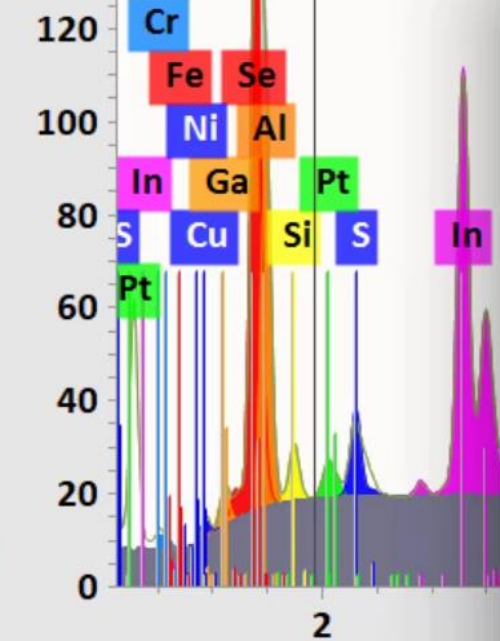


EDIT STANDARD PROPERTIES

Name: CIGS
 Description: CL Quant
 Real time [s]: 110.558
 Life time [s]: 51.663
 Specification in... Mass-% Atomic-%
 Use data from.. [dropdown]
 Element | Atom conc. [%] | Error [%]
 Chromium | [] | []
 Iron | [] | []
 Nickel | [] | []
 Copper | [] | 21
 Gallium | [] | 7
 Selenium | [] | 45
 Indium | [] | 22
 Platinum | [] | []

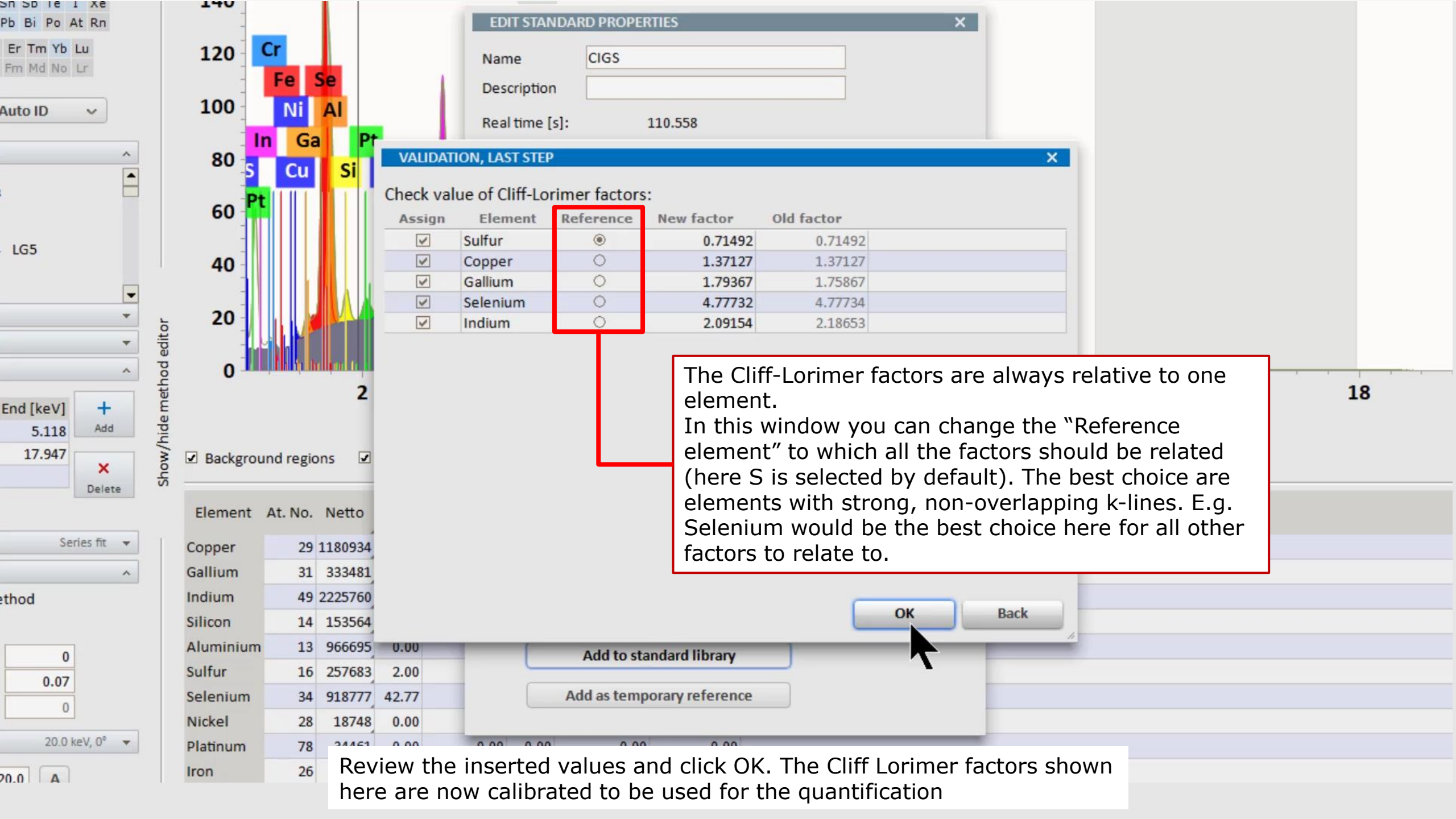
Sum of concentrations [%]: **100.00%**

Add to standard library
 Add as temporary reference



Element	At. No.	Netto	Mass [%]	Mass [%]
Copper	29	1180934	15.92	
Gallium	31	333481	5.71	
Indium	49	2225760	33.60	
Silicon	14	153564	0.00	
Aluminium	13	966695	0.00	
Sulfur	16	257683	2.00	
Selenium	34	918777	42.77	
Nickel	28	18748	0.00	
Platinum	78	34461	0.00	0.00
Iron	26	37	0.00	0.00

Known concentration of the elements is added manually for the experimental calibration of Cliff-Lorimer factors



The Cliff-Lorimer factors are always relative to one element. In this window you can change the "Reference element" to which all the factors should be related (here S is selected by default). The best choice are elements with strong, non-overlapping k-lines. E.g. Selenium would be the best choice here for all other factors to relate to.

Review the inserted values and click OK. The Cliff Lorimer factors shown here are now calibrated to be used for the quantification

Zeta-Factor Quantification method for e-transparent samples

Settings

Elements

Clear all Auto ID

Element finder: Mo, Pa, Cf

Element overview list

Standards

Background settings

SEM
 TEM
 Math

	Start [keV]	End [keV]
1	2.528	2.668
2	10.717	10.807
3	13.057	15.257
4		

Auto Delete

Deconvolution settings: Series fit

Quantification model

P/B - ZAF
 Zeta factor method
 Phi(Rho,Z)
 Cliff-Lorimer

Use standards
 P/B film

Layer density [g/cm³]: 0
 Layer thckn. [μm]: 0.05
 Substrate (mean. AN): 0

Additional settings: 20.0 keV, 0°

Description: automatic element identification, quantification with P/B-ZAF

Load Save To project Apply

Results

Background regions
 Element lines
 Dynamic lines

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Selenium	34	1588855	43.17	43.17	44.52	0.13	0.30
Indium	49	3990205	33.26	33.26	23.59	0.05	0.16
Copper	29	2029122	16.17	16.17	20.72	0.03	0.20

Area density: 42.990 μg/cm²

Density: 5.81 g/cm³ Thickness: **74.00 nm**

Continue with Zeta- Quant only, if you have calculated the Cliff-Lorimer factors before theoretically (using the voltage and angle settings of the measurement) or additionally experimentally, using data from a representative standard spectrum out of the HyperMap. See before in this pdf or the manual for details on this (also shown on slide 26).

In the quanification window, change the quant model to Zeta factor method. Thickness is calculated automatically from the elements present in the spectrum. Then, click "Add to standards" to calculate zeta-factors.

Settings

Elements

Element finder: Mo,Pa,Cf

Element overview list

Standards

Background settings

- SEM
- TEM
- Math

	Start [keV]	End [keV]
1	2.528	2.668
2	10.717	10.807
3	13.057	15.257
4		

Deconvolution settings: Series fit

Quantification model

- P/B - ZAF
- Zeta factor method
- Phi(Rho,Z)
- Cliff-Lorimer

Use standards

- P/B film

Layer density [g/cm³]: 0

Layer thckn. [μm]: 0.05

Substrate (mean. AN): 0

Additional settings: 20.0 keV, 0°

Description: automatic element identification, quantification with P/B-ZAF

Buttons: Load, Save, To project, Apply

Name: CIGS-ZETA

Description: 20kV-1.9nA

Real time [s]: 188.637

Life time [s]: 83.880

Specification in... Mass-% Atomic-%

Use data from..

Element	Atom conc. [%]	Error [%]
Sulfur	4.69	
Chromium		
Iron		
Nickel		
Copper	20.72	
Gallium	6.49	
Selenium	44.52	
Indium	23.58	

Sum of concentrations [%]: 100.00%

Thickness [nm]: 74

Density [g/cm³]: 5.81

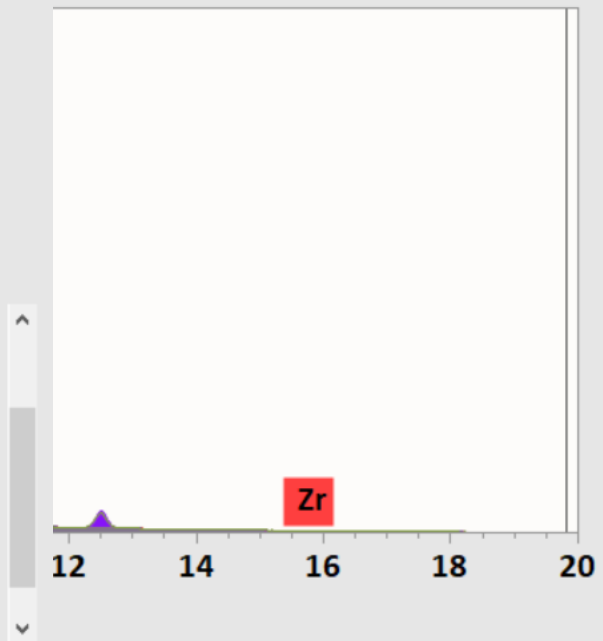
Beam current [pA]: 1960

Buttons: Add to standard library, Add as temporary reference

	28	34787	0.00	0.00	0.00	0.00	0.00
Nickel							
Iron							

Area density: 42.990 μg/cm²

Density: 5.81 g/cm³ Thickness: 74.00 nm



Fact I/O

- All
- Orig. 1.00
- Bkg. 1.00
- Se 1.00
- In 1.00
- Cu 1.00
- Ga 1.00
- S 1.00
- Al 1.00
- Ni 1.00
- Fe 1.00
- Cr 1.00
- Zr 1.00
- Pt 1.00
- Si 1.00
- O 1.00
- Deconv. 1.00

Buttons: Zoom, Scale, Options, Delete

6]

30

1.6

20

14

19

10

Buttons: I/O, Cx, Coat, Depth, Options

Enter the beam current value in pA

Settings

Elements

Clear all Auto ID

Element finder: Mo,Pa,Cf

Element overview list

Standards

Background settings

- SEM
- TEM
- Math

	Start [keV]	End [keV]
1	2.528	2.668
2	10.717	10.807
3	13.057	15.257
4		

Auto Delete

Deconvolution settings: Series fit

Quantification model

- P/B - ZAF
- Zeta factor method
- Phi(Rho,Z)
- Cliff-Lorimer

Use standards

- P/B film

Layer density [g/cm³]: 0

Layer thckn. [μm]: 0.05

Substrate (mean. AN): 0

Additional settings: 20.0 keV, 0°

EDIT STANDARD PROPERTIES

Name: CIGS-ZETA

Description: 20kV-1.9nA

Real time [s]: 188.637

Life time [s]: 83.880

Specification in... Mass-% Atomic-%

Use data from..

Element	Atom conc. [%]	Error [%]
Sulfur	5	
Chromium		
Iron		
Nickel		
Copper	21	
Gallium	7	
Selenium	45	
Indium	22	

Sum of concentrations [%]: 100.00%

Thickness [nm]: 74

Density [g/cm³]: 5.77

Beam current [pA]: 1960

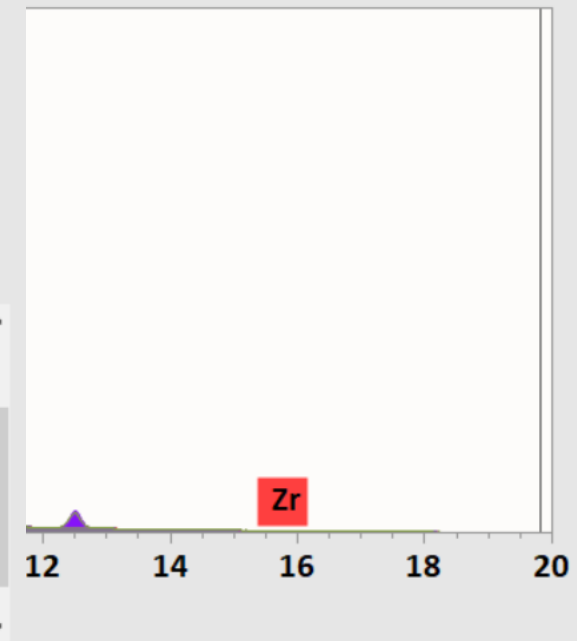
Add to standard library

Add as temporary reference

NICKEL	28	34/8/	0.00	0.00	0.00	0.00	0.00
Iron	26	62700	0.00	0.00	0.00	0.00	0.00

Area density: 42.990 μg/cm²

Density: 5.81 g/cm³ Thickness: 74.00 nm



All Fact

- Orig. 1.00
- Bkg. 1.00
- Se 1.00
- In 1.00
- Cu 1.00
- Ga 1.00
- S 1.00
- Al 1.00
- Ni 1.00
- Fe 1.00
- Cr 1.00
- Zr 1.00
- Pt 1.00
- Si 1.00
- O 1.00
- Deconv. 1.00

I/O Zoom Scale Options Delete

6]
30
16
20
34
39
30

I/O Cx Coat Depth Options

Description: automatic element identification, quantification with P/B-ZAF

Settings

Elements

Clear all Auto ID

Element finder Mo,Pa,Cf

Element overview list

Standards

Background settings

SEM TEM Math

	Start [keV]	End [keV]
1	2.528	2.668
2	10.717	10.807
3	13.057	15.257
4		

Auto

Deconvolution settings Series fit

Quantification model

P/B - ZAF Zeta factor method

Phi(Rho,Z) Cliff-Lorimer

Use standards

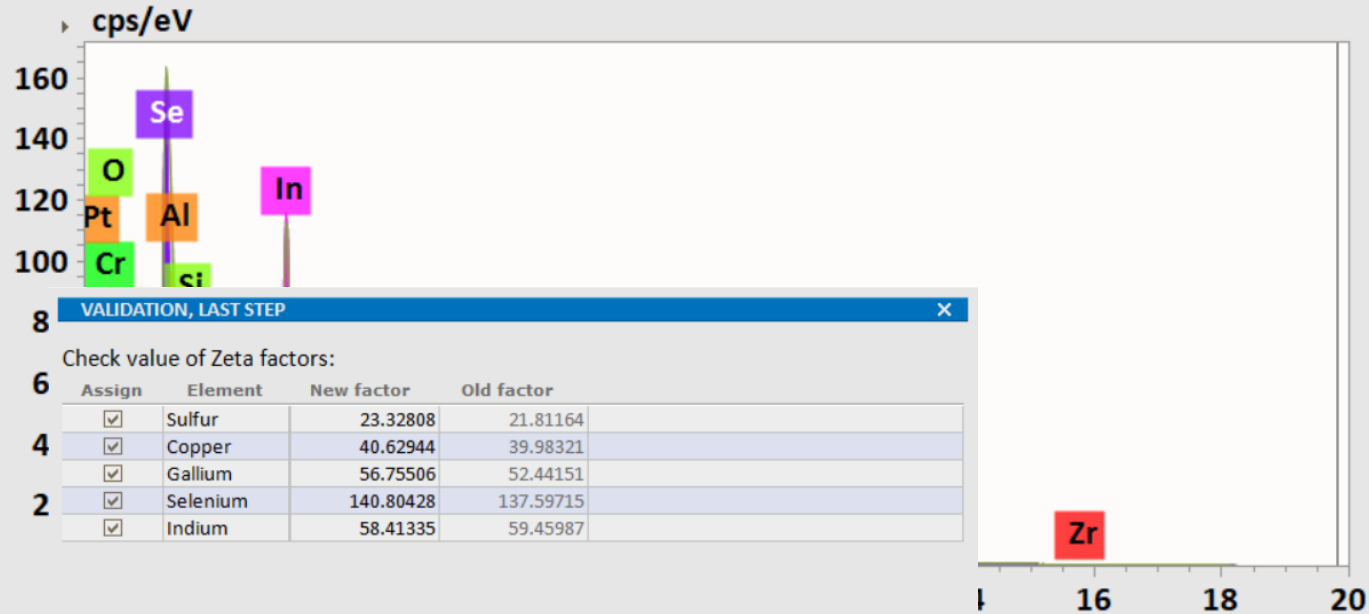
P/B film Layer density [g/cm³] 0

Layer thckn. [μm] 0.05

Substrate (mean. AN) 0

Additional settings 20.0 keV, 0°

Results



8 VALIDATION, LAST STEP

6 Check value of Zeta factors:

Assign	Element	New factor	Old factor
<input checked="" type="checkbox"/>	Sulfur	23.32808	21.81164
<input checked="" type="checkbox"/>	Copper	40.62944	39.98321
<input checked="" type="checkbox"/>	Gallium	56.75506	52.44151
<input checked="" type="checkbox"/>	Selenium	140.80428	137.59715
<input checked="" type="checkbox"/>	Indium	58.41335	59.45987

All Fact

Orig. 1.00

Bkg. 1.00

Se 1.00

In 1.00

Cu 1.00

Ga 1.00

S 1.00

Al 1.00

Ni 1.00

Fe 1.00

Cr 1.00

Zr 1.00

Pt 1.00

Si 1.00

O 1.00

Deconv. 1.00

I/O Zoom Scale Options Delete

Show/hide method editor

In this case, zeta factors have been calculated before. So changes between "old" and "new" factor are small. Originally the zeta-factors would change from the Cliff-Lorimer factors. See also next slides.

Area density: 42.990 μg/cm²

Density 5.81 g/cm³ Thickness 74.00 nm

Element	Area	Factor	Old Factor	Ratio	Depth	Coat
Selenium	140.80428	1.00	1.00	0.49	0.02	0.34
Indium	58.41335	1.00	1.00	0.01	0.01	0.39
Copper	40.62944	1.00	1.00	0.00	0.00	0.00
Gallium	56.75506	1.00	1.00	0.00	0.00	0.00
Sulfur	23.32808	1.85	1.85	0.00	0.00	0.00
Aluminium	16.34748	0.00	0.00	0.00	0.00	0.00
Nickel	28.34787	0.00	0.00	0.00	0.00	0.00
Iron	26.62708	0.00	0.00	0.00	0.00	0.00

OK Back

CIGS-2a(mod.)

Date: 29/09/2020 Elevation angle: 48.0° WDS elevation angle: 0.0°
 High voltage: 20.0 keV Azimuth angle: 45.0° WDS azimuth angle: 0.0°
 Calibration: Copper reference Tilt angle: 0.0°
 Standards: 3 Beam entrance angle: 42.0°

Bulk Electron transp.

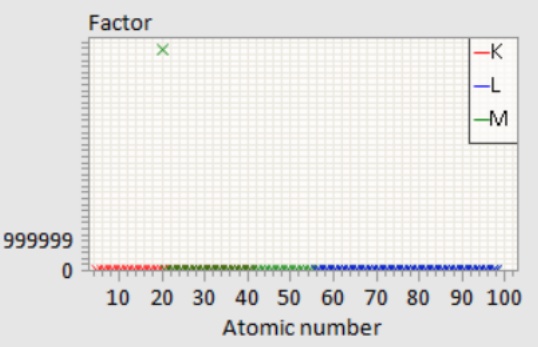
Cliff-Lorimer factors Zeta factors

Legend: 0.000 - Undefined data
 1.234 - Calculated data from theory
 1.234 - Calibrated data

Export

AN	EL.	K	L	M
29	Cu	40.629	53.027	0.000
30	Zn	1.667	22.798	0.000
31	Ga	56.755	14.414	0.000
32	Ge	2.383	8.386	0.000
33	As	2.849	5.823	0.000
34	Se	140.804	4.259	0.000
35	Br	4.202	2.224	0.000

Se..	Ref.	Standard
K		
L		
M		

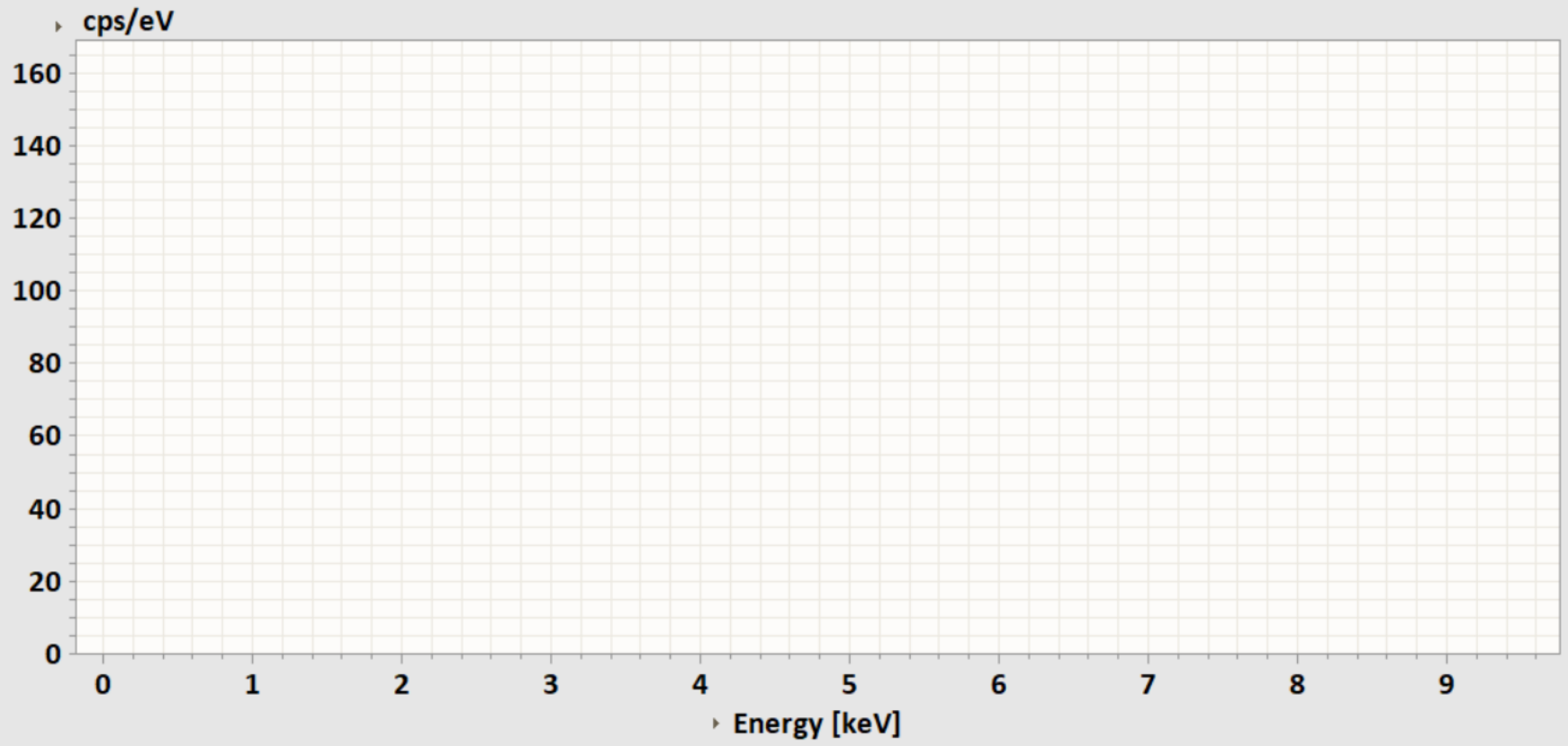


Scale

Reset **Fit to Stds**

Validate

EDS Default



All cps/eV Factor Certification values [Mass-%] Sort: Element

I/O

I/O

Elements

Search

Zoom

Scale

Delete

Options

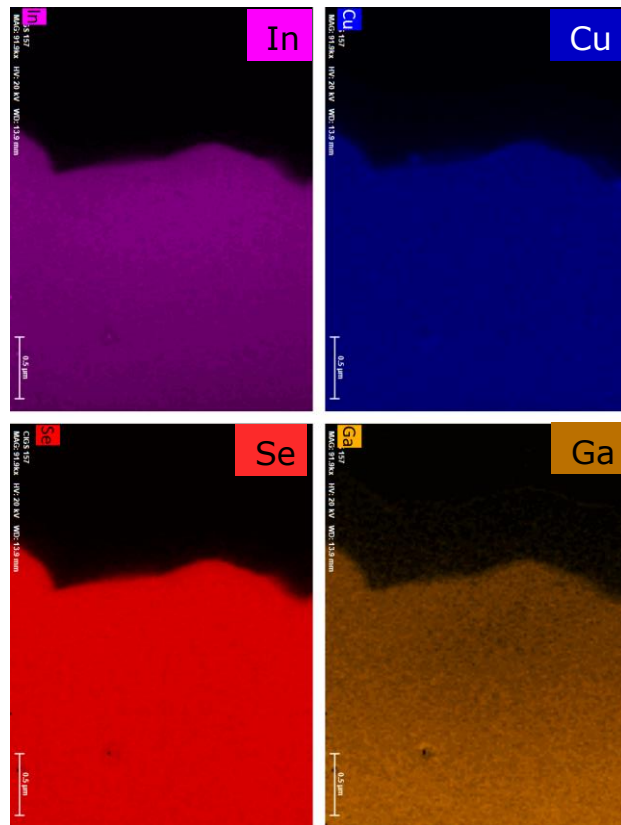
In the standards library, In RED, you can now see the calibrated Zeta factors for the given beam current. You can then click "fit to standards" to interpolate the theoretical zeta factors for other elements for the given e-beam conditions using the Cliff-Lorimer factors calculated before.

Application example: Cu(In,Ga)Se₂ solar cell (contd...)

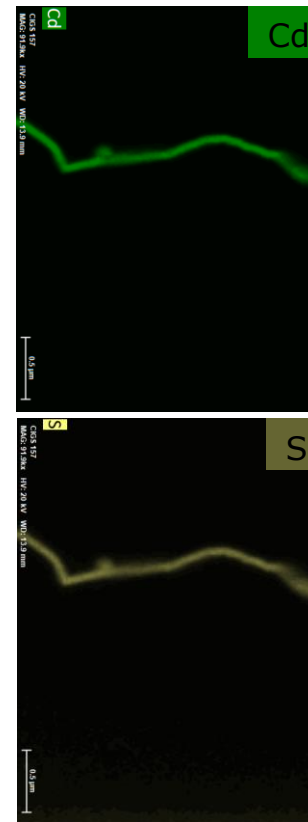
Quantified map in atomic %



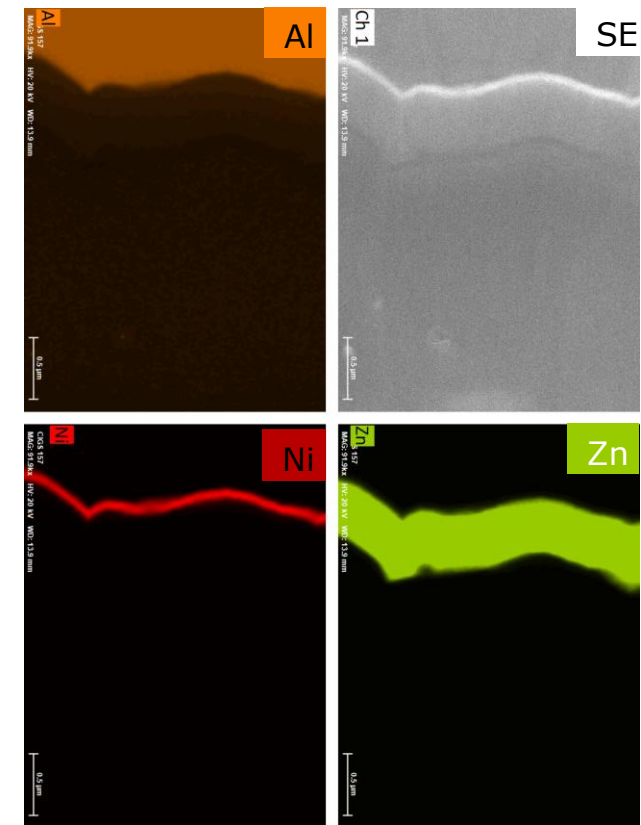
Cu(In,Ga)Se₂



CdS



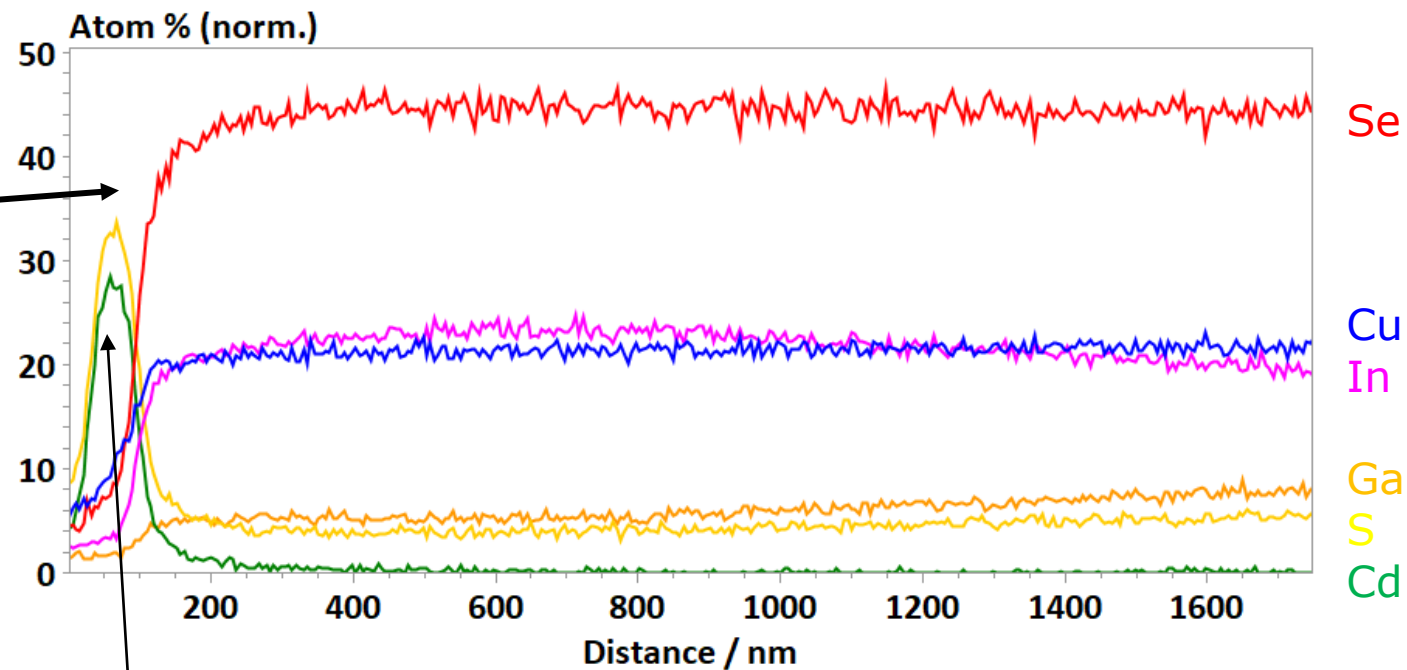
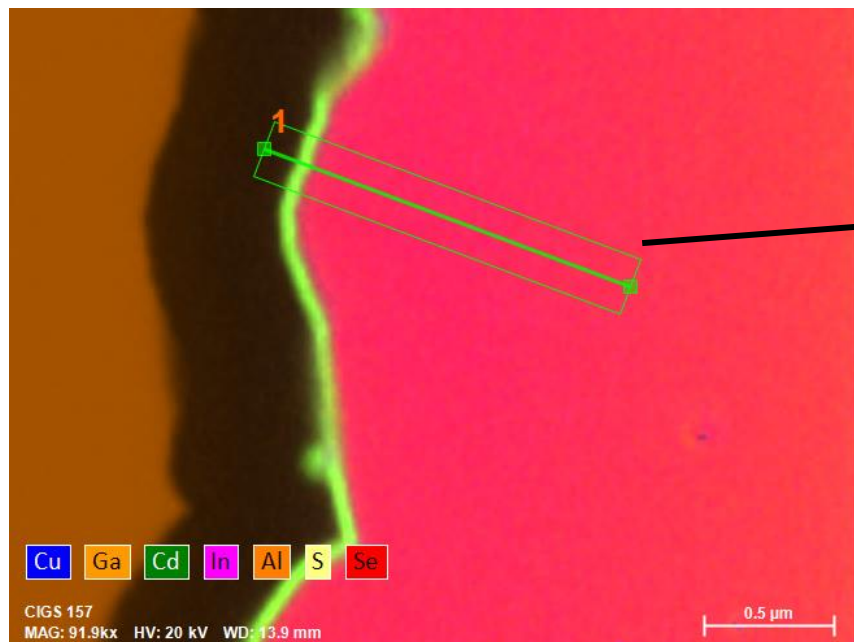
External contacts



(Cliff-Lorimer quantification)

Application example: Cu(InGa)Se₂ solar cell

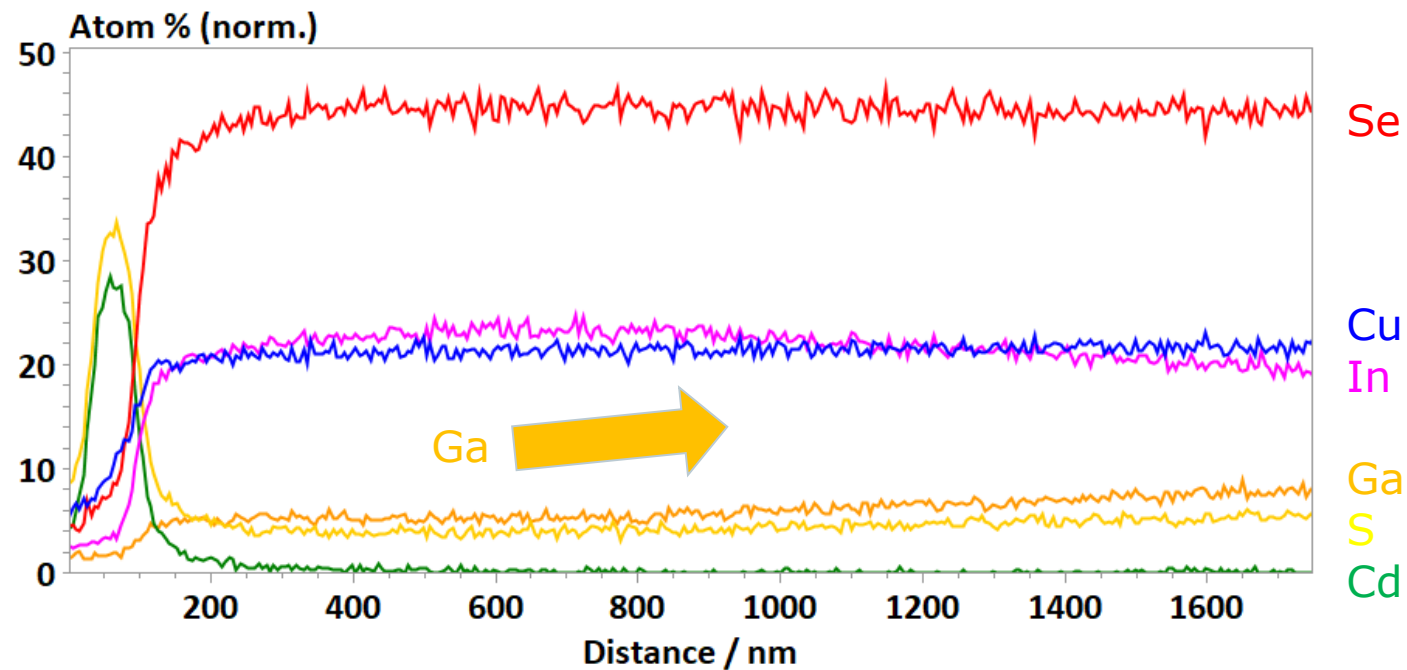
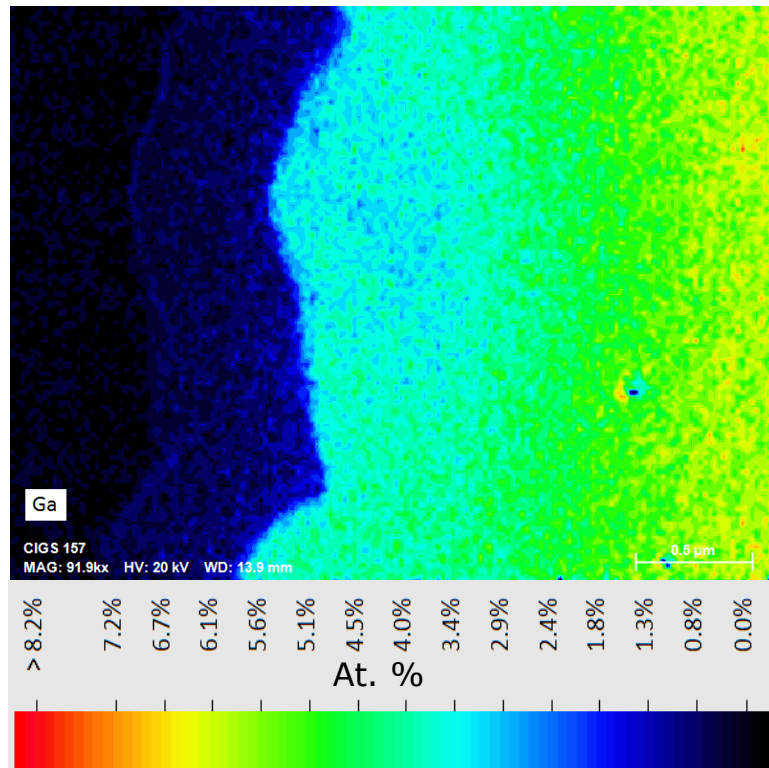
EDS Line scan in Atomic %



Thin CdS buffer layer (~60-80 nm)

Application example: Cu(InGa)Se₂ solar cell

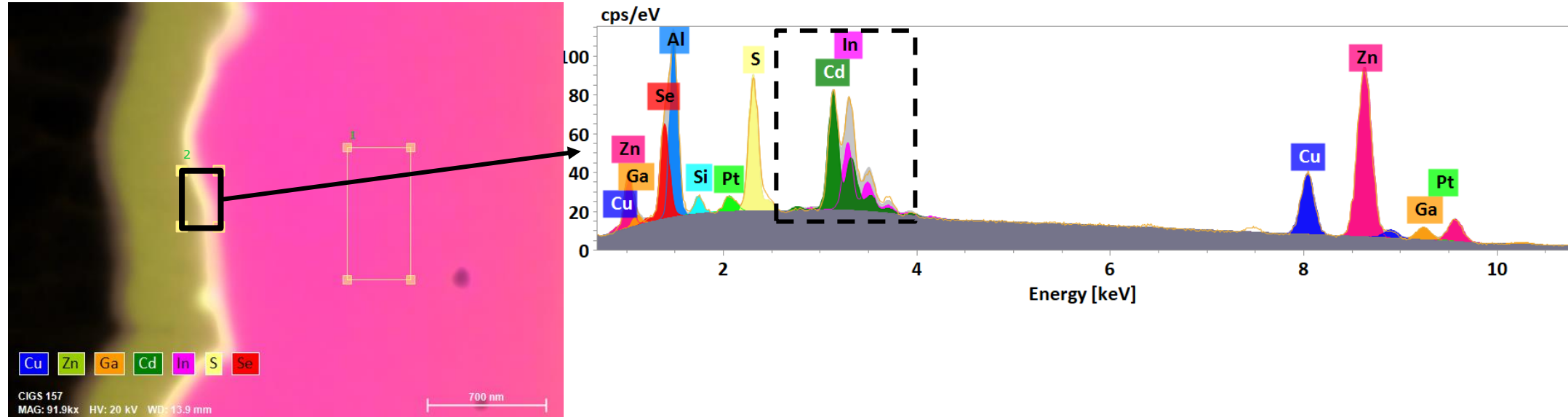
EDS Line scan in Atomic %



Ga grading in CIGS absorber detected by EDS

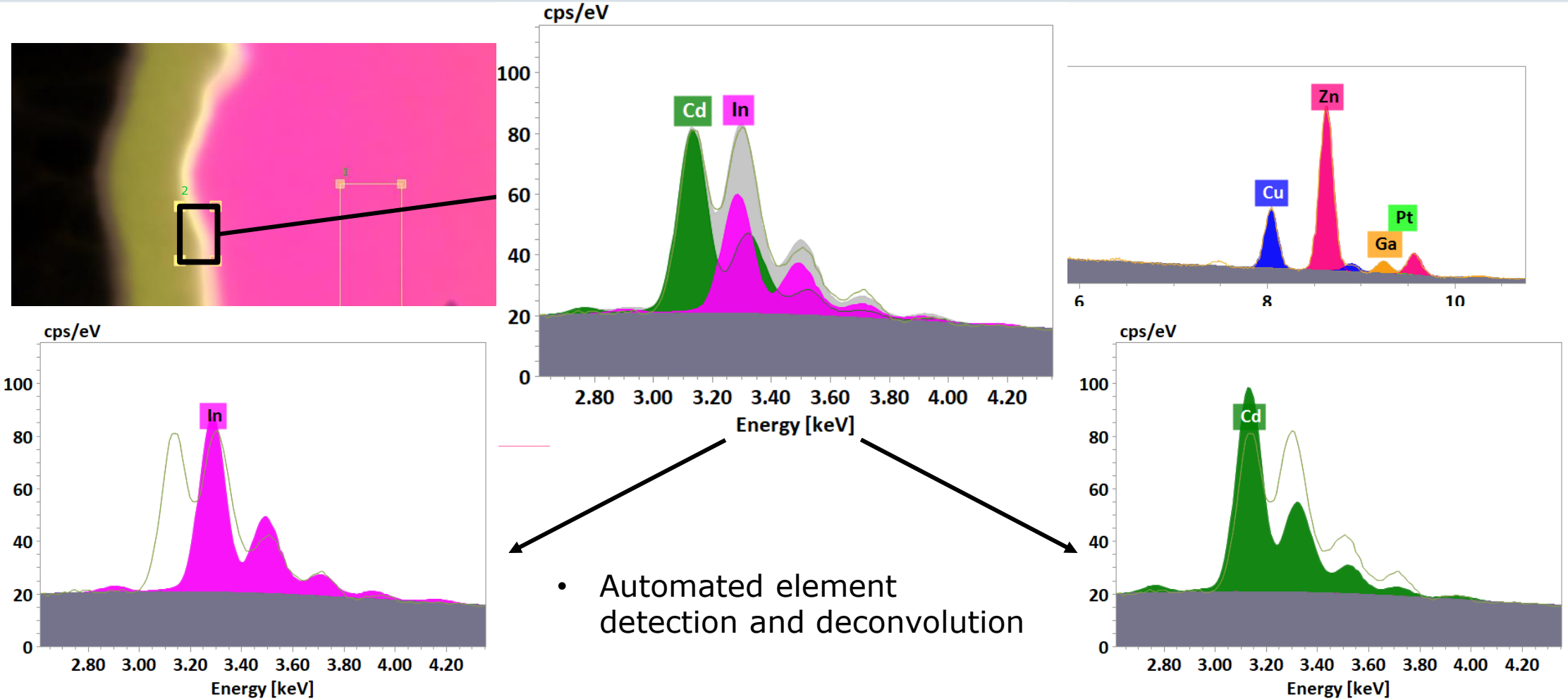
Application example: Cu(In,Ga)Se₂ solar cell

EDS mapping – automated peak deconvolution

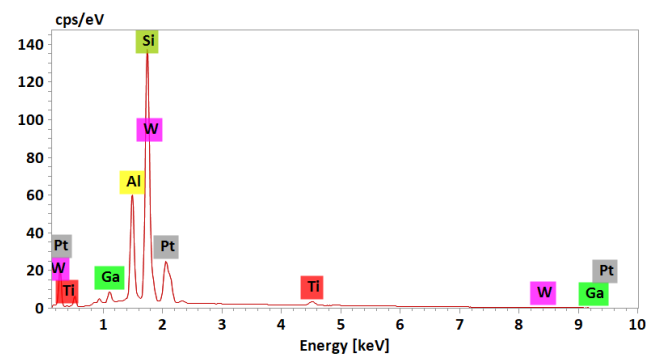


Application example: Cu(In,Ga)Se₂ solar cell

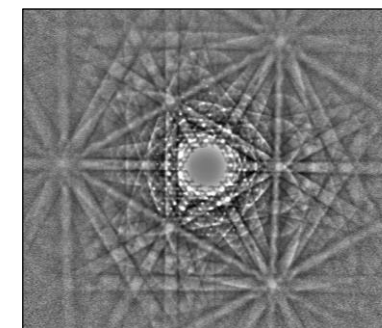
EDS mapping – automated peak deconvolution



Simultaneous chemical (EDS) and microstructural (TKD) characterization



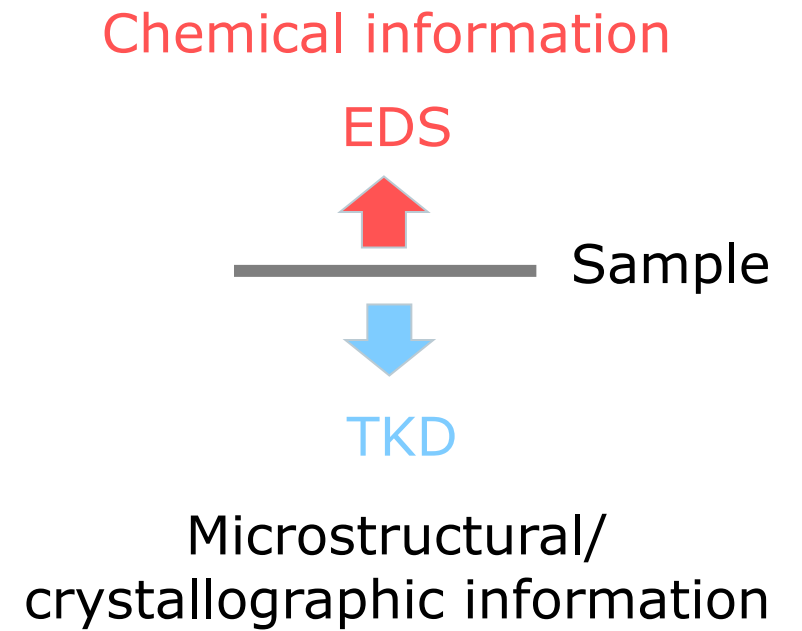
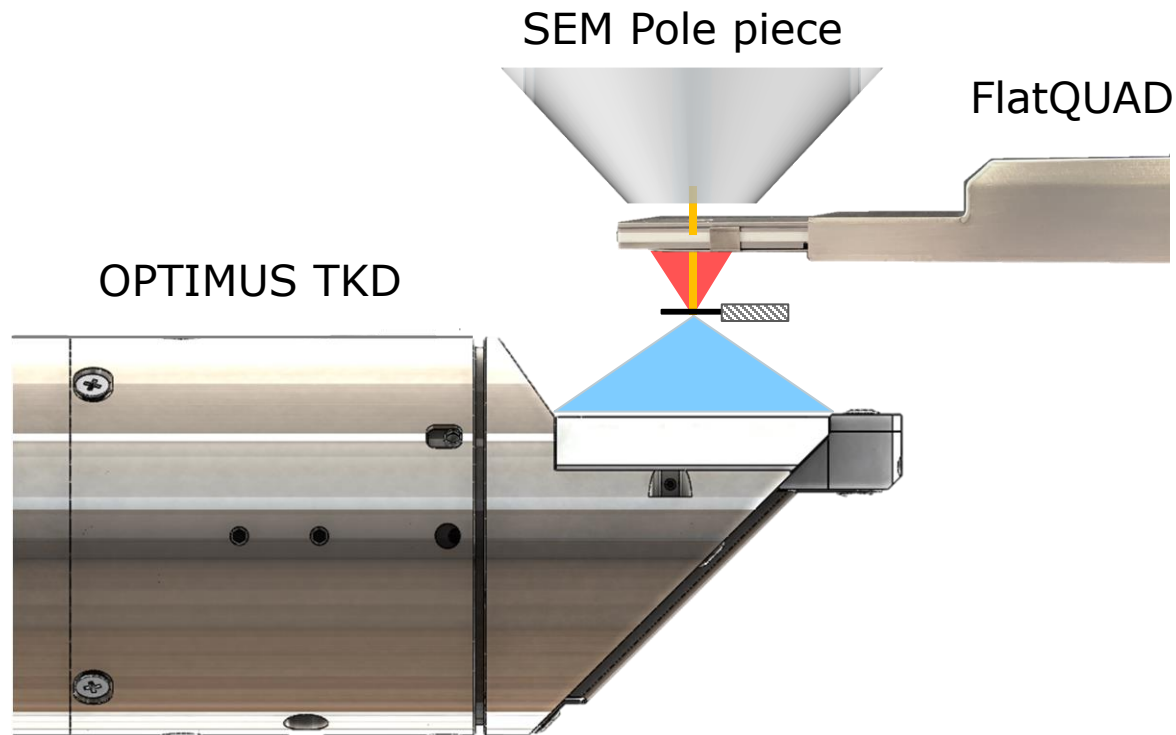
EDS spectrum



Kikuchi pattern

EDS/TKD simultaneous measurement

XFlash FlatQUAD with OPTIMUS™ TKD

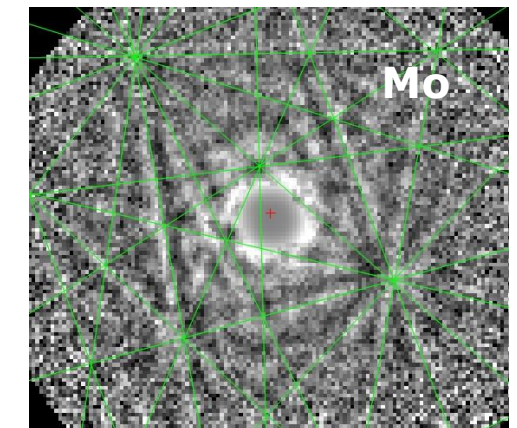
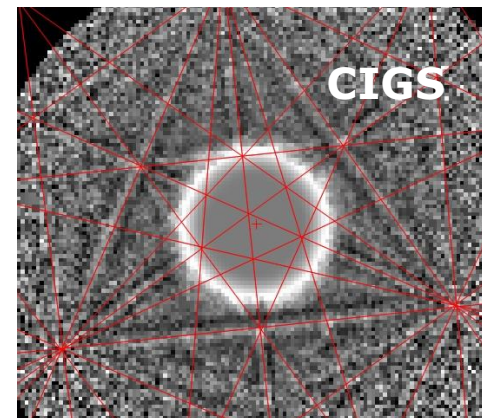
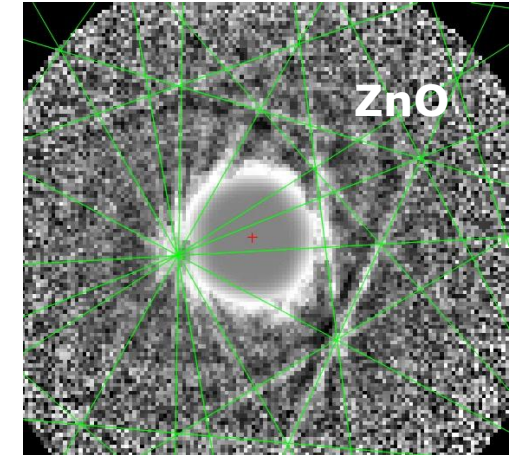
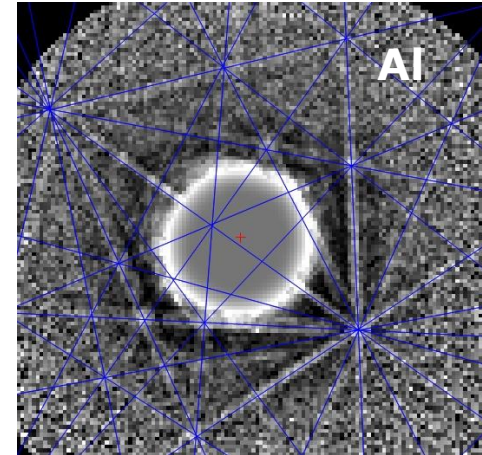
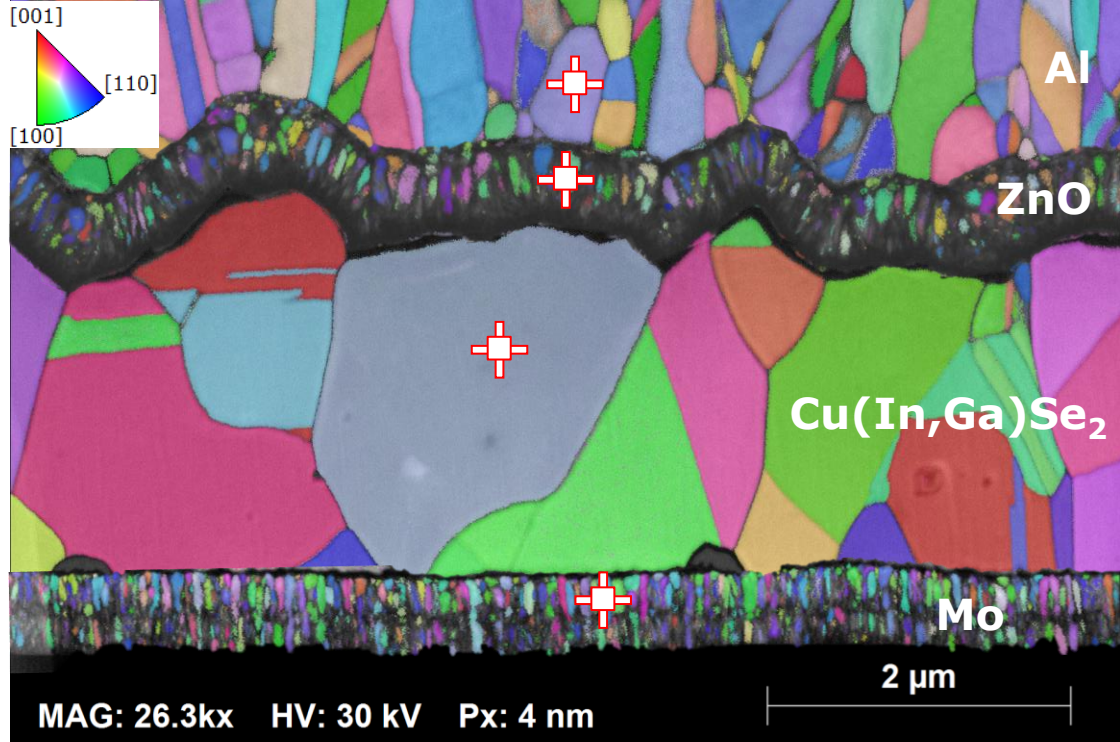


Application example: $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ solar cell

Crystallographic and orientational mapping using OPTIMUS TKD



IPF-Z map

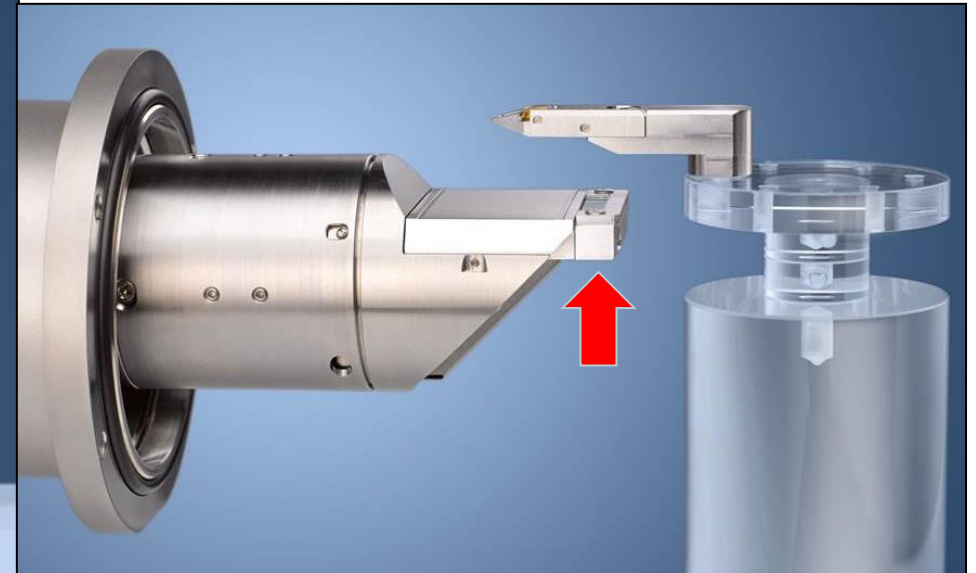
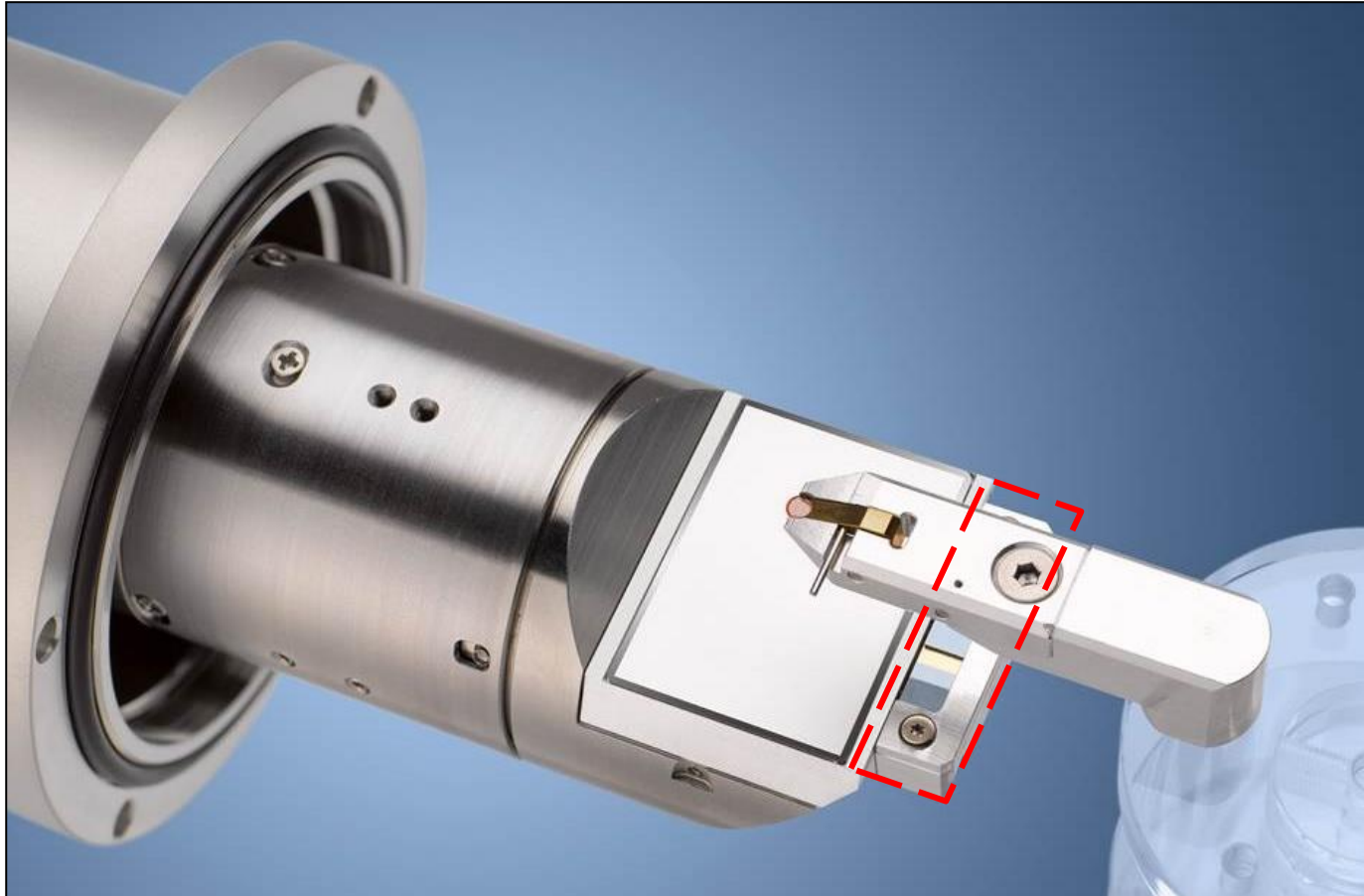


Mapping parameters:

- 30kV; 1.6 nA; Step size: 4nm
- Acq. speed: 330 fps; **Map size: 1.93 million pixels**

ARGUS imaging

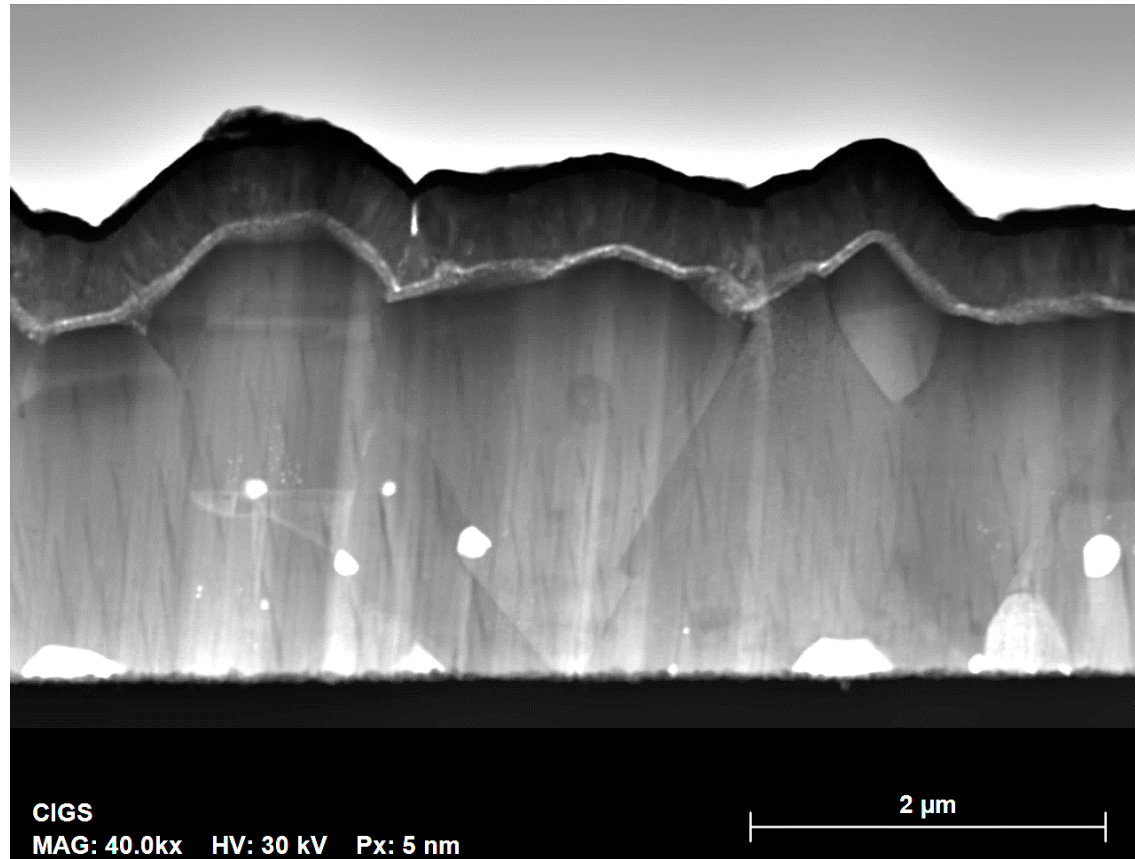
Color coded orientation contrast imaging



3x ARGUS diodes for STEM-like
DF and BF imaging for e^-
transparent sample

ARGUS imaging

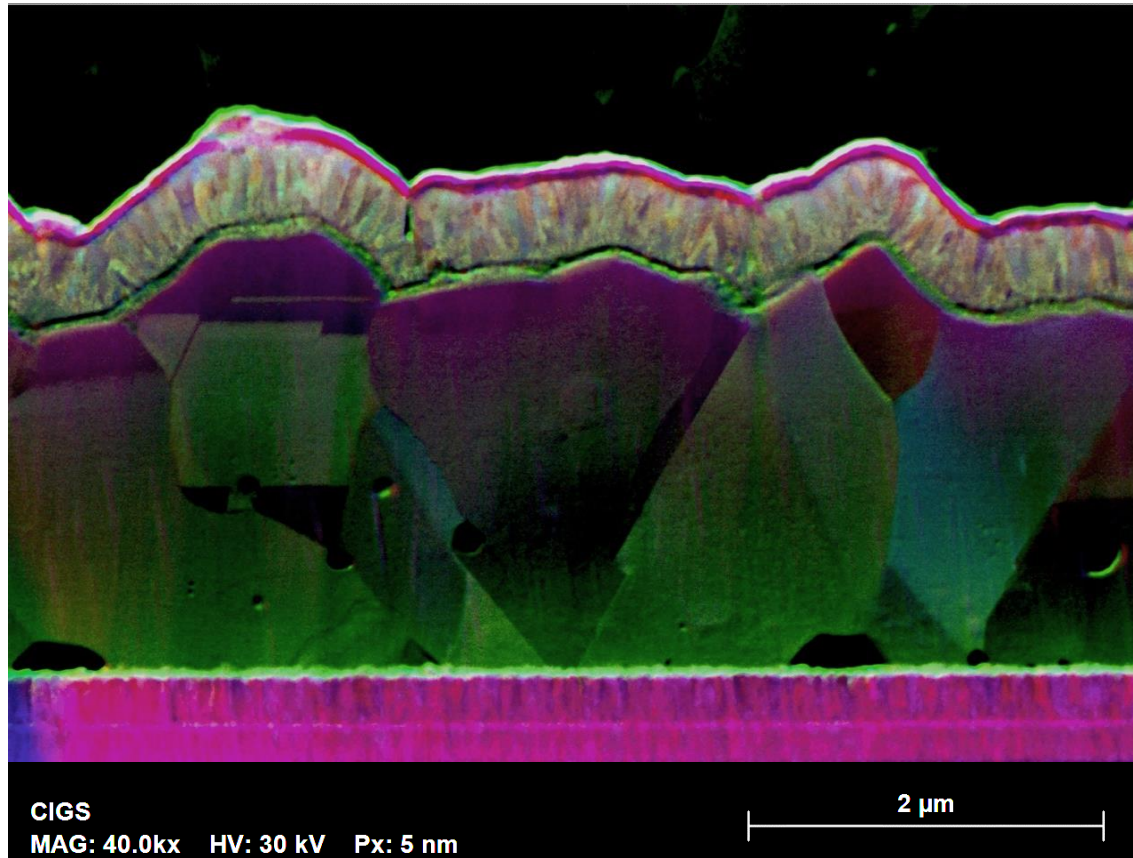
Color coded orientation contrast imaging



- Bright field mode imaging (direct detection)

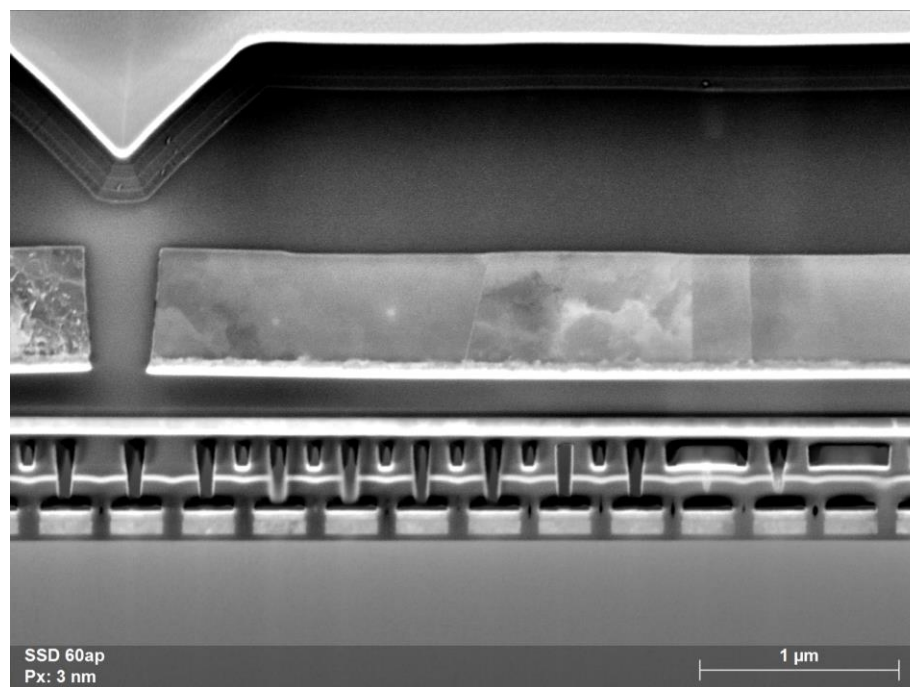
ARGUS imaging

Color coded orientation contrast imaging



- Color coded dark field-like imaging (High angle scattered signal)

Application example: SSD

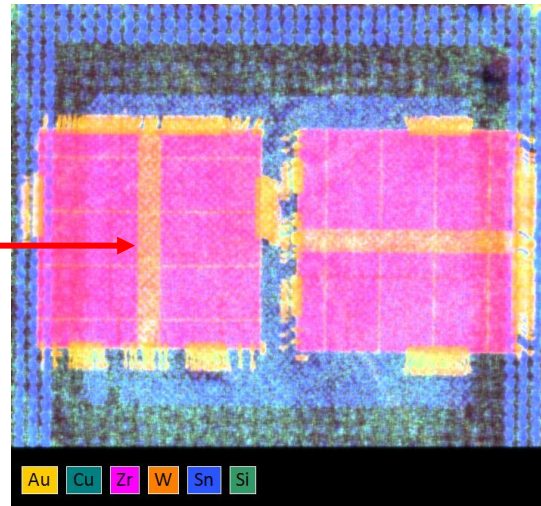
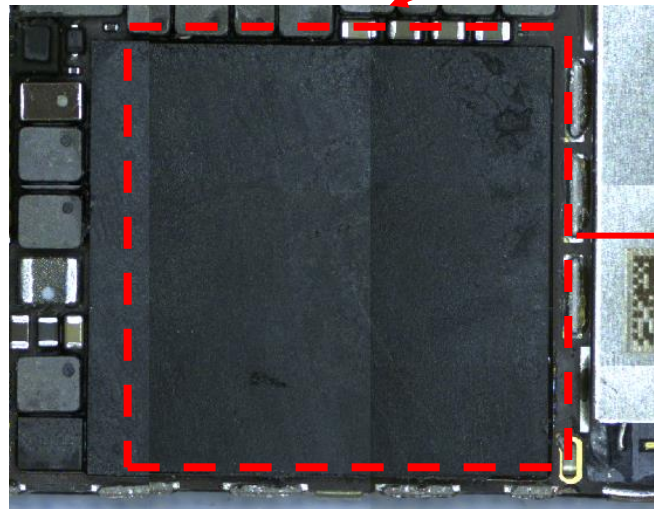
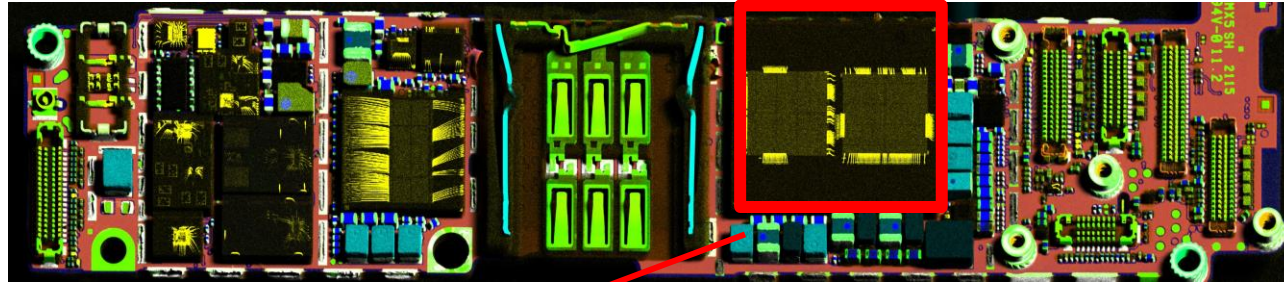


Large area mapping

Locating region of interest using μ -XRF



Smartphone motherboard μ -XRF map



- Large area mapping using μ -XRF



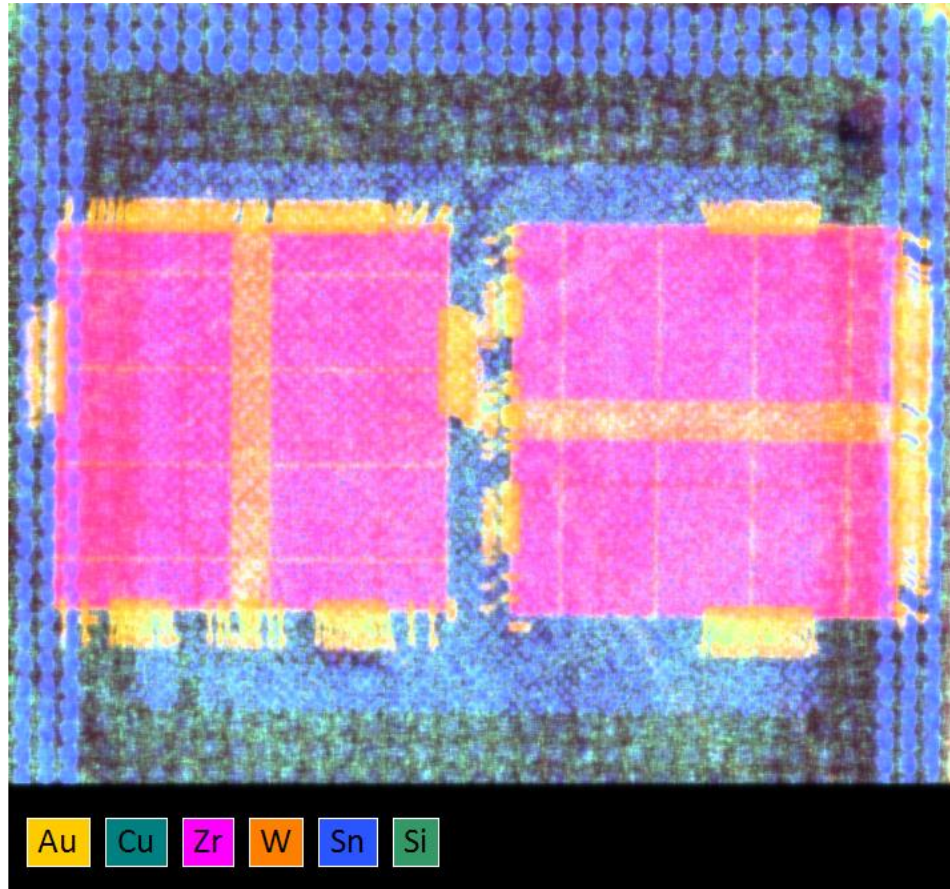
- Locating the area for lift out on the sample

Large area mapping

Locating region of interest using μ -XRF



Smartphone motherboard μ -XRF map



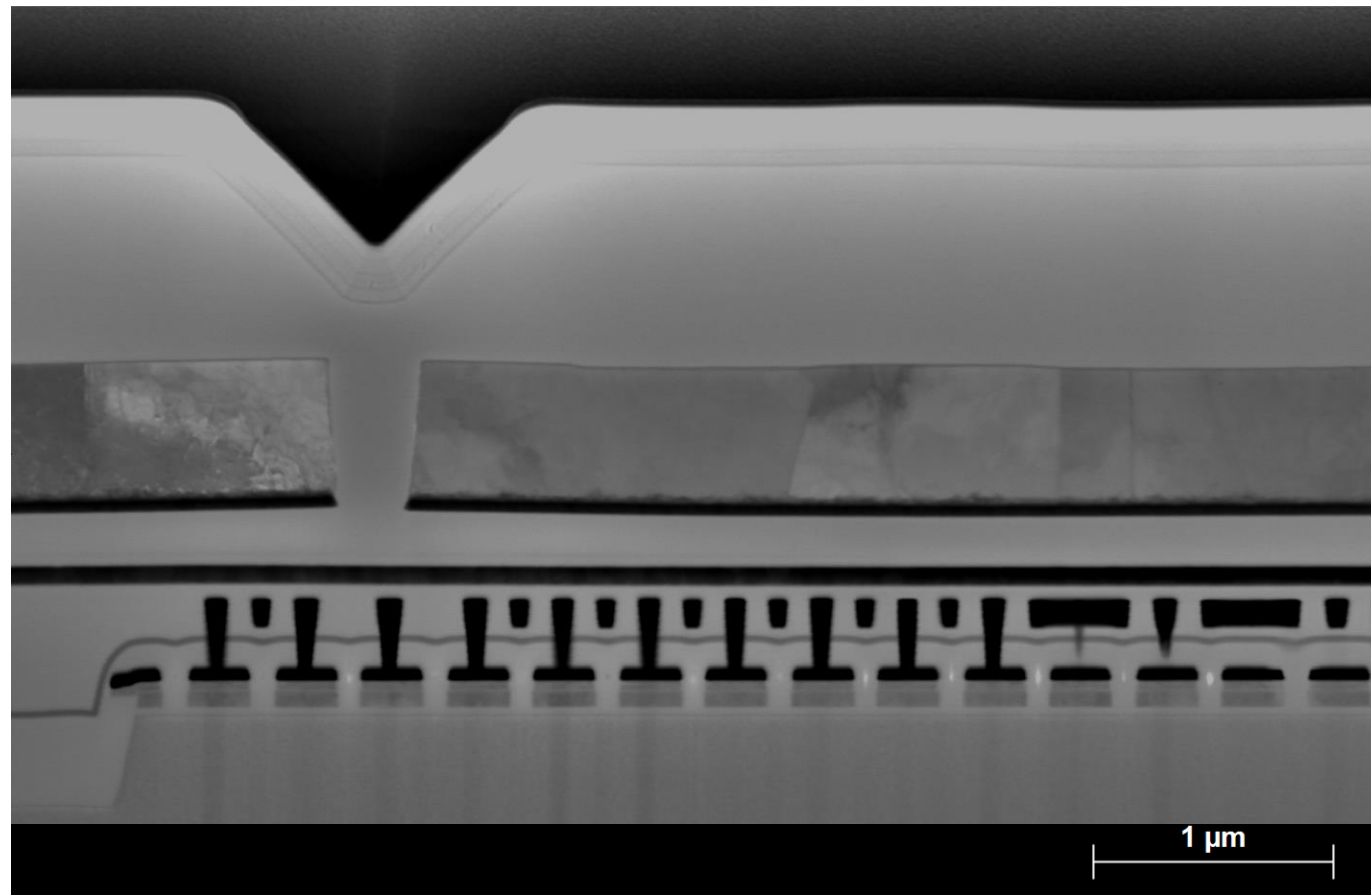
- Large area mapping using μ -XRF



- Locating the area for lift out on the sample

Application example: SSD

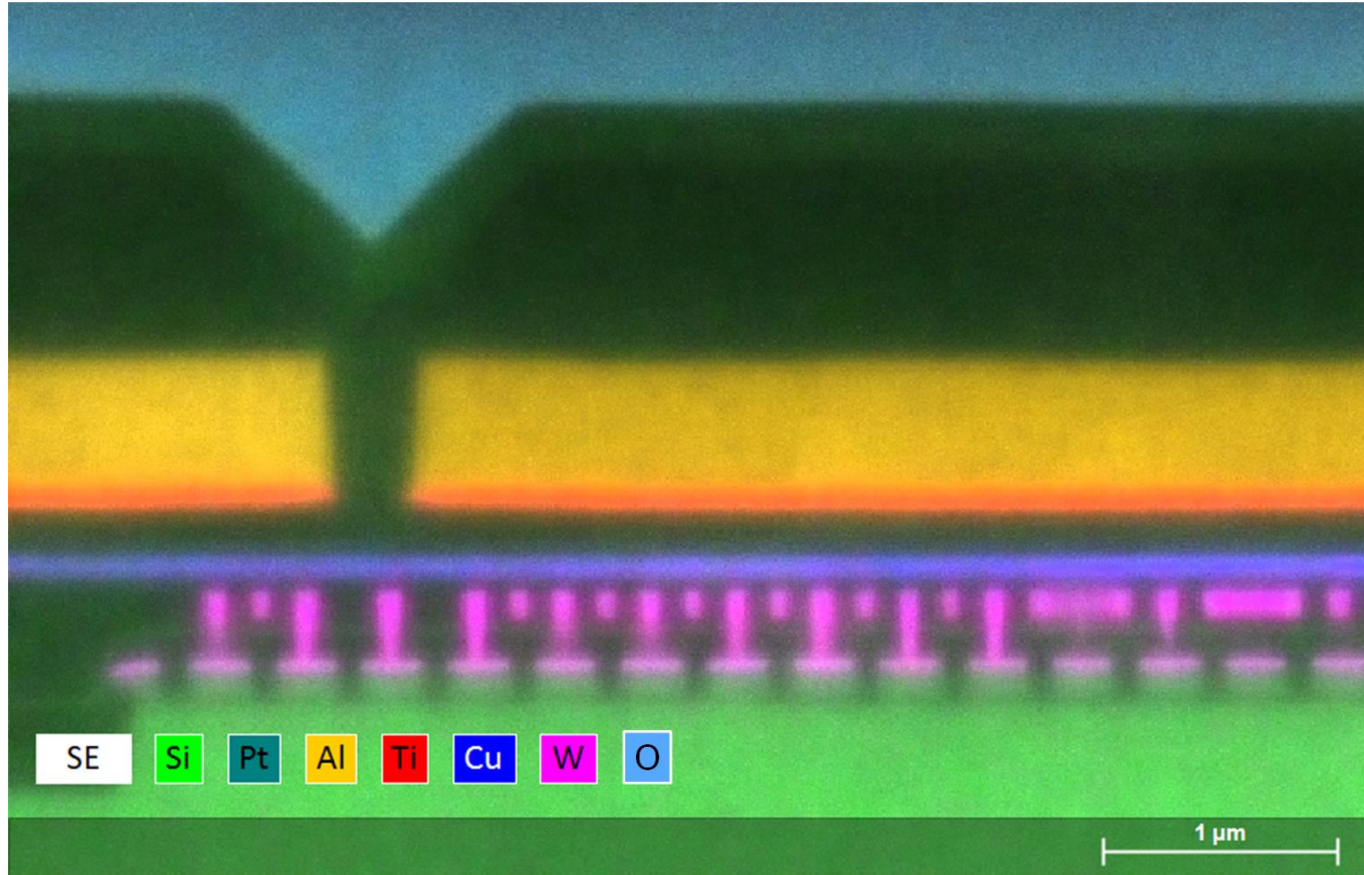
EDS mapping – individual element profile



STEM Bright field

Application example: SSD

EDS mapping – individual element profile



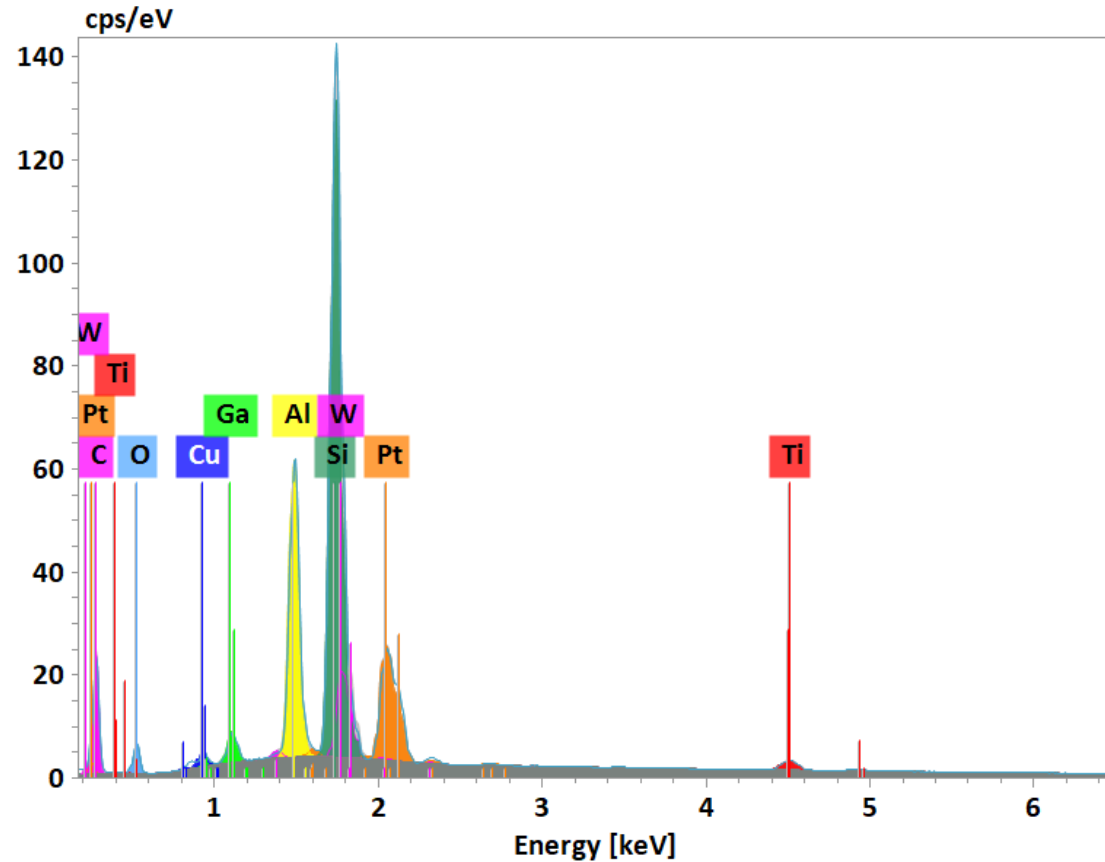
EDS map

EDS mapping parameters:

- High voltage: 10 kV
- Abs. current: 410 pA
- WD: 9 mm
- Mag: 35,000 x
- **Map time: 300 s**
- Map size: 800 × 533 px
- Input counts: 86.6 Kcps
- Output counts: 36.1 Kcps
- **Total counts: 1.08E+07 (10.8 M)**

Application example: SSD

EDS mapping – Spectrum and mapping details

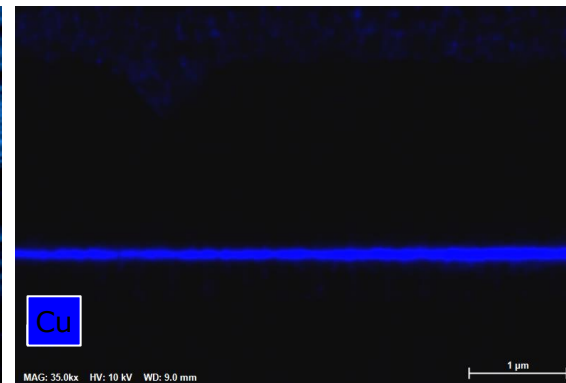
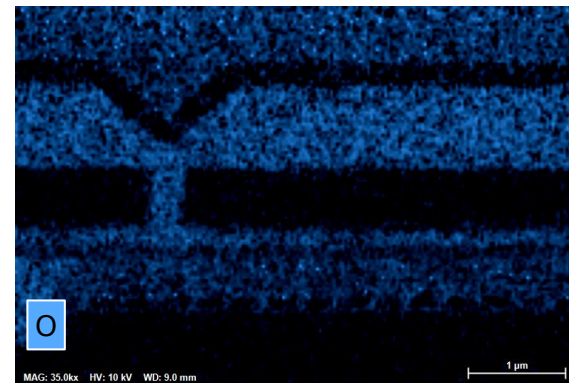
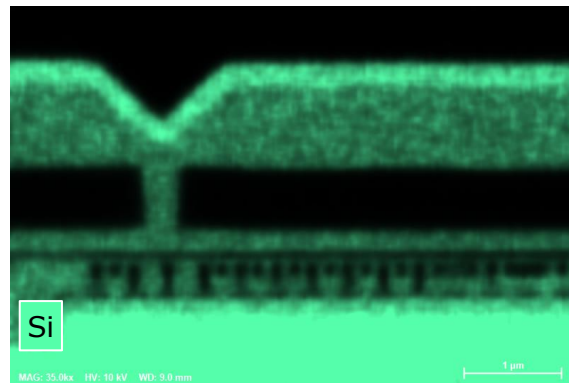
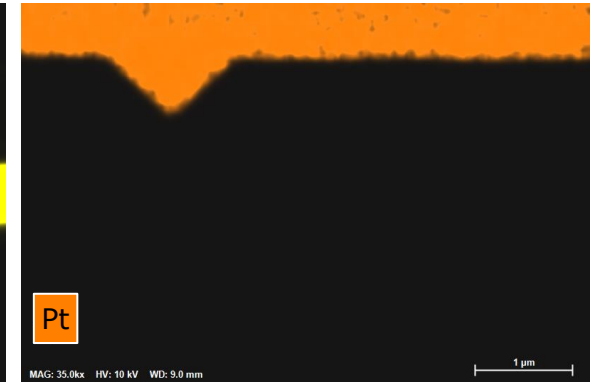
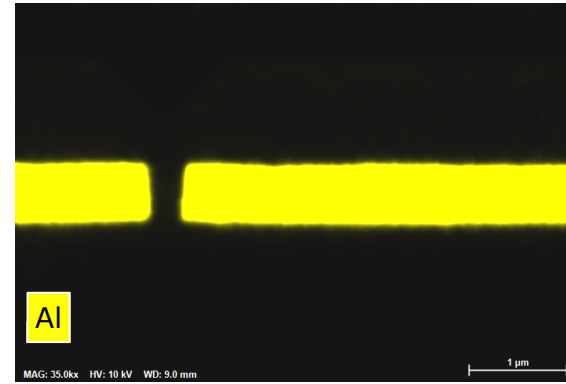
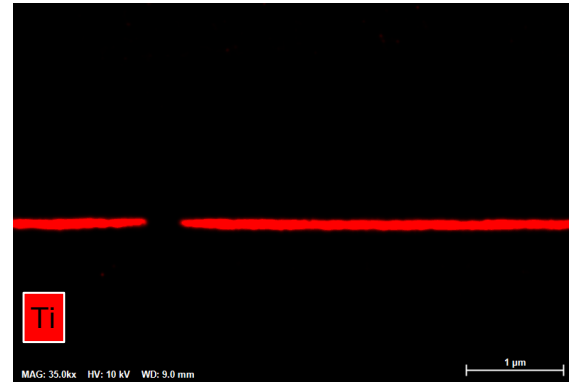
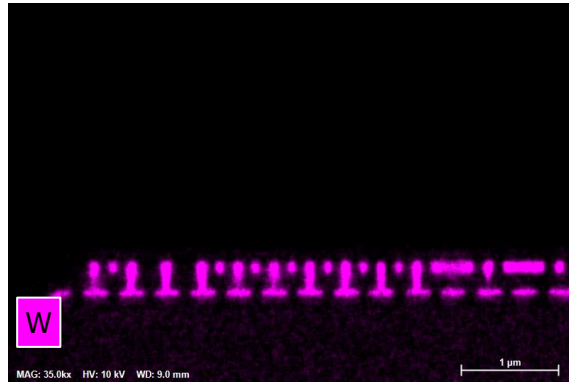


EDS mapping parameters:

- High voltage: 10 kV
- Abs. current: 410 pA
- WD: 9 mm
- Mag: 35,000 x
- **Map time: 300 s**
- Input counts: 86.6 Kcps
- Output counts: 36.1 Kcps
- **Total counts: 1.08E+07 (10.8 M)**

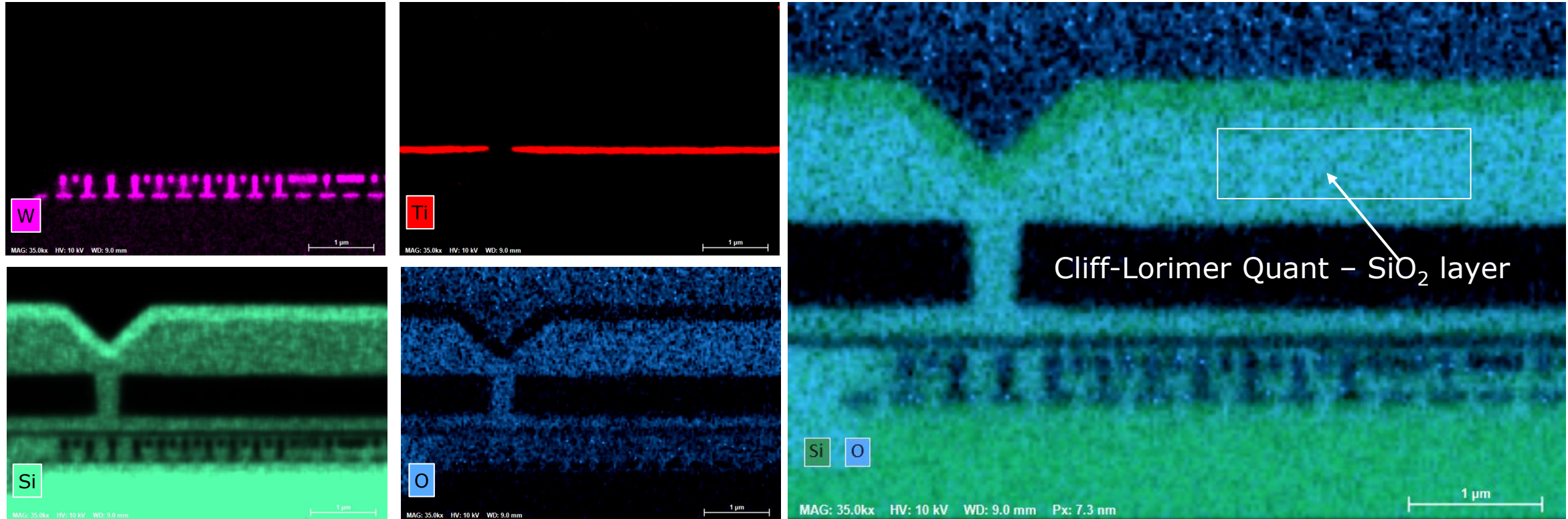
Application example: SSD

Quantified map in atomic %



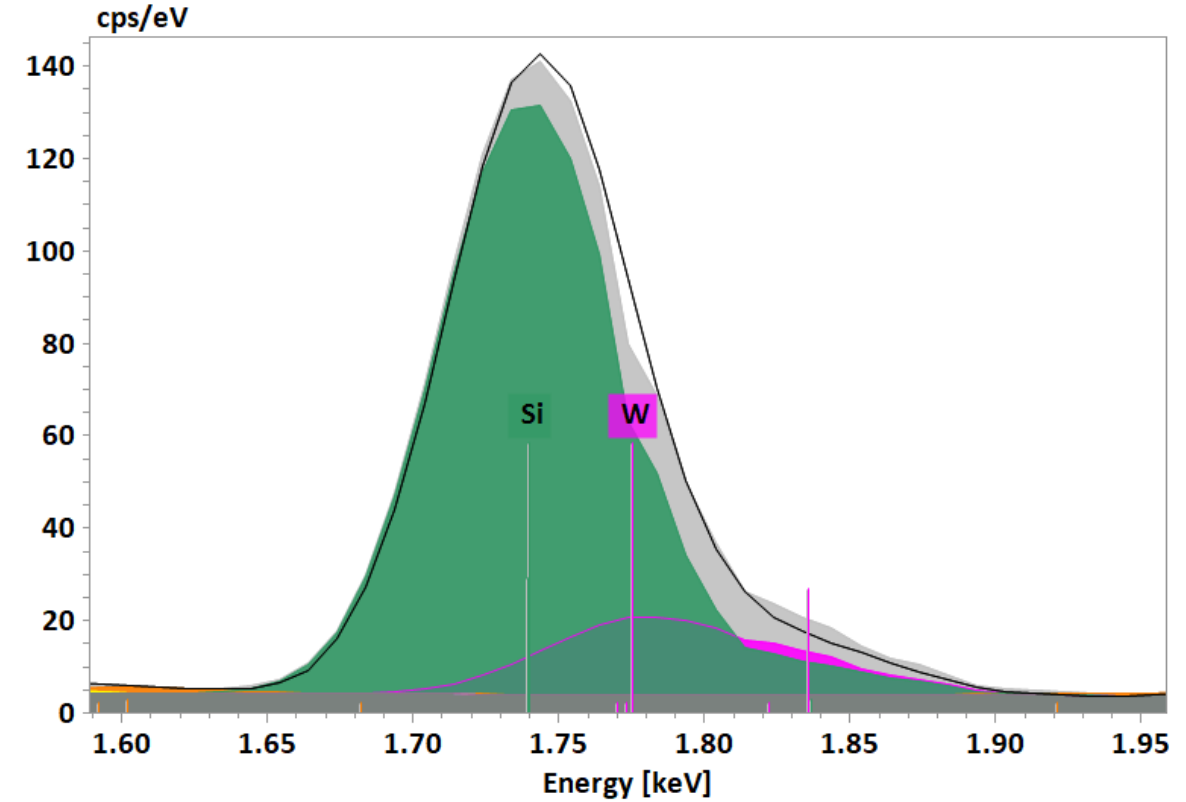
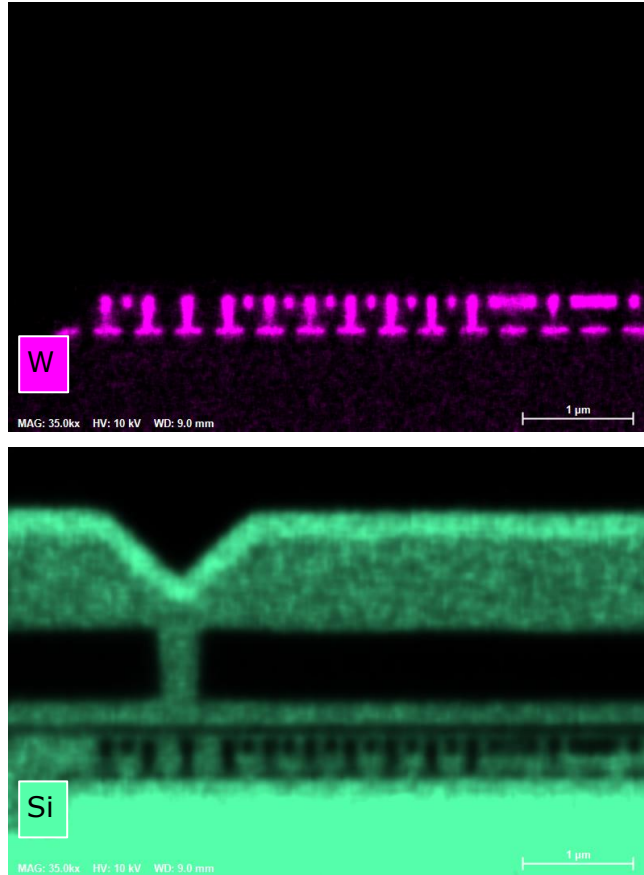
Application example: SSD

Quantified map in atomic %



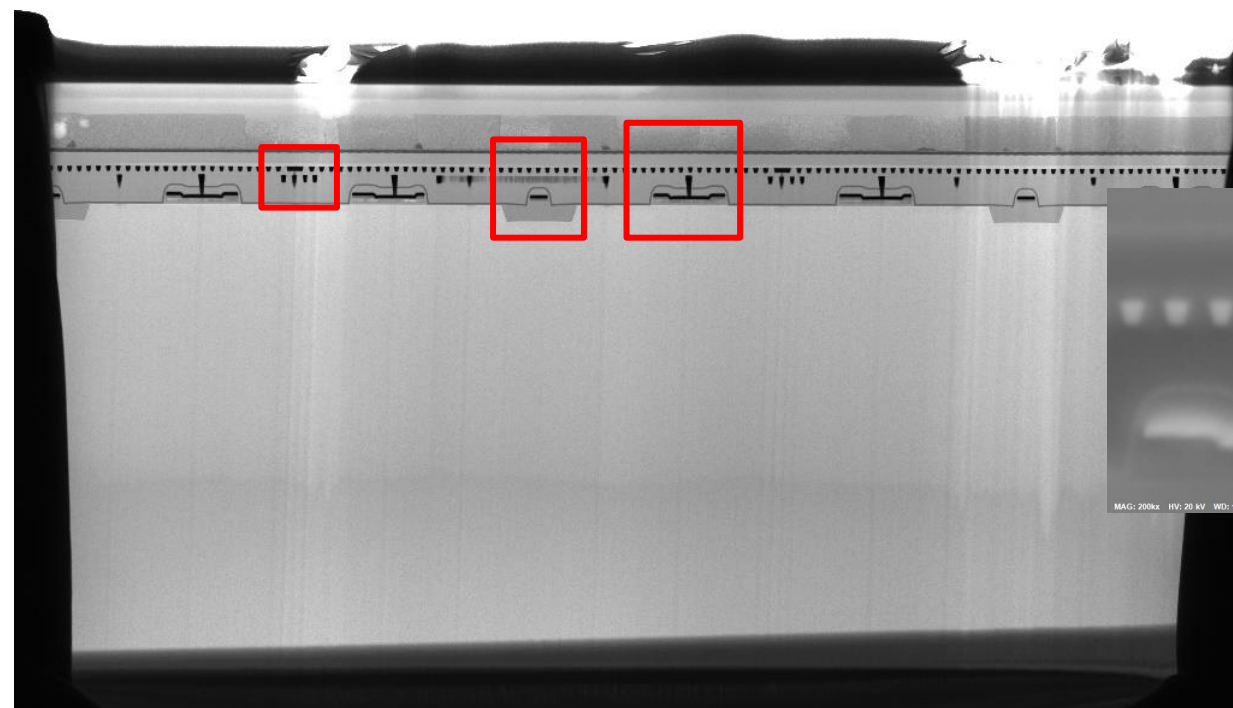
Application example: SSD

Quantified map in atomic %

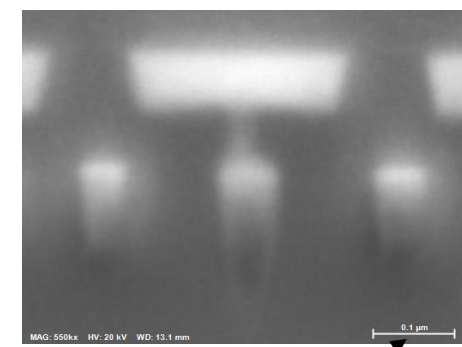
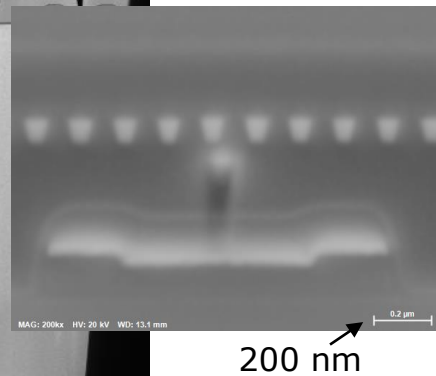


Si and W – automated deconvolution

Application example: SSD-2 Lamella #2



SEM HV: 30.0 kV	WD: 6.99 mm		LYRA3 TESCAN	
SEM MAG: 13.5 kx	Det: STEM Bright		5 μm	
View field: 20.5 μm	Date(m/d/y): 08/14/20		Bruker Nano	



100 nm

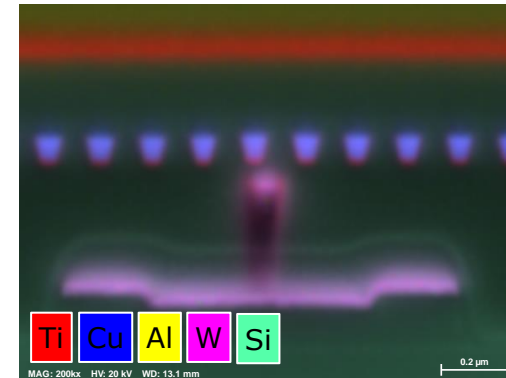
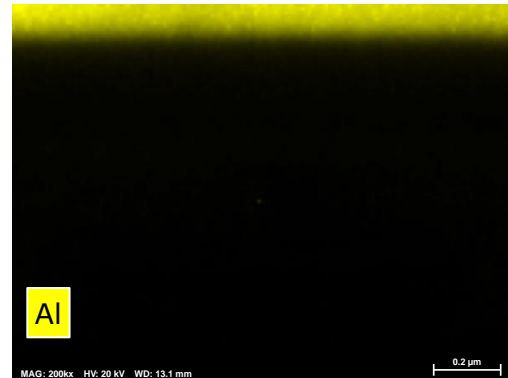
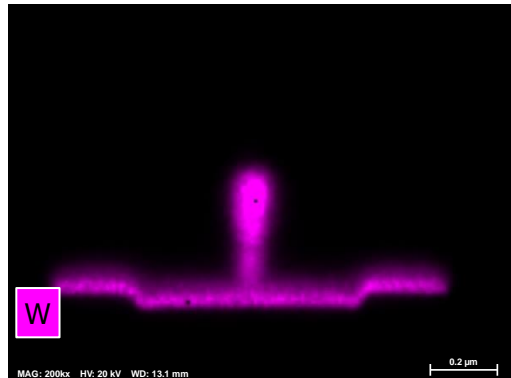
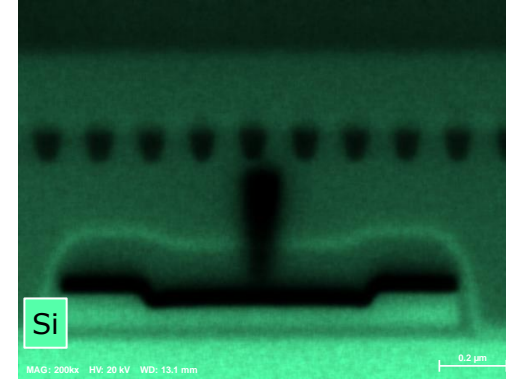
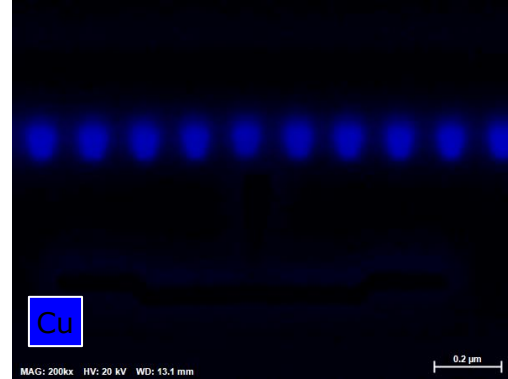
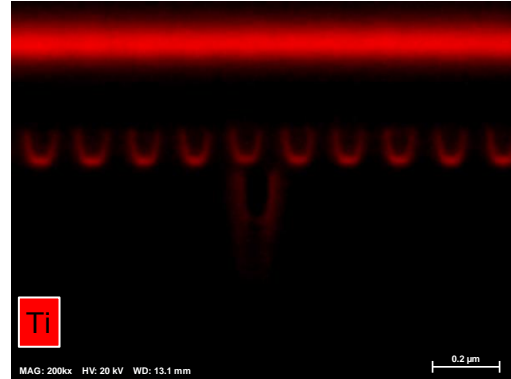
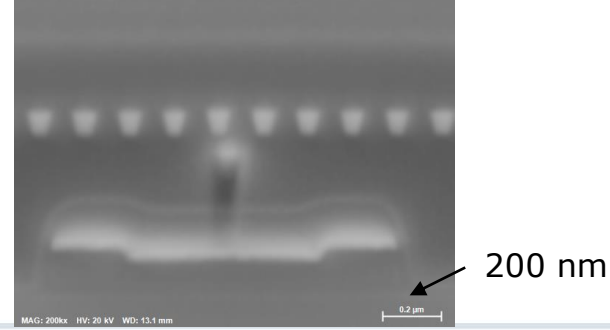


200 nm



Application example: SSD-2

Quantified map in atomic %

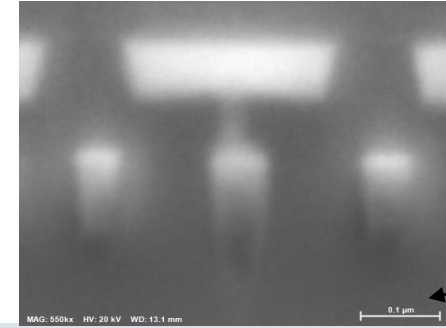


EDS mapping parameters:

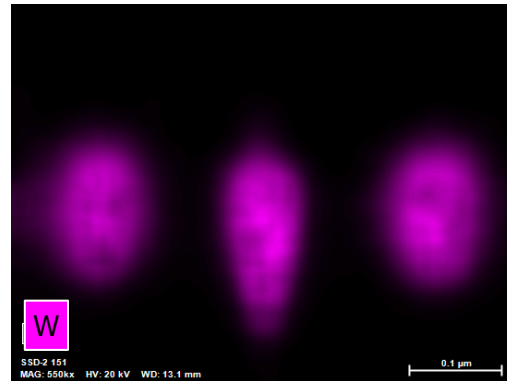
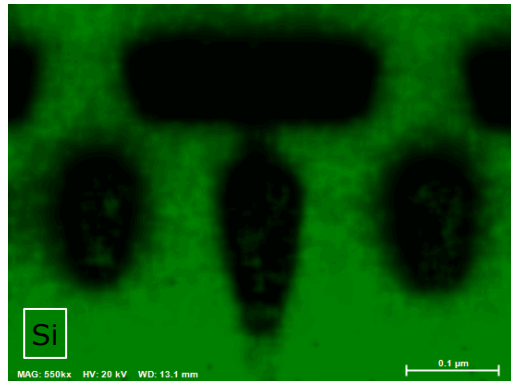
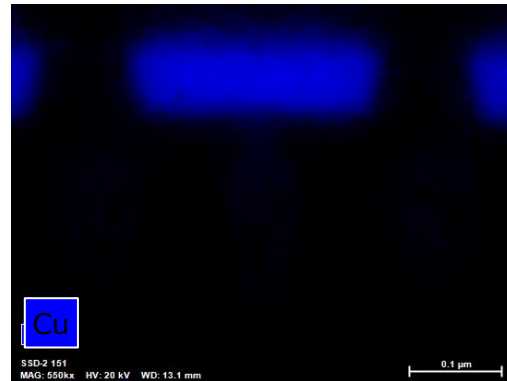
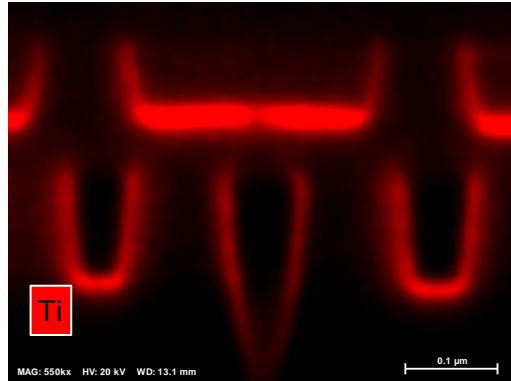
- High voltage: 20 kV
- Abs. current: 350 pA
- WD: 13.1 mm
- **Mag: 200,000 X**
- Map time: 20 m
- Input counts: 298.2 Kcps
- Output counts: 170 Kcps
- **Total counts: 2.02E+08**
(0.2 B)

Application example: SSD-2

EDS mapping at high magnification in SEM



100 nm



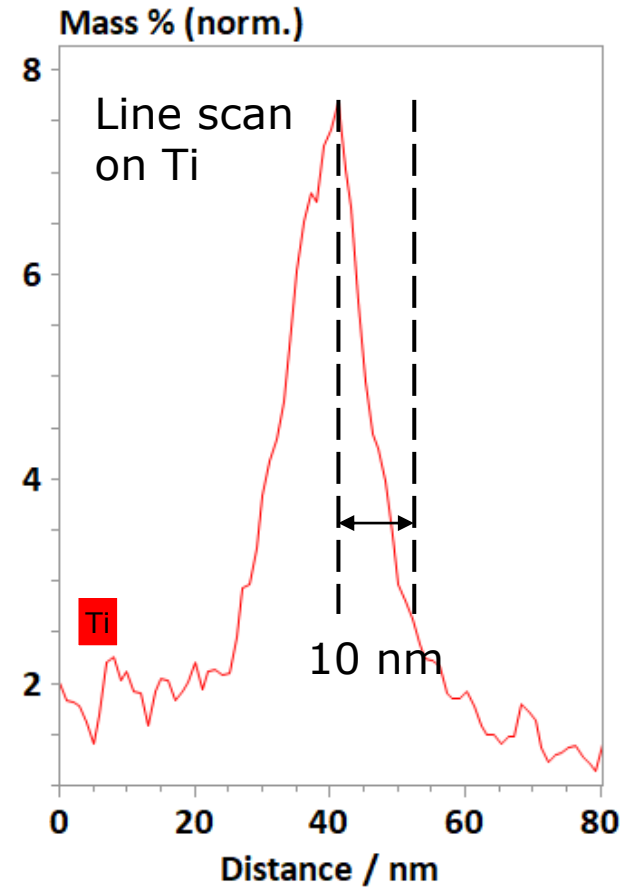
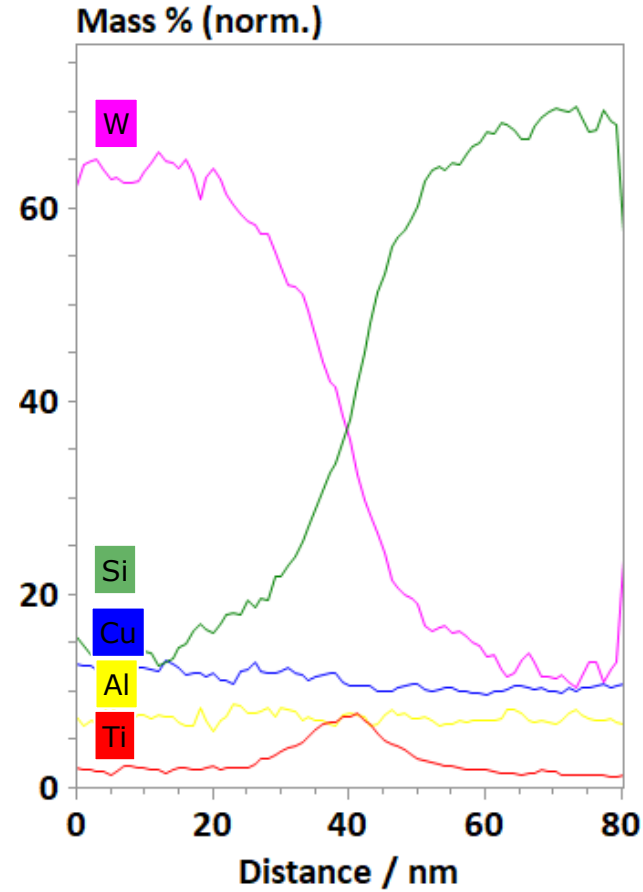
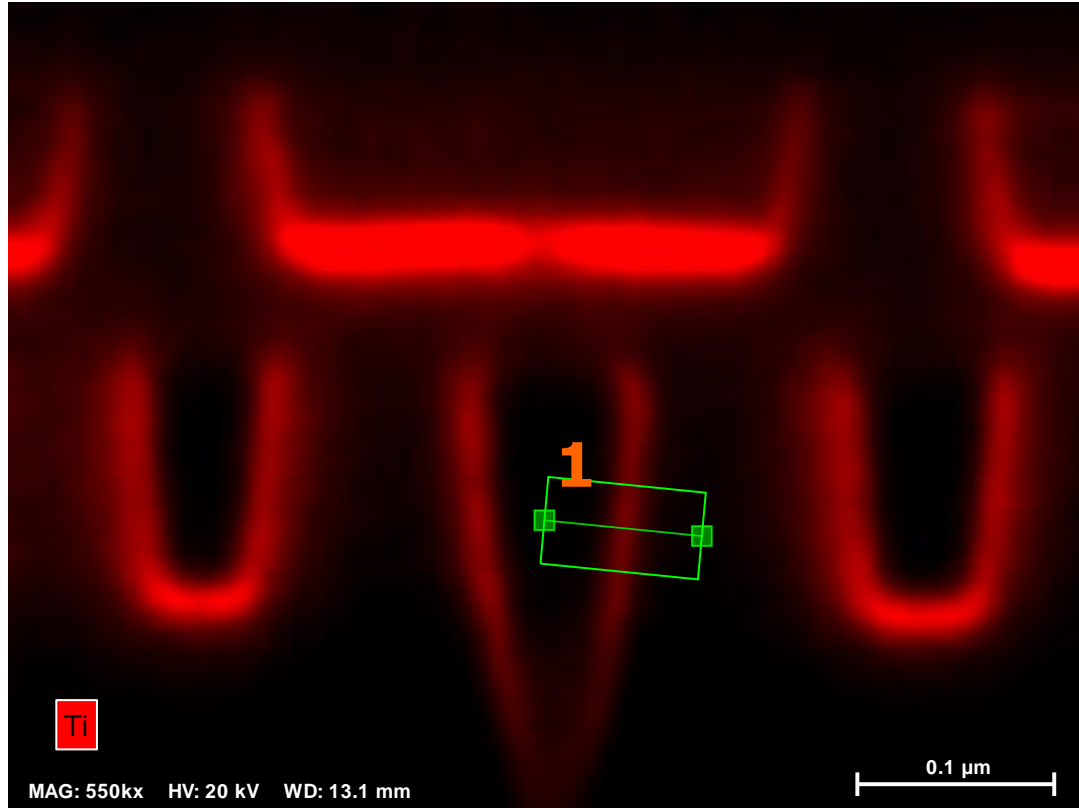
EDS mapping parameters:

- High voltage: 20 kV
- Abs. current: 350 pA
- WD: 13.1 mm
- **Mag: 550,000 X**
- **Map time: 6 m**
- Input counts: 366.6 Kcps
- Output counts: 180.5 Kcps
- **Total counts: 7.28E+07 (70 M)**

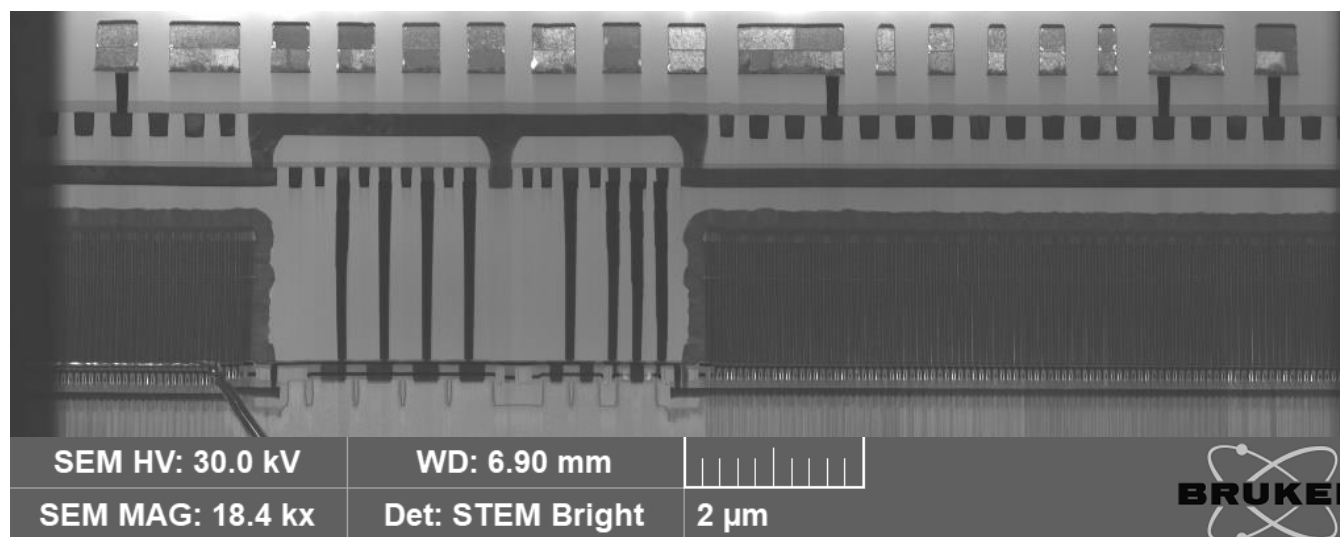
Quantified map in atomic %

Application example: SSD-2

EDS mapping – Line scan

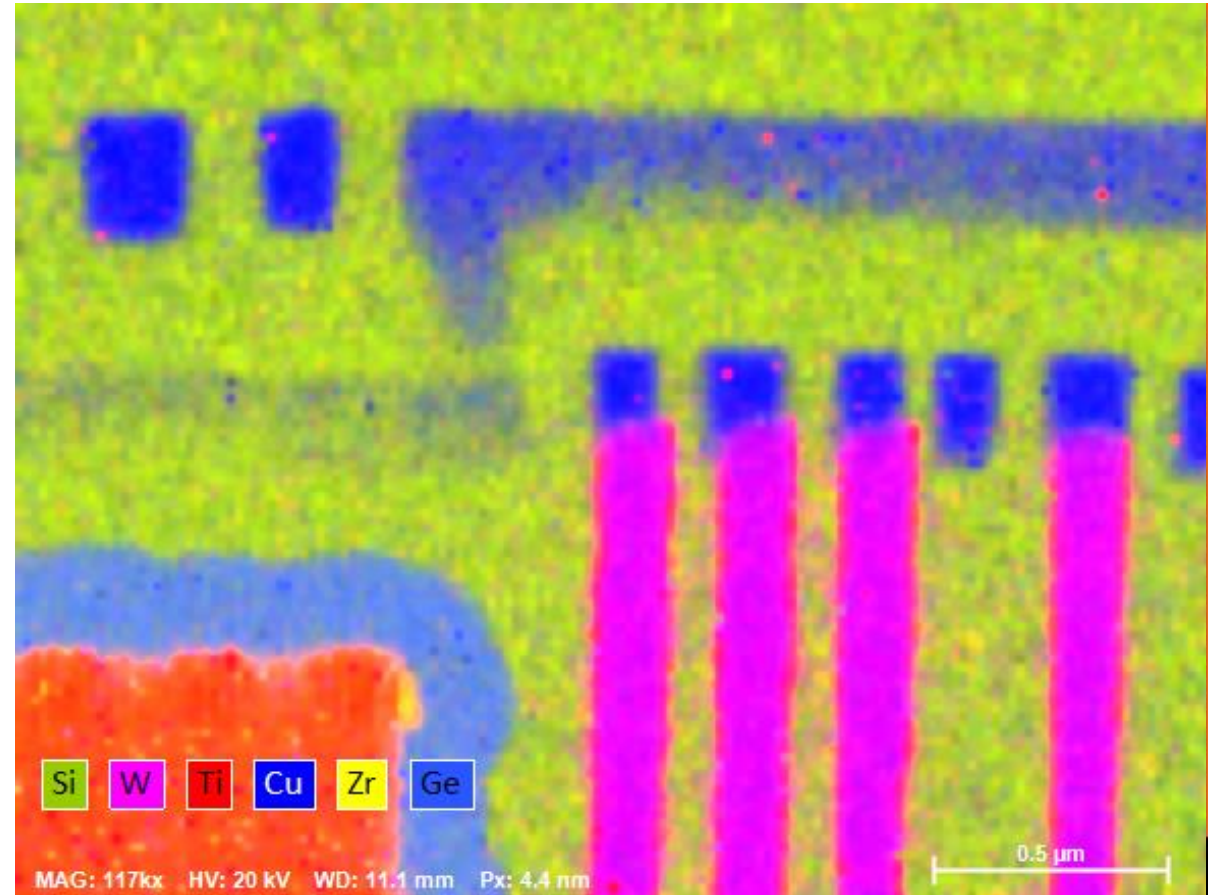
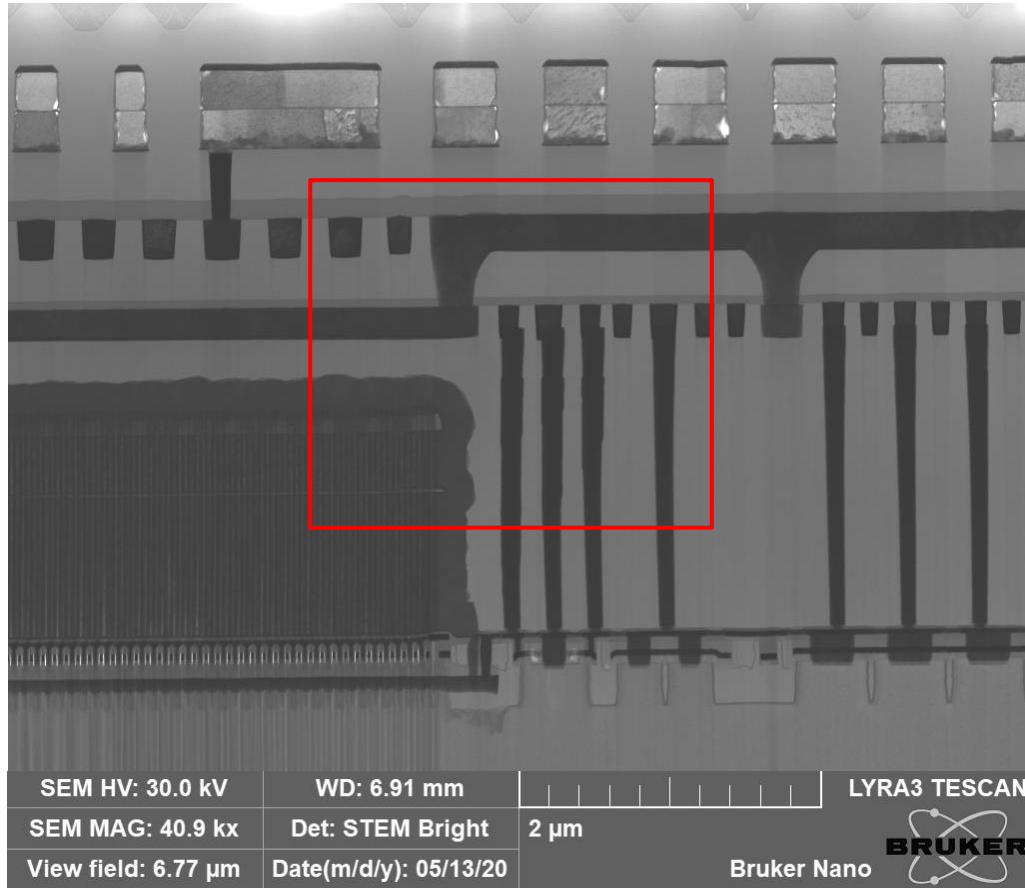


Application example: Microprocessor



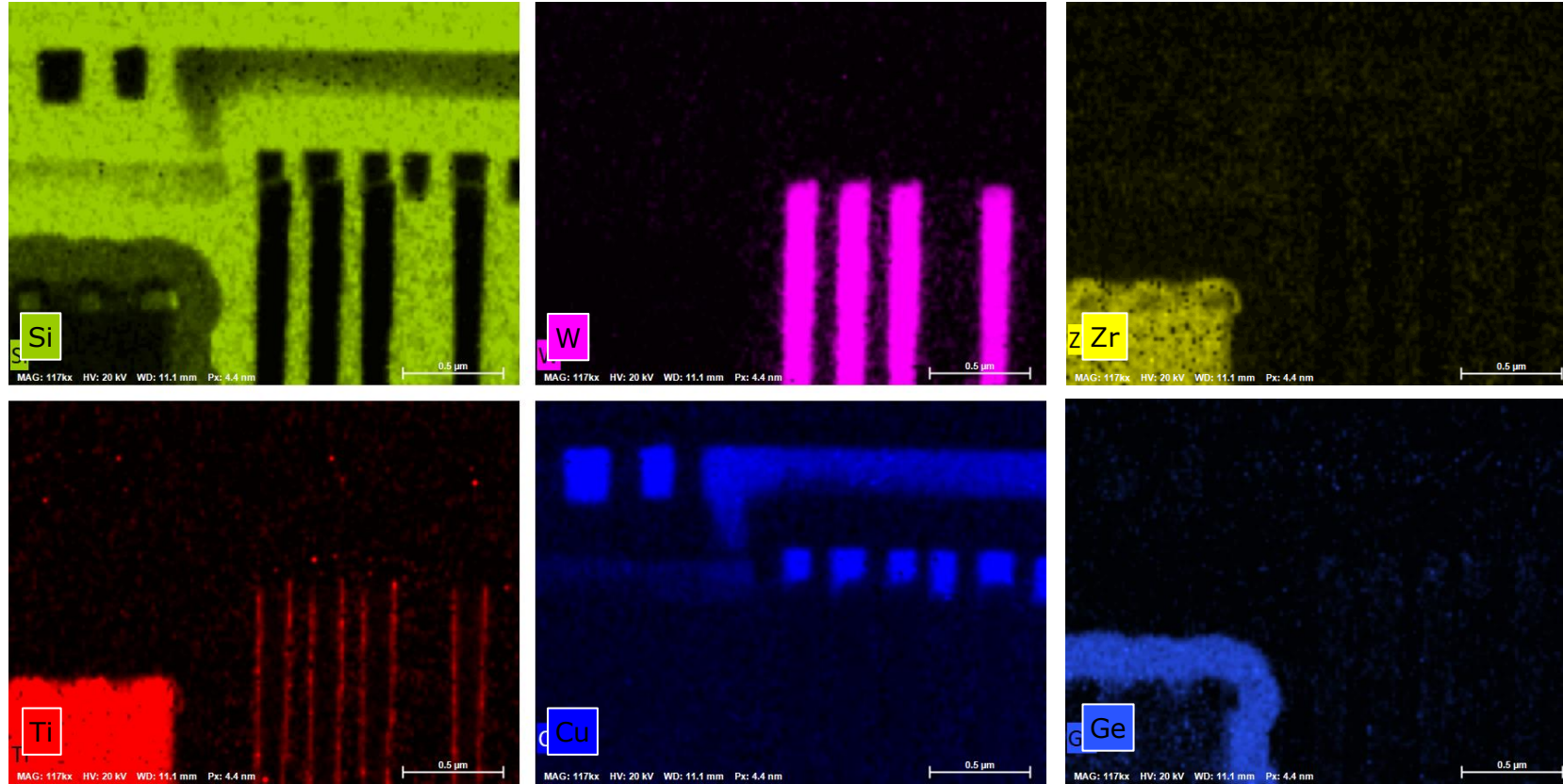
Application example: Microprocessor

EDS mapping – Quantified map in atomic %



Application example: Microprocessor

EDS mapping

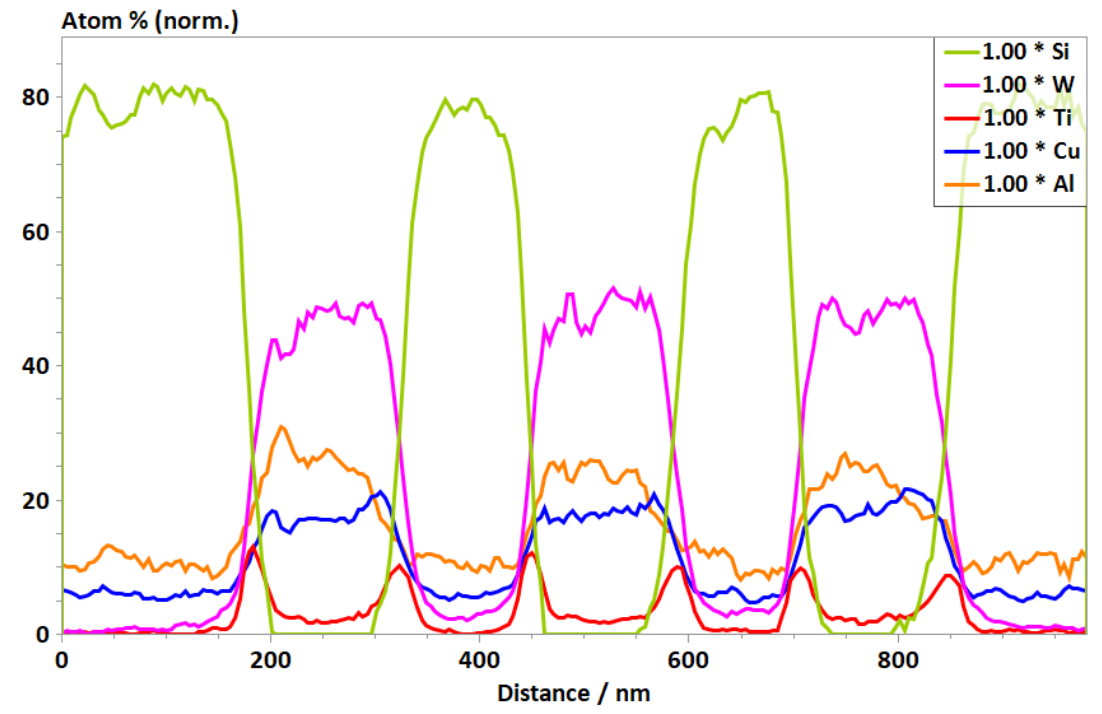
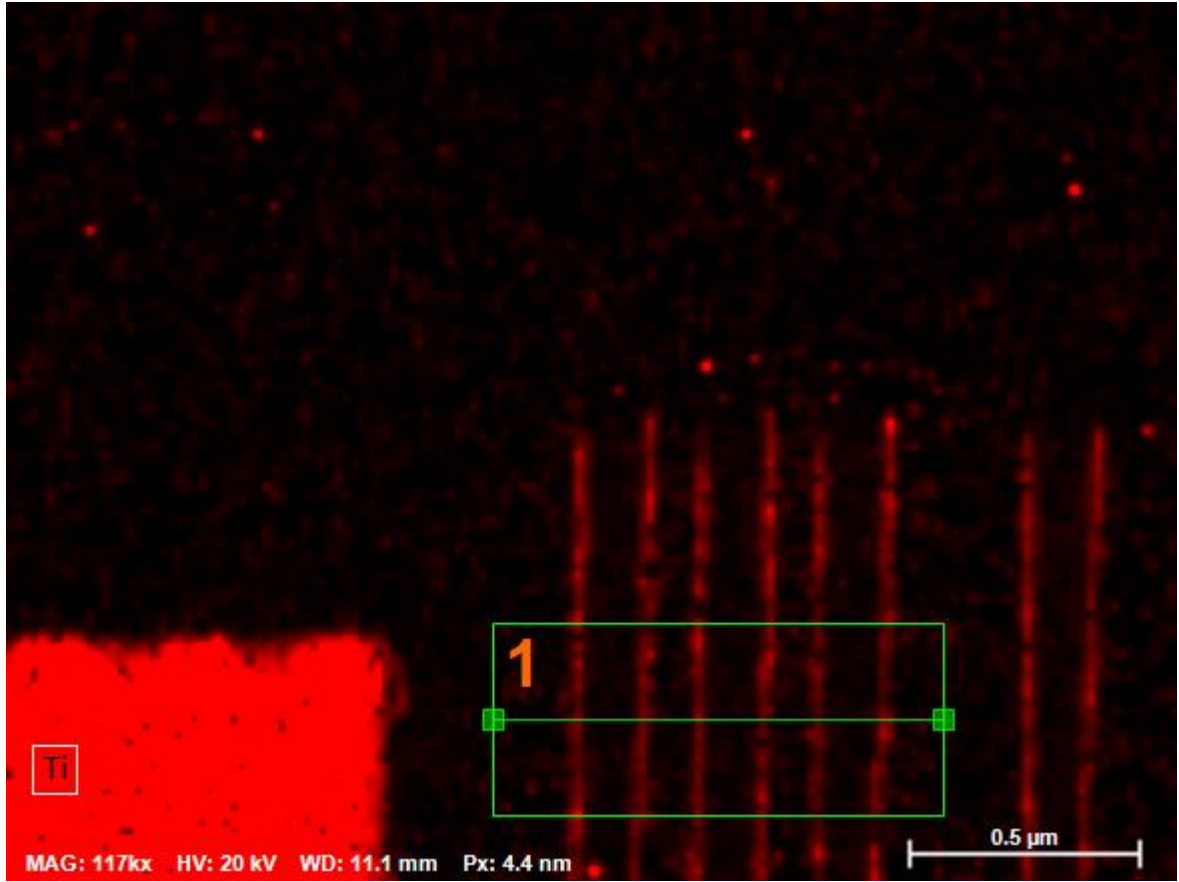


EDS mapping parameters:

- High voltage: 20 kV
- Abs. current: 350 pA
- WD: 11.1 mm
- Mag: 177,000 X
- Map time: 2 m
- Input counts: 64.0 Kcps
- Output counts: 53.2 Kcps
- Total counts: 6.838E+06 (6.8 M)

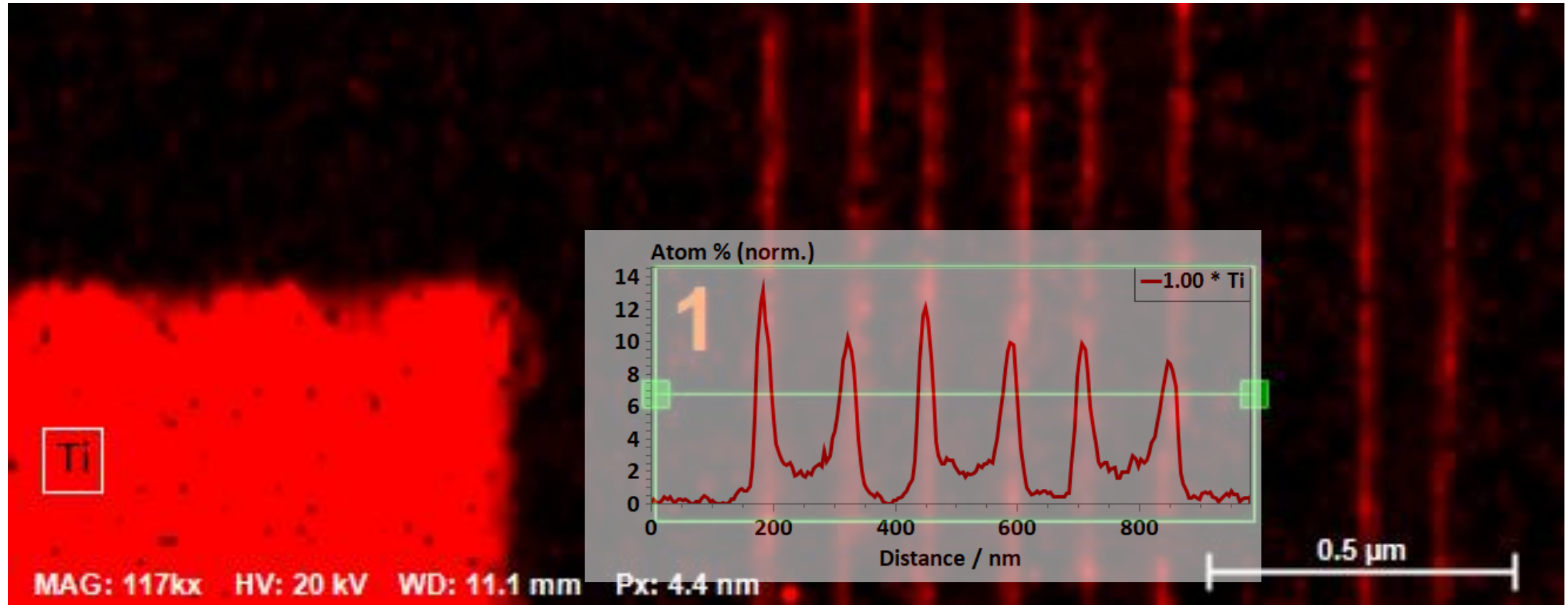
Application example: Microprocessor

EDS Line scan – Quantified line scan in Atomic %



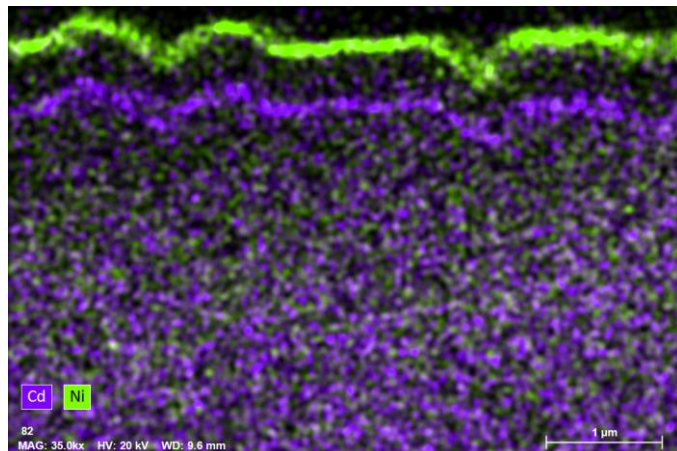
Application example: Microprocessor

EDS Line scan - overlap



Conventional detector vs. FlatQUAD

FQ ideal for thin lamellae, nanoparticles and low x-ray yield samples
20 kV, 35000 X, WD 9.6 mm, 410 pA



Conventional EDS detector:

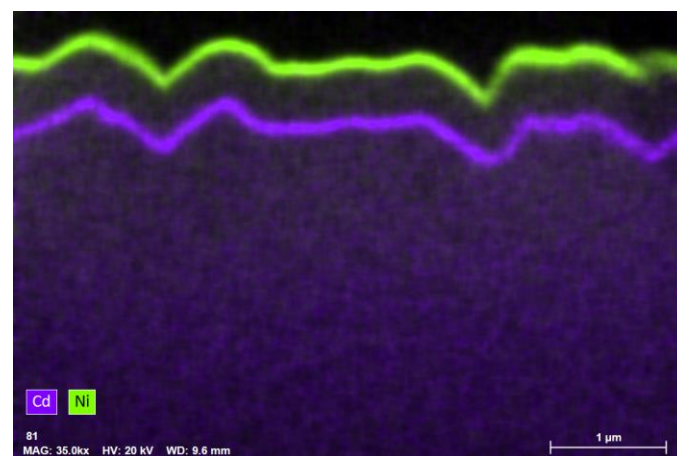
Size/solid angle: 60 mm², 0.0253 sr

Map time: 300 s

Total counts: 2.4E06 (2.4 M)

Input counts: 7.7 kcps

Output counts: 7.6 kcps



FlatQUAD:

Size/solid angle: 60 mm², 0.95 sr

Map time: 300 s

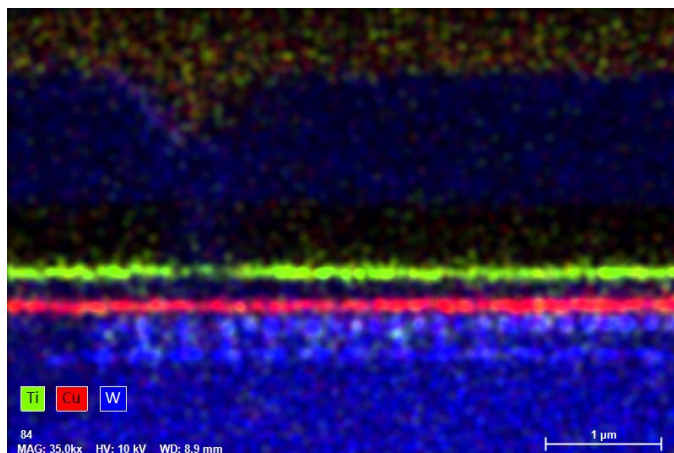
Total counts: 3.9E07 (39 M)

Input counts: 218.8 kcps

Output counts: 124.9 kcps

Conventional detector vs. FlatQUAD

FQ ideal for thin lamellae, nanoparticles and low x-ray yield samples
10 kV, 35000 X, WD 9.0 mm, 280 pA



Conventional EDS detector:

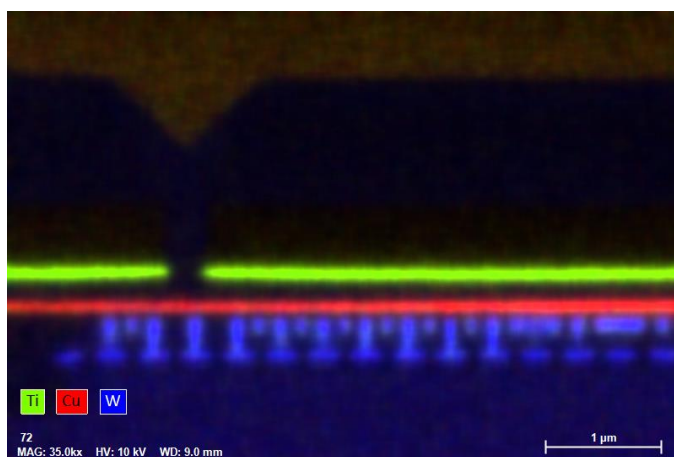
Size/solid angle: 60 mm², 0.0253 sr

Map time: 300 s

Total counts: 6.2E05 (0.62 M)

Input counts: 2.02 kcps

Output counts: 2.02 kcps



FlatQUAD:

Size/solid angle: 60 mm², 0.95 sr

Map time: 300 s

Total counts: 1.08E07 (10.8 M)

Input counts: 86.8 kcps

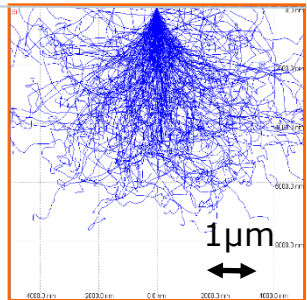
Output counts: 36.1 kcps

Spatial Resolution for Bulk and Electron Transparent Specimens

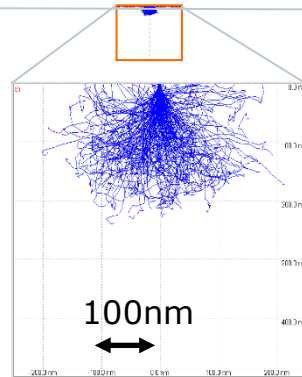


SEM: bulk

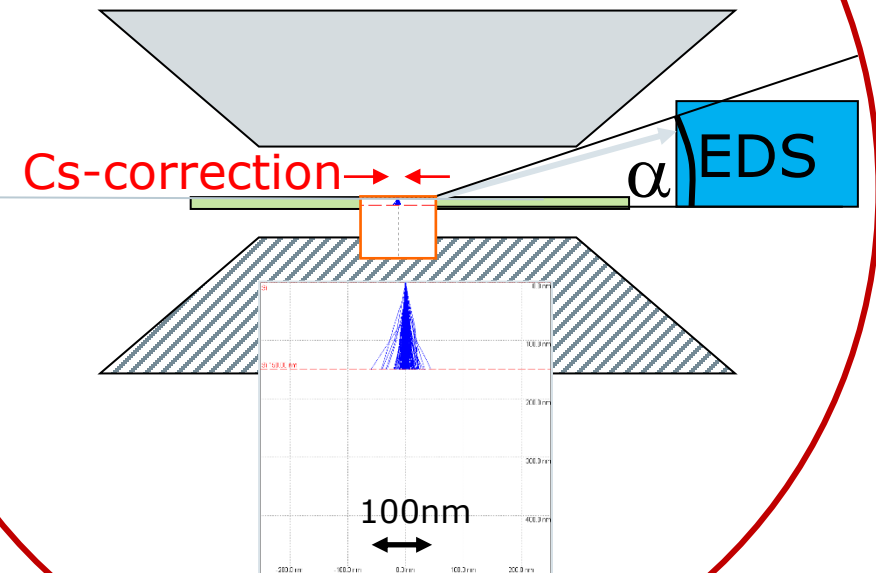
High voltage
30kV



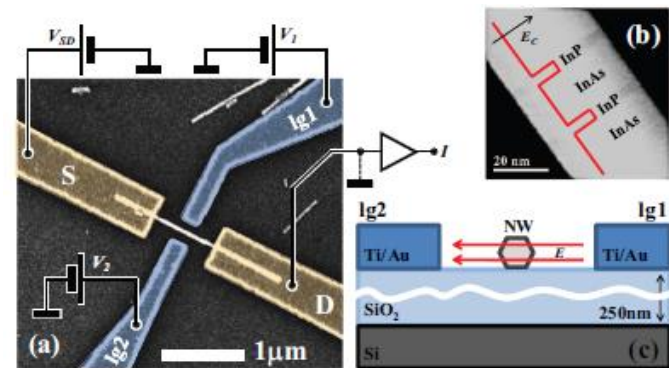
Lower voltage
4kV



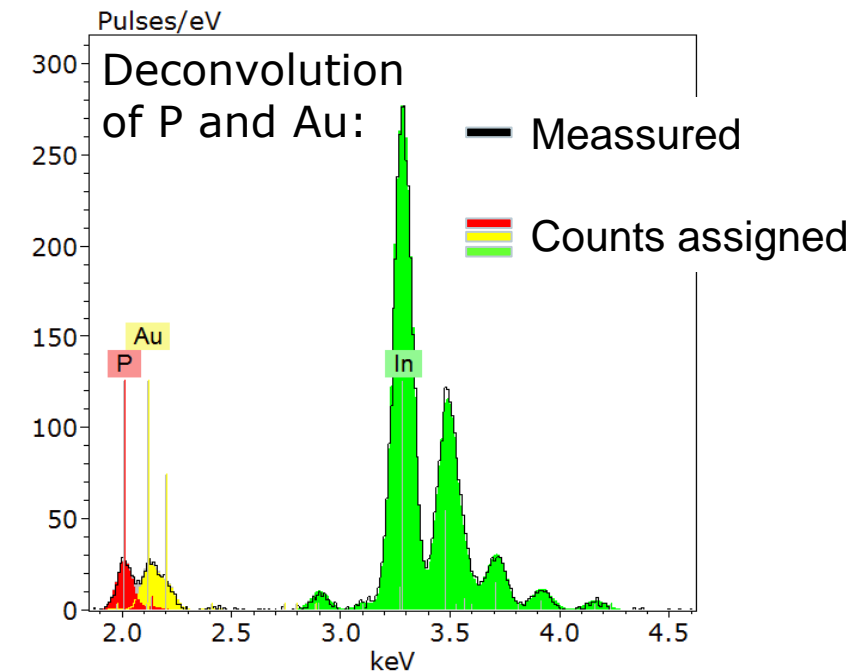
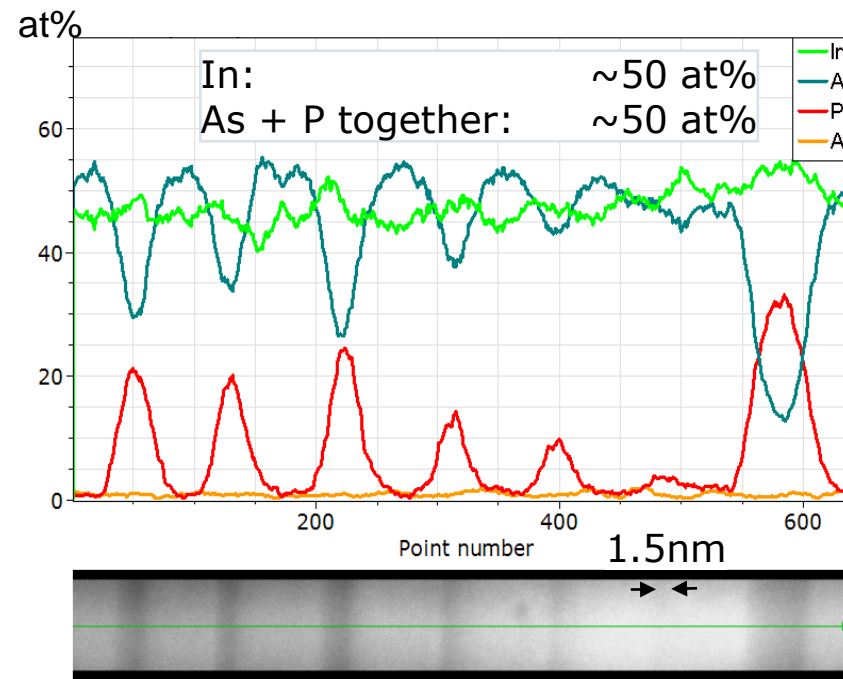
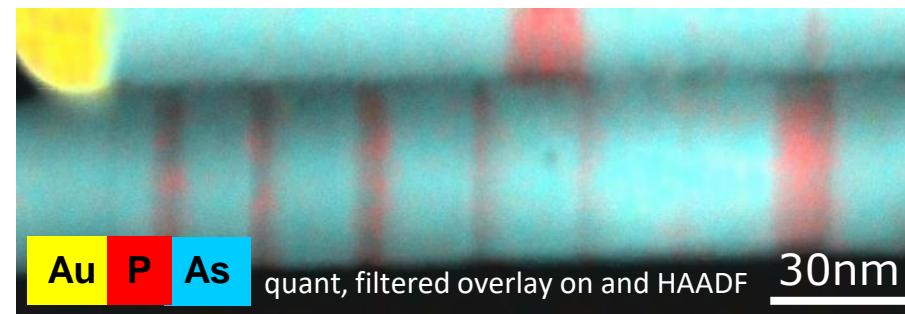
S/TEM, T-SEM: thin specimen,
small probe



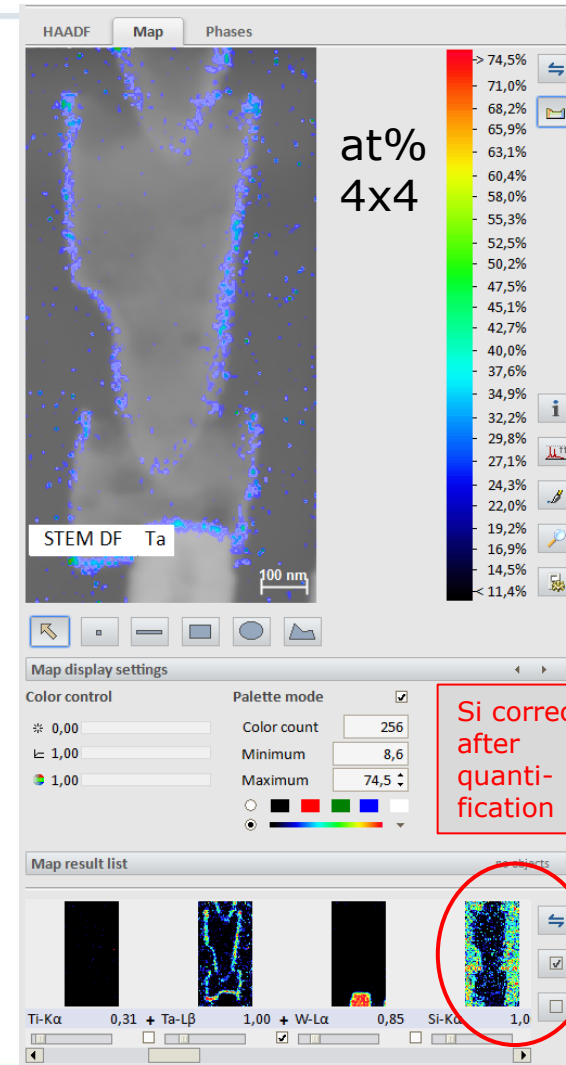
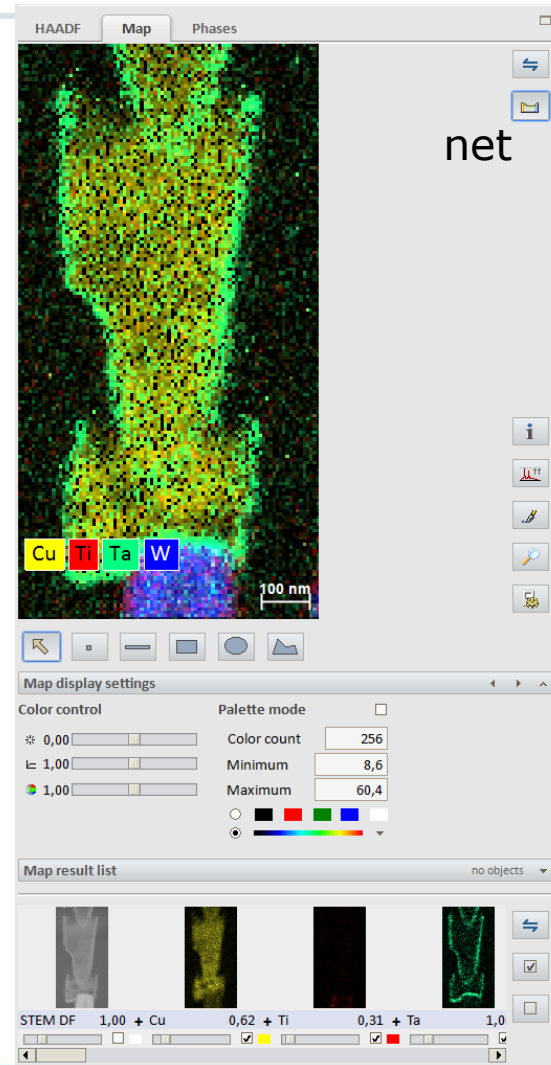
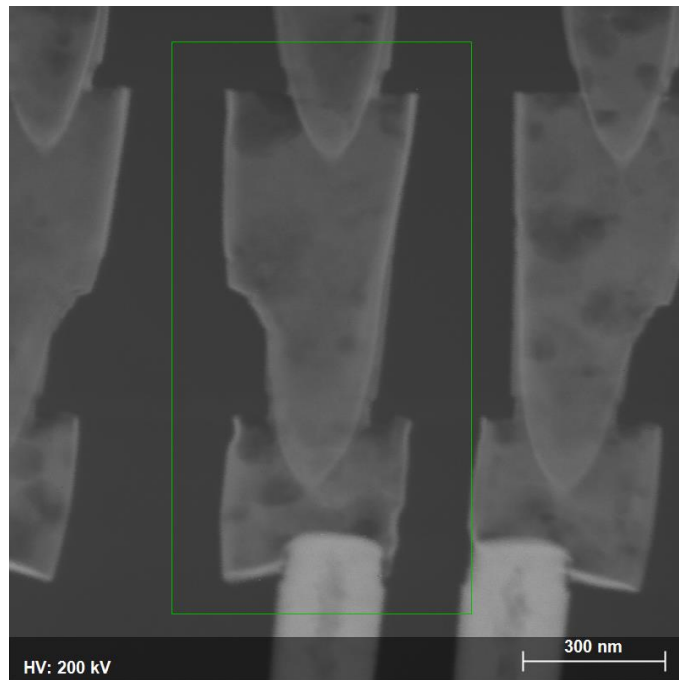
ED(X)S With 30mm² Standard EDS Detectors Using Standard STEM; Collection Angle: ~ 0.1 sr; Cliff-Lorimer Quantification



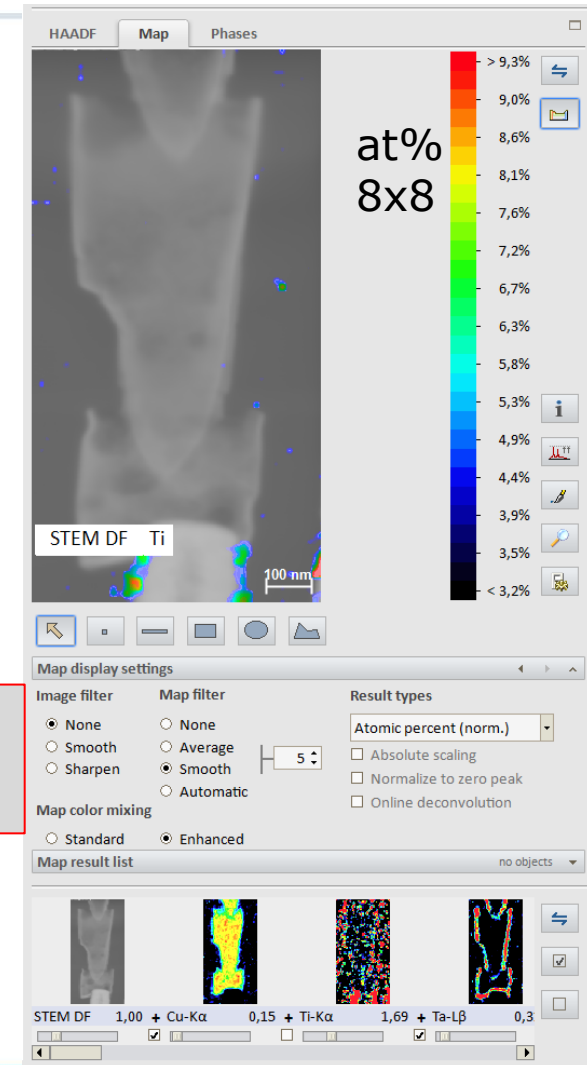
Nanorods for Single e⁻ transistor:



ED(X)S With 30mm² Standard EDS Detectors Using Standard STEM; Collection Angle: ~ 0.1 sr; Cliff-Lorimer Quantification



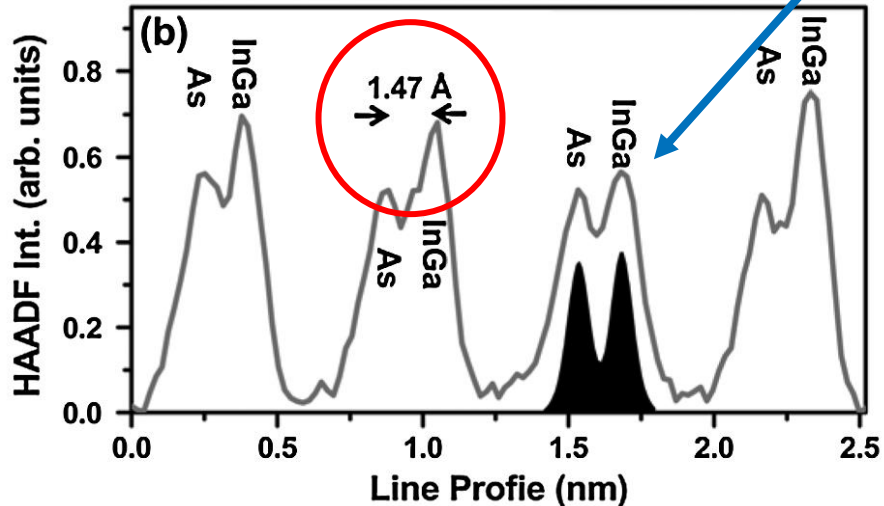
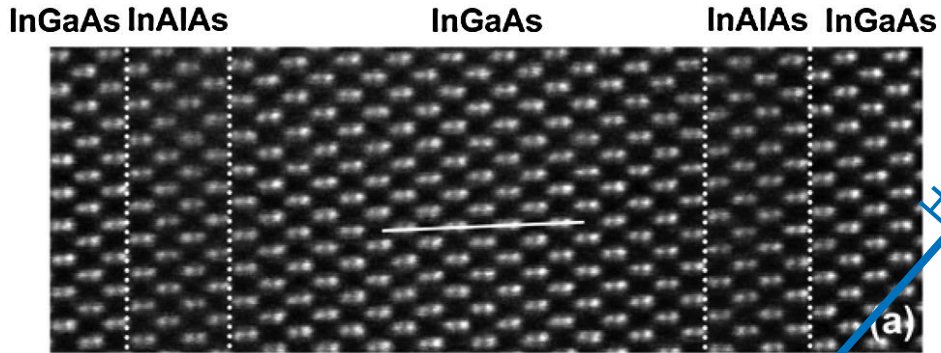
Si correct after quantification



ED(X)S With 30mm² Standard EDS Detectors Using **Cs-corrected** STEM; Collection Angle: ~ 0.1 sr

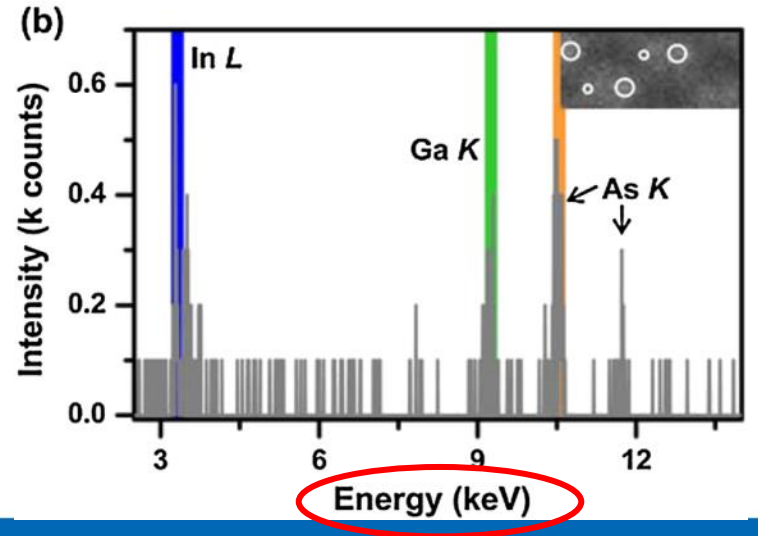
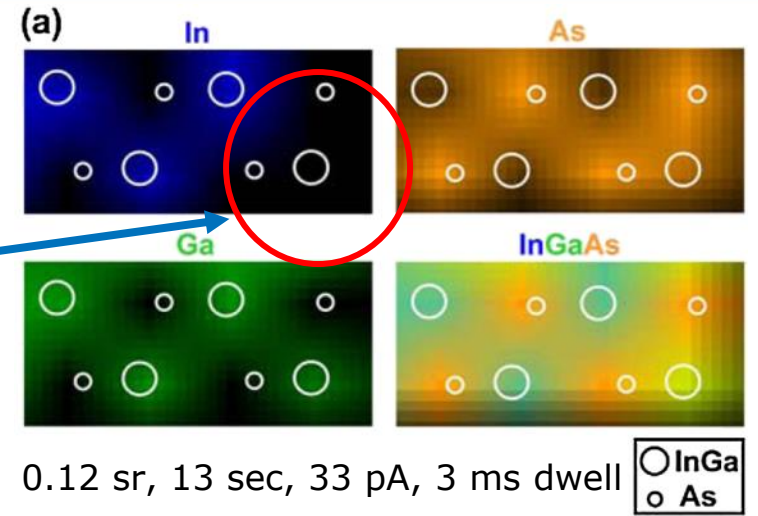


First atom column mapping using SDD



Indium missing
in one atomic
column

EDS



Forbes, ... Mc Comb et al.:
Simulation needed, to
correctly interpret atom
column EDS!

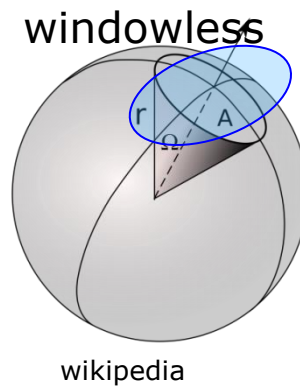
100 mm² Oval Detector Area, Windowless: XFlash[®]T 100 oval



EDXS from 0.4 sr to 0.7 sr depending on geometry. This is the real solid angle for a flat SDD (see wiki below).

Wrong: $100\text{mm}^2 / (10.5\text{mm})^2 = 0.91\text{sr}$; Correct: 0.65sr

TOA: $\sim 13^\circ$



Single Atom ID:

R. M. Stroud et al., *APL* **108**, 163101 (2016) *open access*

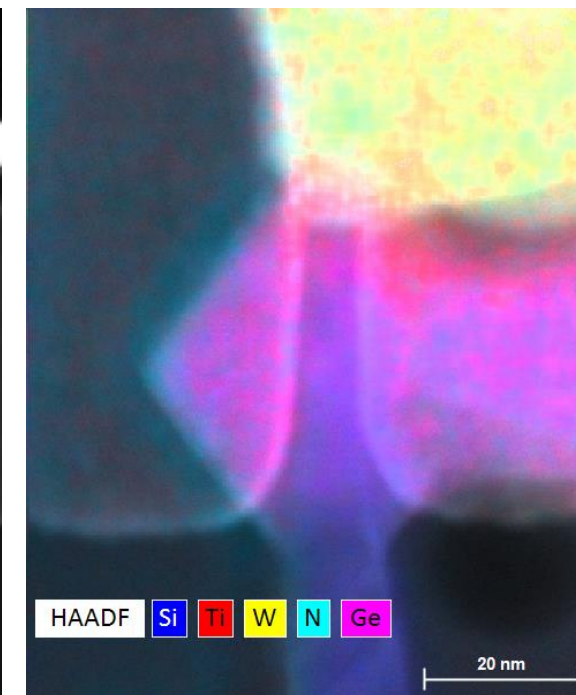
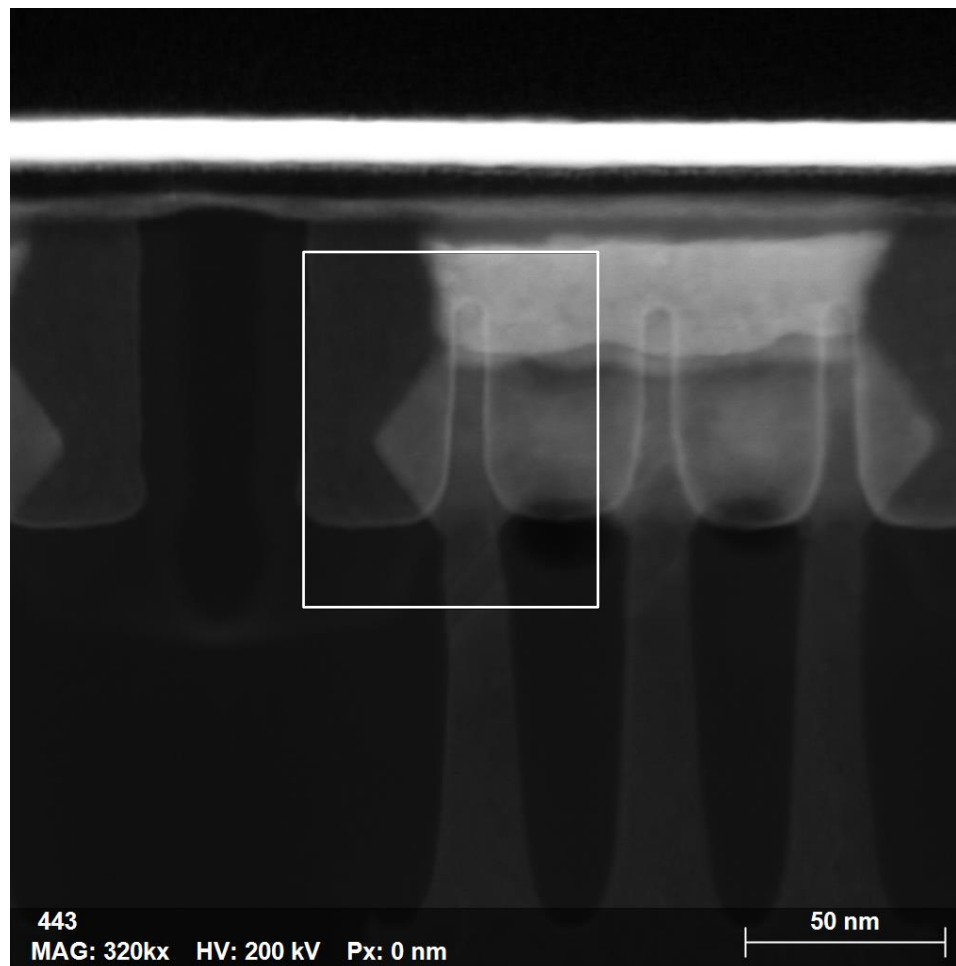
T. C. Lovejoy et al., *APL* **100**, 154101 (2012): 30mm², 0.1sr

ED(X)S with 100mm² windowless oval detector area using Cs-corrected STEM; Collection angle: ~ 0.4 sr
Raw data, acquisition time 24min



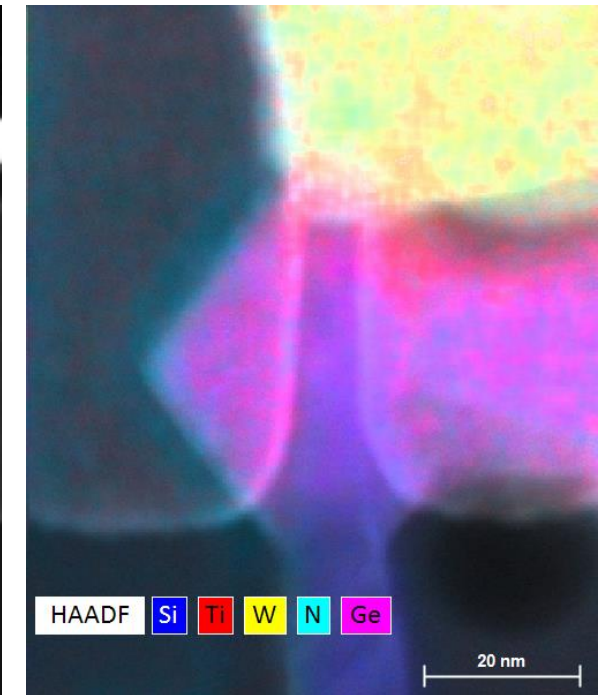
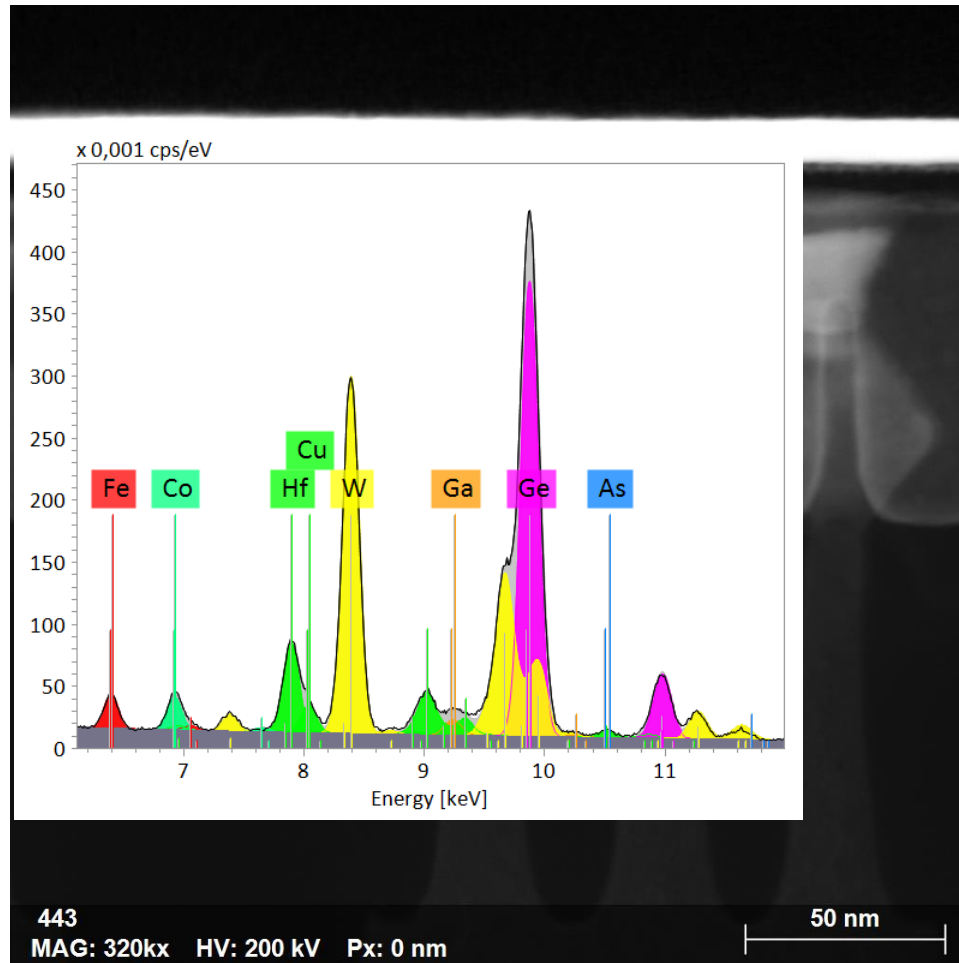
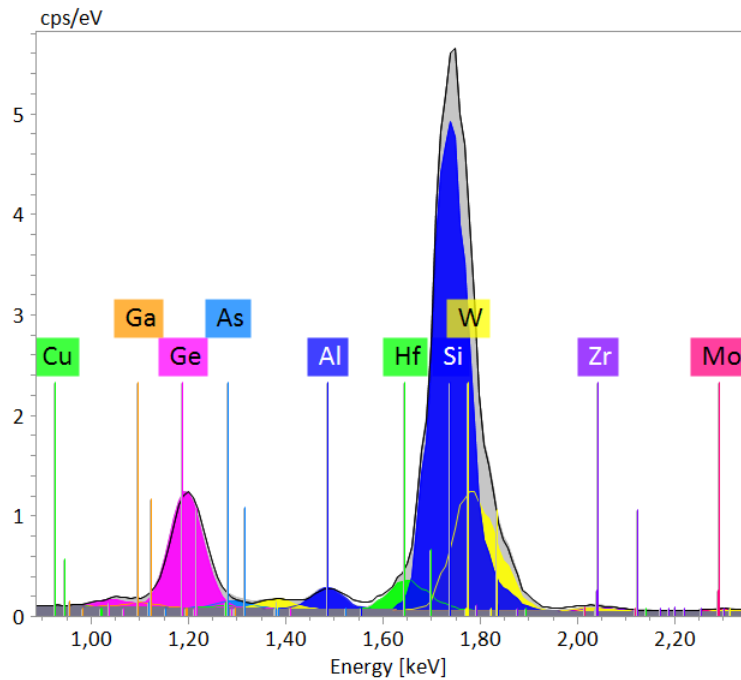
TFS Titan 80-300 with Bruker XFlash[®]T 100 oval EDS detector at ACE.

Quantitative element mapping of nanostructures.



ED(X)S with 100mm² windowless oval detector area using Cs-corrected STEM; Collection angle: ~ 0.4 sr

Raw data, acquisition time 24min

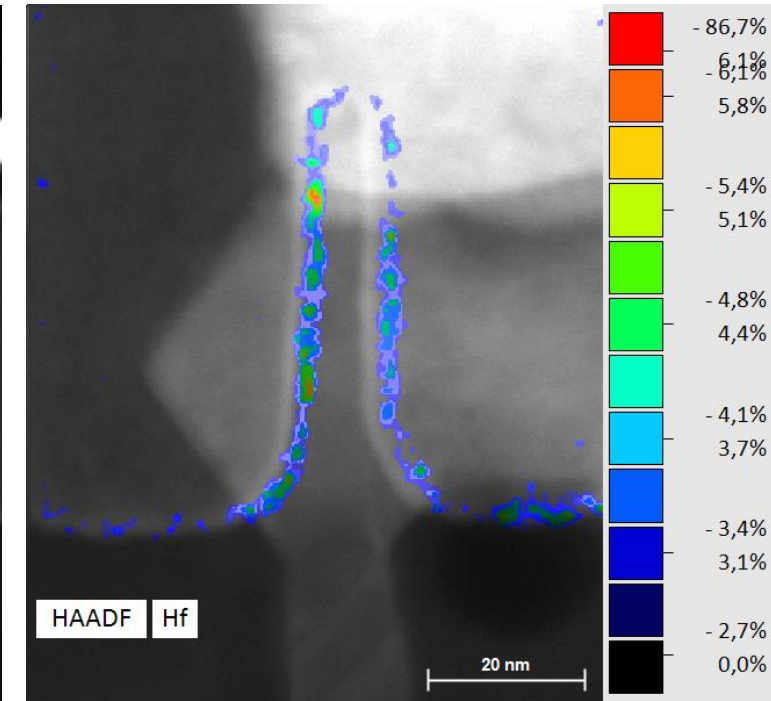
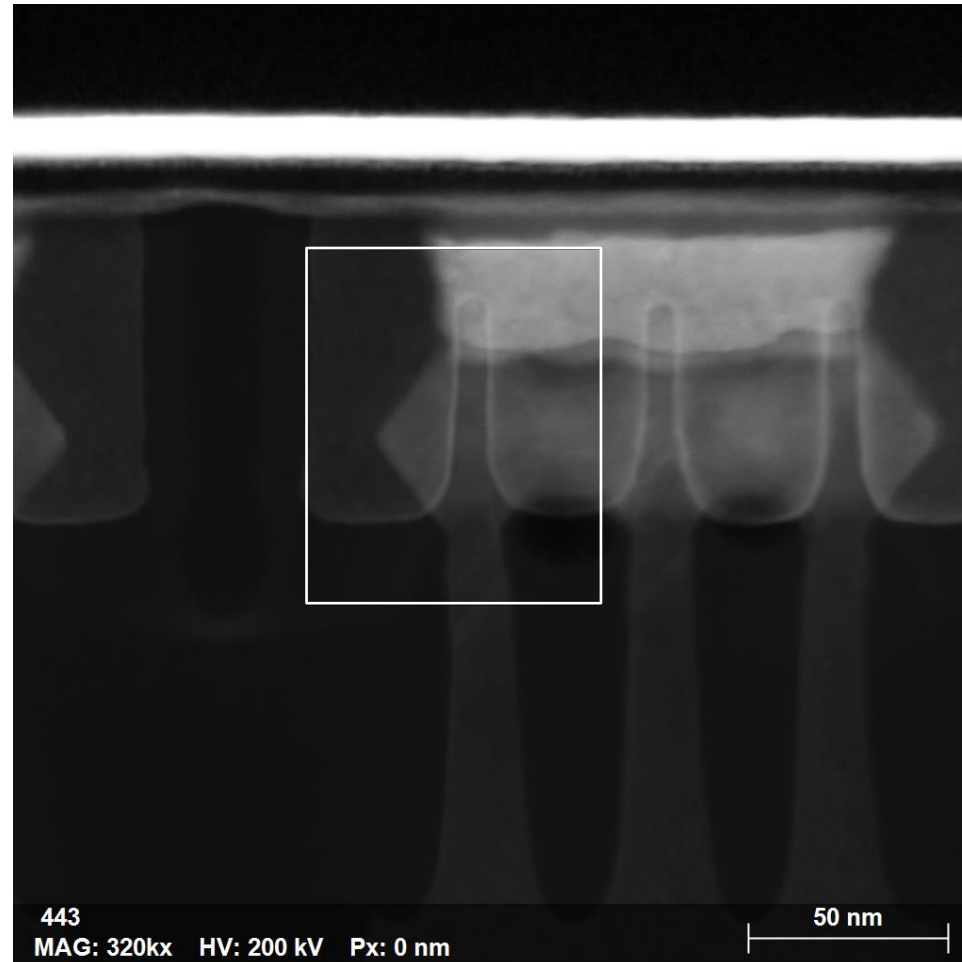


ED(X)S with 100mm² windowless oval detector area using Cs-corrected STEM; Collection angle: ~ 0.4 sr
Cliff-Lorimer Quantification: at%



TFS Titan 80-300 with Bruker XFlash[®]T 100 oval EDS detector at ACE.

Quantitative element mapping of nanostructures.

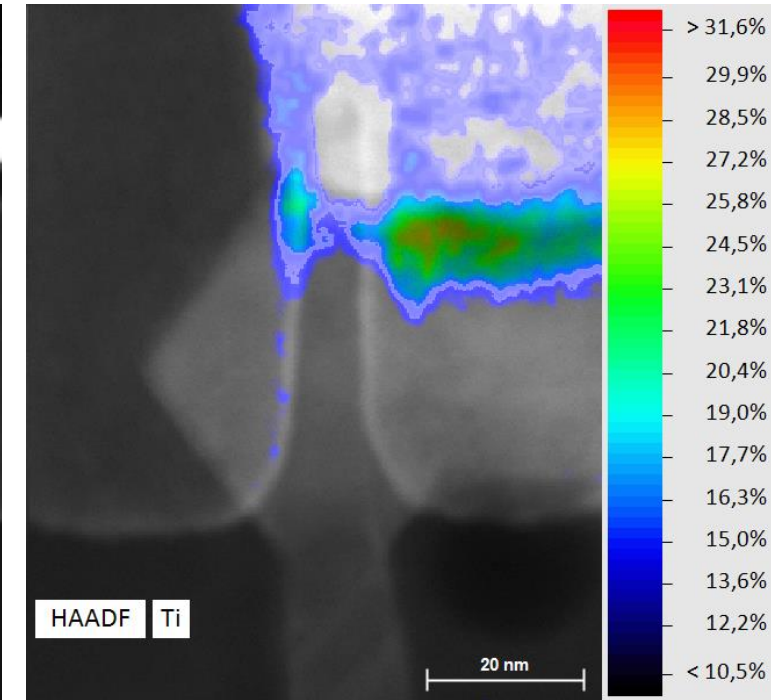
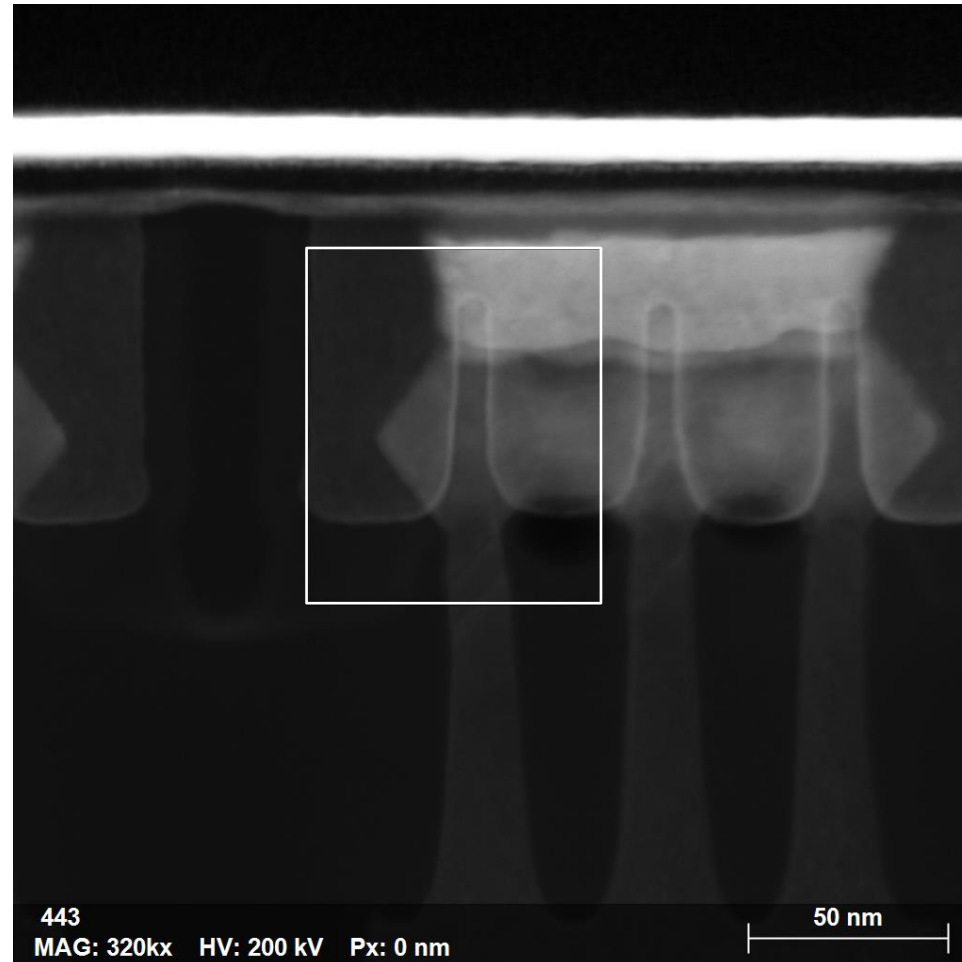


ED(X)S with 100mm² windowless oval detector area using Cs-corrected STEM; Collection angle: ~ 0.4 sr
Cliff-Lorimer Quantification: at%



TFS Titan 80-300 with Bruker XFlash[®]T 100 oval EDS detector at ACE.

Quantitative element mapping of nanostructures.

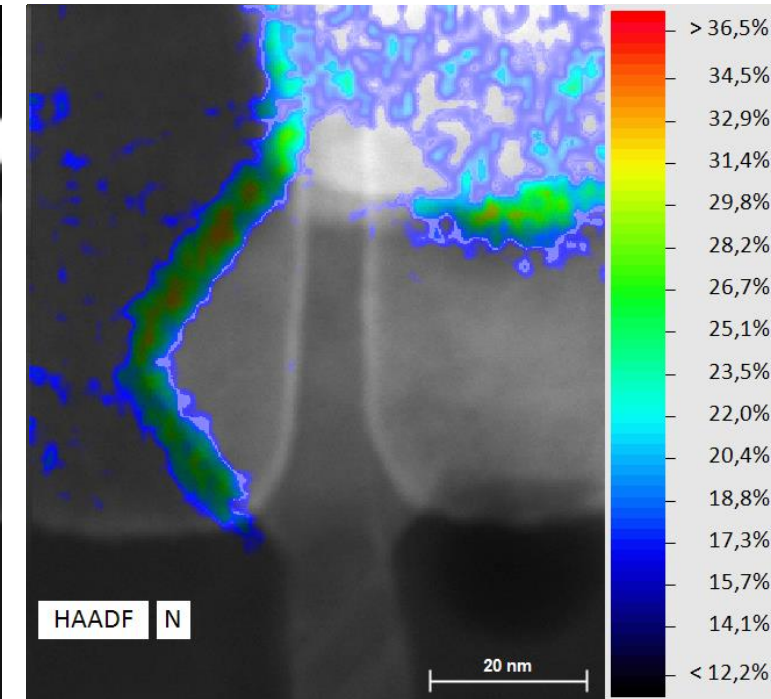
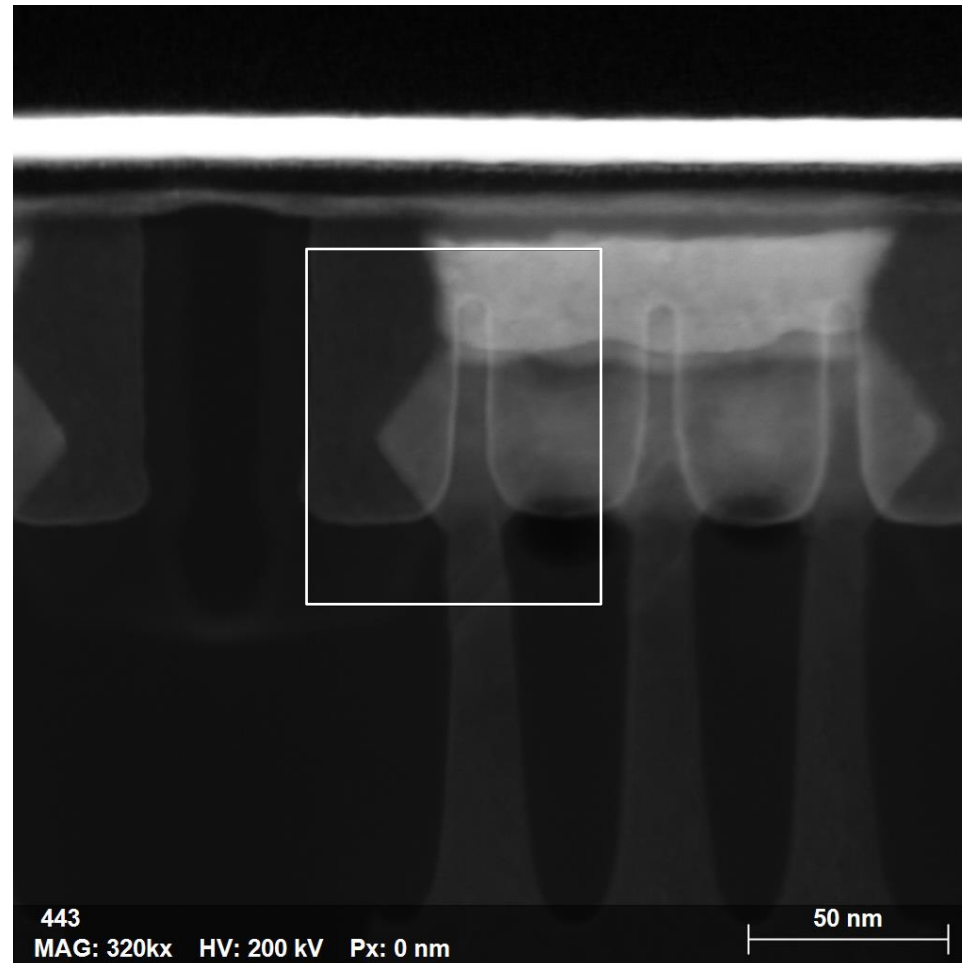


ED(X)S with 100mm² windowless oval detector area using Cs-corrected STEM; Collection angle: ~ 0.4 sr
Cliff-Lorimer Quantification: at%



TFS Titan 80-300 with Bruker XFlash[®]T 100 oval EDS detector at ACE.

Quantitative element mapping of nanostructures.

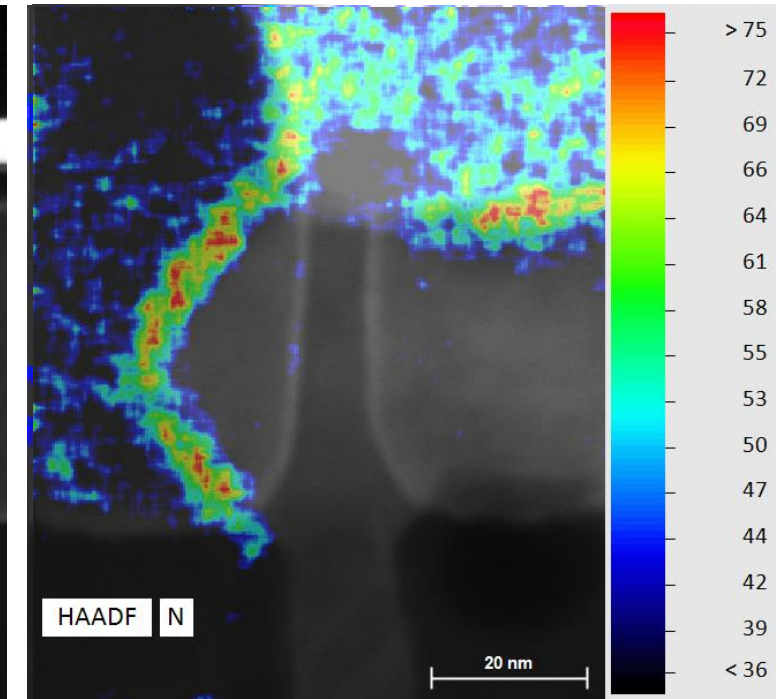
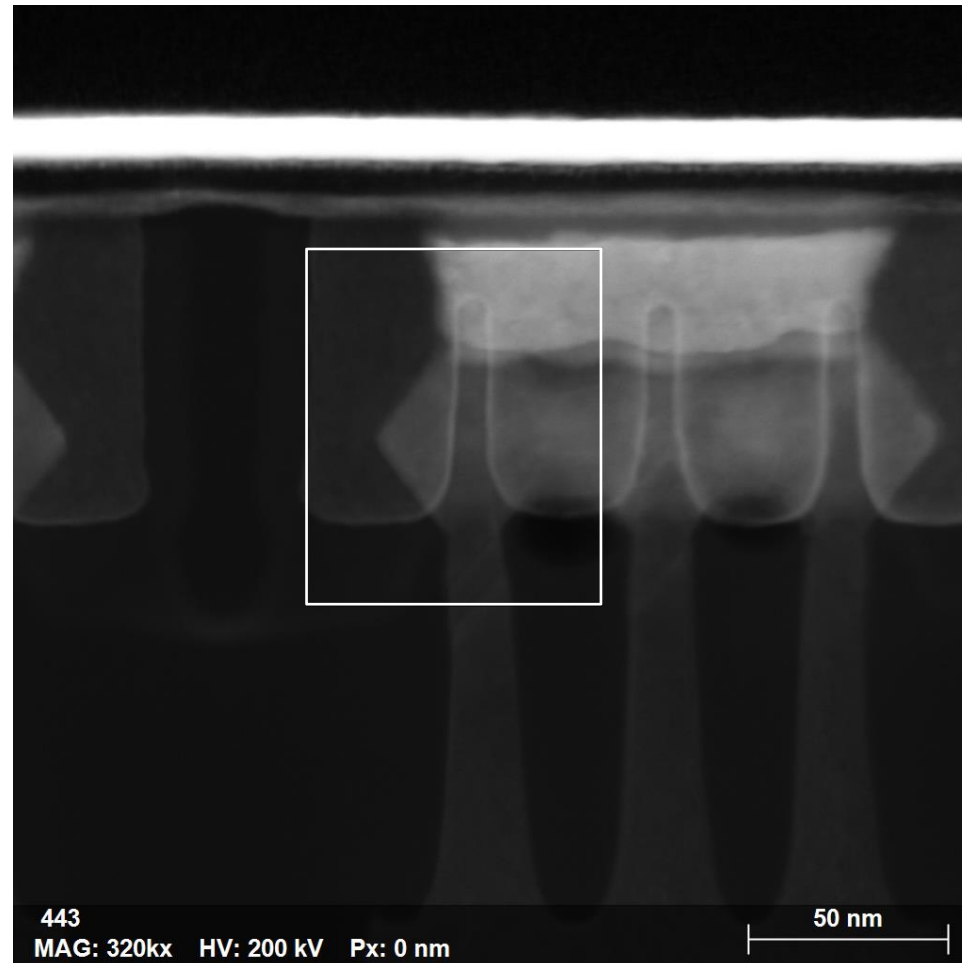


ED(X)S with 100mm² windowless oval detector area using Cs-corrected STEM; Collection angle: ~ 0.4 sr
Raw data, acquisition time 24min, arbitr. units scaled to 100



TFS Titan 80-300 with Bruker XFlash[®]T 100 oval EDS detector at ACE.

Quantitative element mapping of nanostructures.



EDXS with 100 mm² windowless oval detector area; Nion UltraSTEM, Cs-corrected, high brightness source (CFEG); ~0.7sr



NRL UltraSTEM200 with
Bruker XFlash®T 100 oval
EDS detector @ 200 kV.

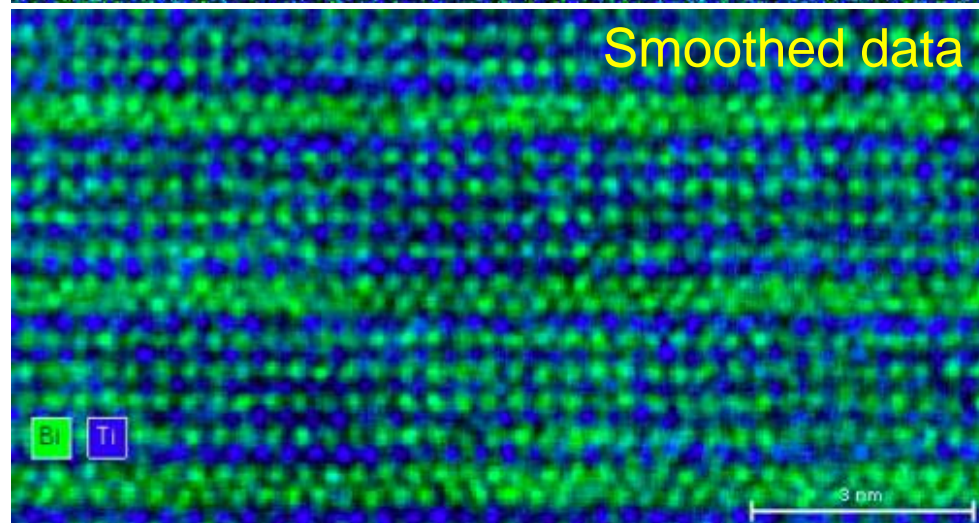
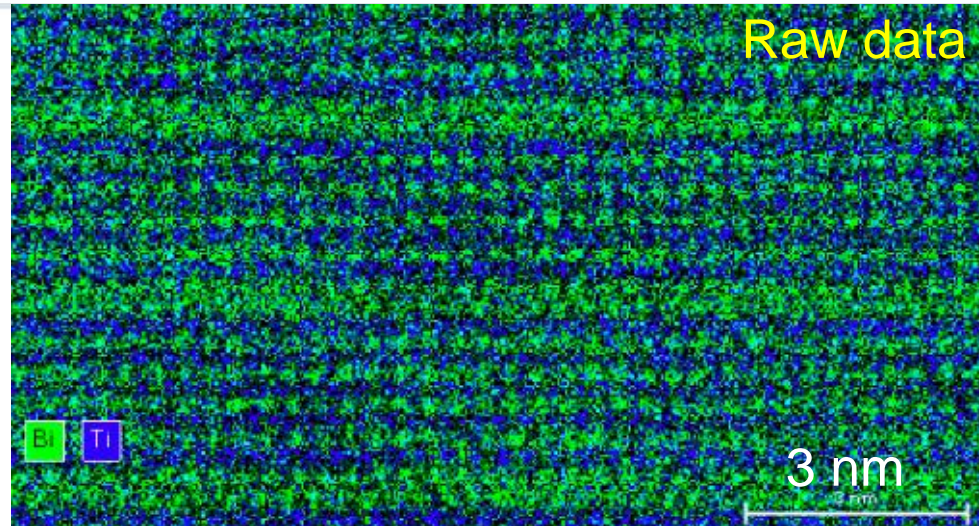
Individual atom columns
can be identified.

Specimen:



See:

*"Direct atomic scale
determination of magnetic
ion partition in a room
temperature multiferroic
material", by L. Keeney et al.*



TCD (Trinity College Dublin) Nion
UltraSTEM200XE 200 kV with
Bruker 100 mm² XFlash SD detector,
100 mm² windowless SDD; 0.7 sr
collection angle.

432x225 pixels,
4.1 msec/pix => 400 sec for map.

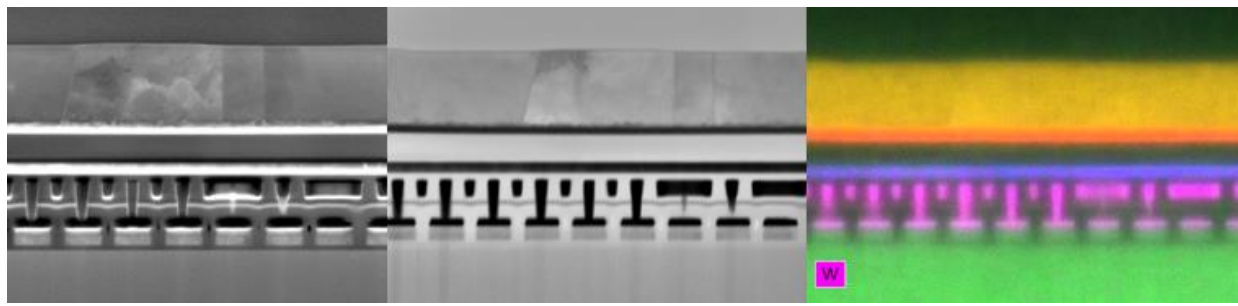
No drift correction.
Bi = green, Ti = blue.

*courtesy Lynette Keeney, Clive
Downing and Valeria Nicolosi. TCD,
Ireland.*

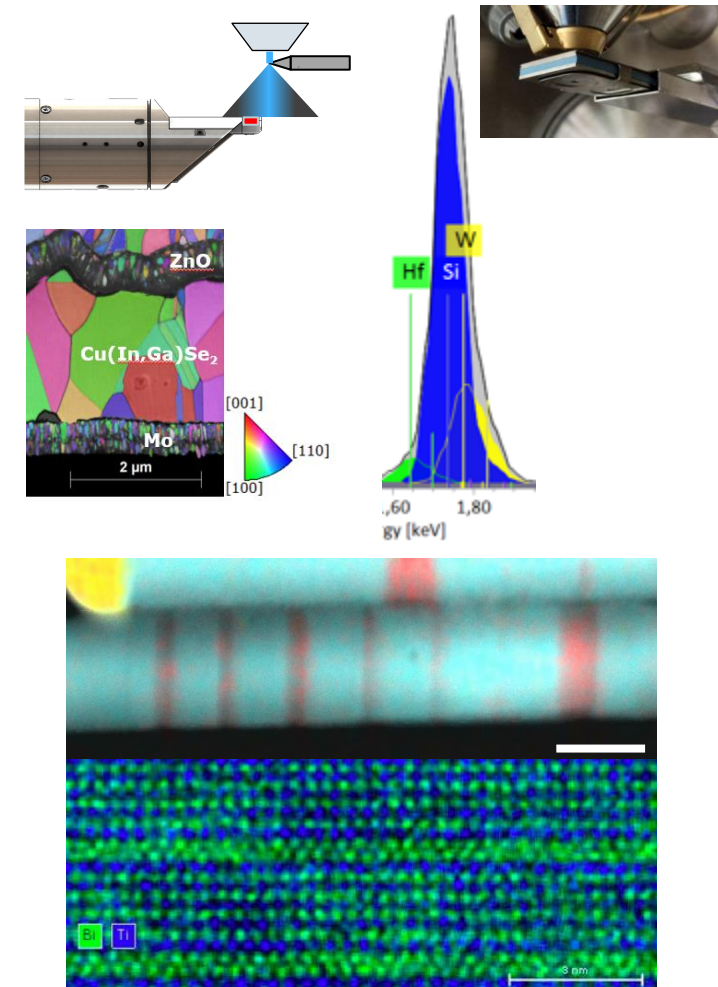
Atom column EDS needs simulation
for correct interpretation

**B. D. Forbes et al., PHYSICAL REVIEW
B **86**, 024108 (2012)**

Summary

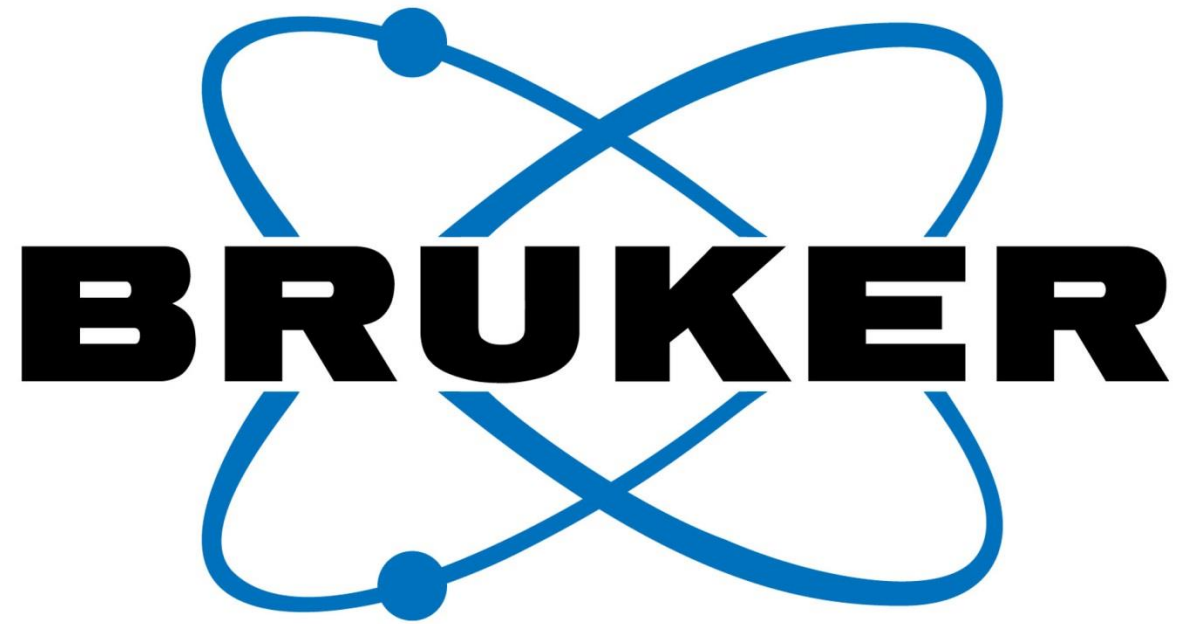


- SEM/FIB are valuable tools for the investigation of semiconductor lamellae using EDS > T-SEM.
- High collection angles and thus fast precise analysis can be achieved with the annular high solid angle XFlash® FlatQUAD detector.
- T-SEM invites for the combination with diffraction techniques, such as TKD, and with micro-XRF.
- Quantitative element analysis with EDS is possible via the relative Cliff-Lorimer and the absolute Zeta-factor method, also for SEM-typical voltages and specimens of considerable thickness.
- Few nm-resolution can be achieved routinely in standard STEM EDS, even with small detector areas (30mm²) at high collection angles.
- The combination of electron source type, Cs-correction and EDS geometry in STEM defines the availability of atomic resolution.



Are there any questions?

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



Innovation with Integrity