Pain Points of Existing Elemental Analysis Techniques and a New Solution

ZEROK NANOTECH

EDX/EELS

- Long sample-prep times
- 3D analysis infeasible
- Low-Z elements challenging

Site-Specific SIMS

- Resolution limited to ~50 nm with high yield (CAMECA NanoSIMS), or
- Can get a high resolution FIB (Ga, He, Ne) with a time-of-flight SIMS analyzer. But low secondary ion yields from these beams usually results in poor lateral resolution. Additionally, time-of-flight analyzers necessitate **long** acquisition times.

These points are addressable by

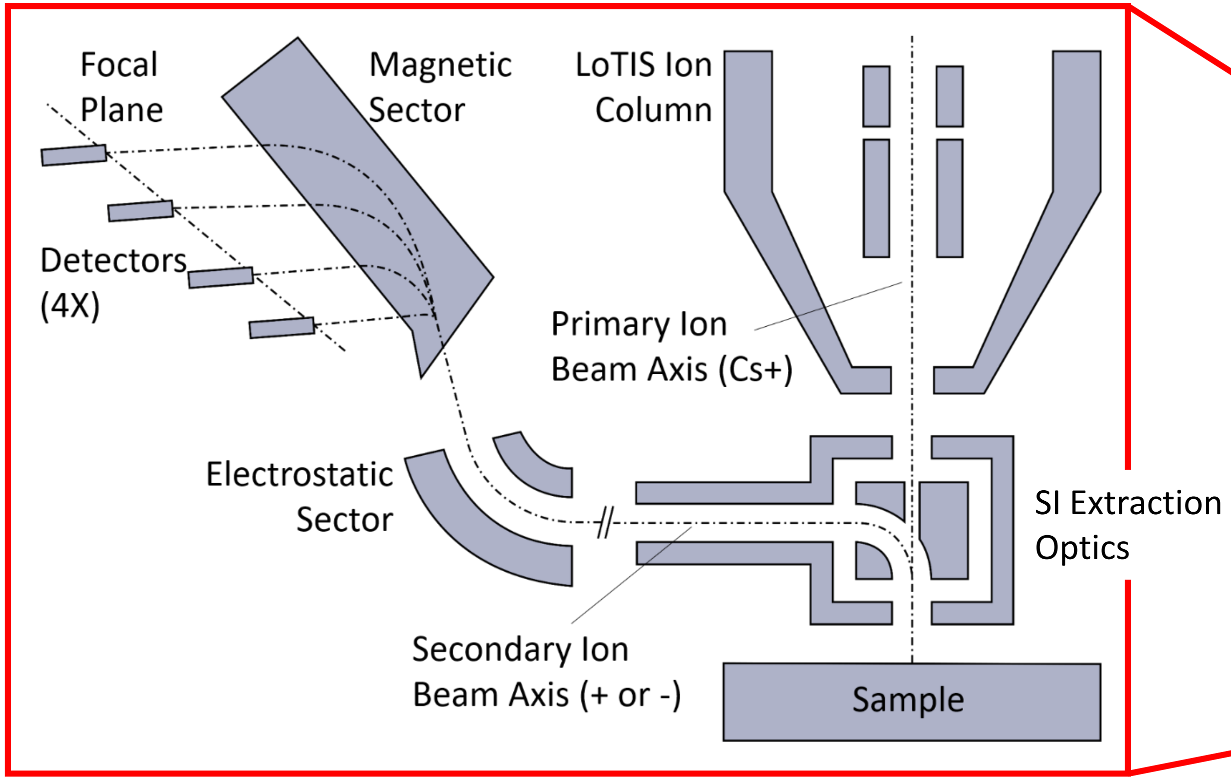
SIMS:ZERO

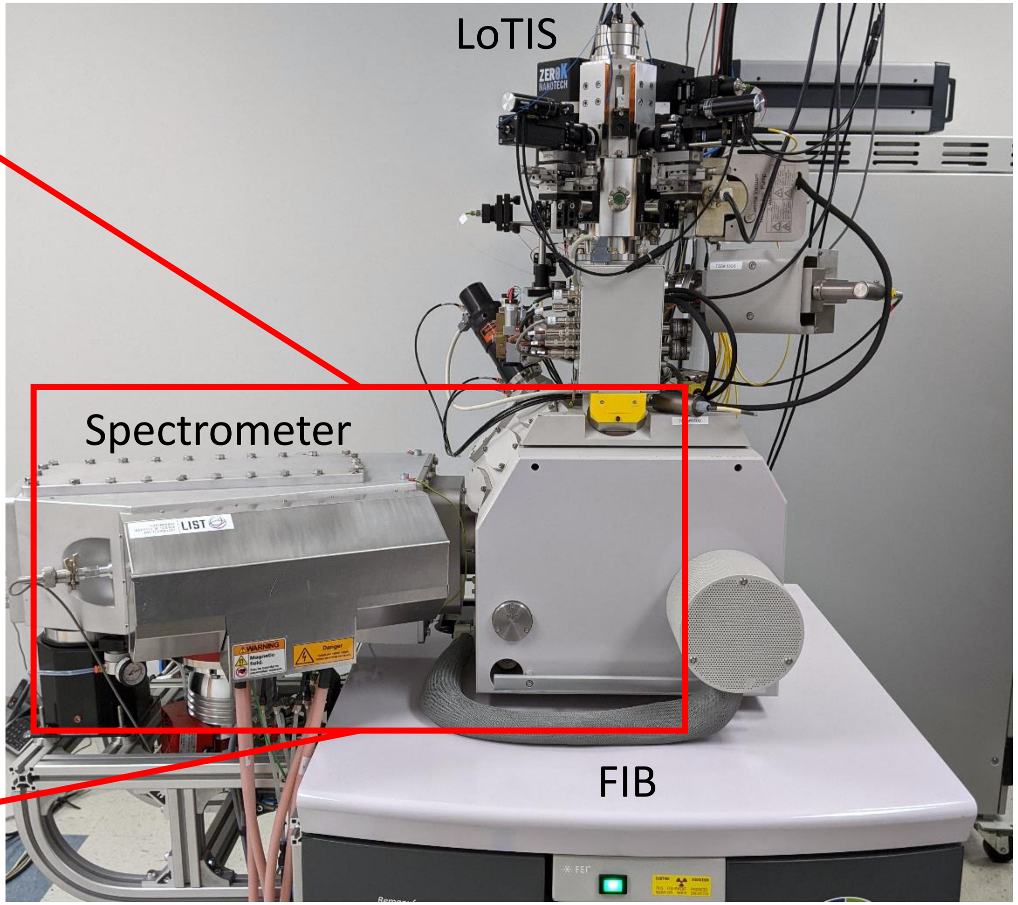
- Few-nanometer resolution (slide 4)
- High secondary ion yield (slides 6,7)
- Integrated sample-prep and analysis capability (slides 8-18)

SIMS:ZERO

Instrument Overview

Cs+ FIB:ZERO (zeroK) and SIMS spectrometer (LIST: Luxembourg Institute of Science and Technology) on a 600 series FIB (FEI)

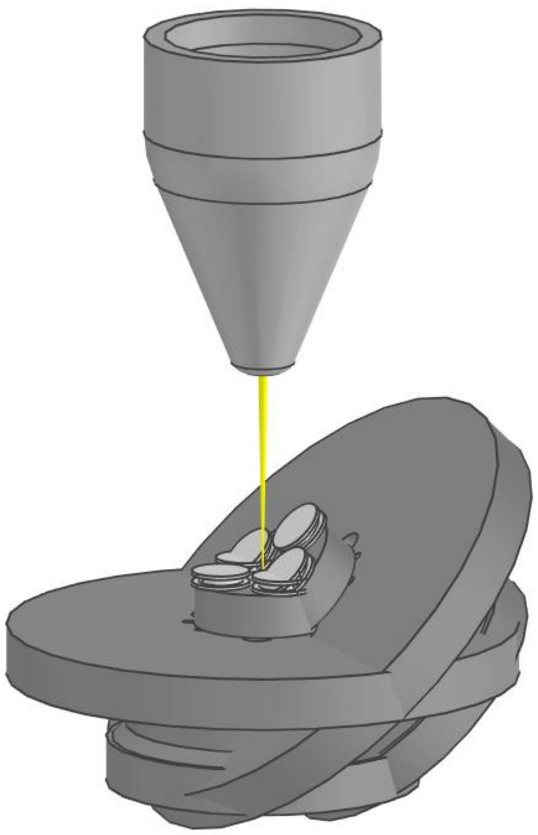


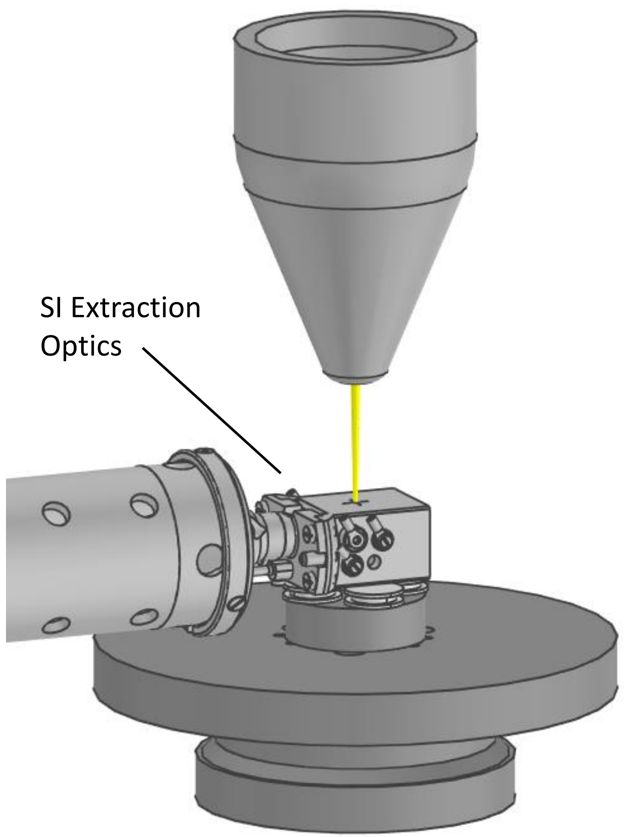


- FIB online 6/2020
- SIMS online 5/2021

FIB / SIMS Combination

Sample Prep, Nanofabrication / Analysis, Process Control





LoTIS capabilities

- 2-16 keV Cs+ beam
- Up to 5nA beam current
- Spotsize <2nm at low current
- Good spotsizes even at low beam energy

FIB Mode (SIMS Extraction Optics Retracted)

- Milling
- Sample Preparation (eg Sectioning, Polishing)
- Nanofabrication
- Gas-assisted processes (eg Platinum Deposition)
- Tilt stage

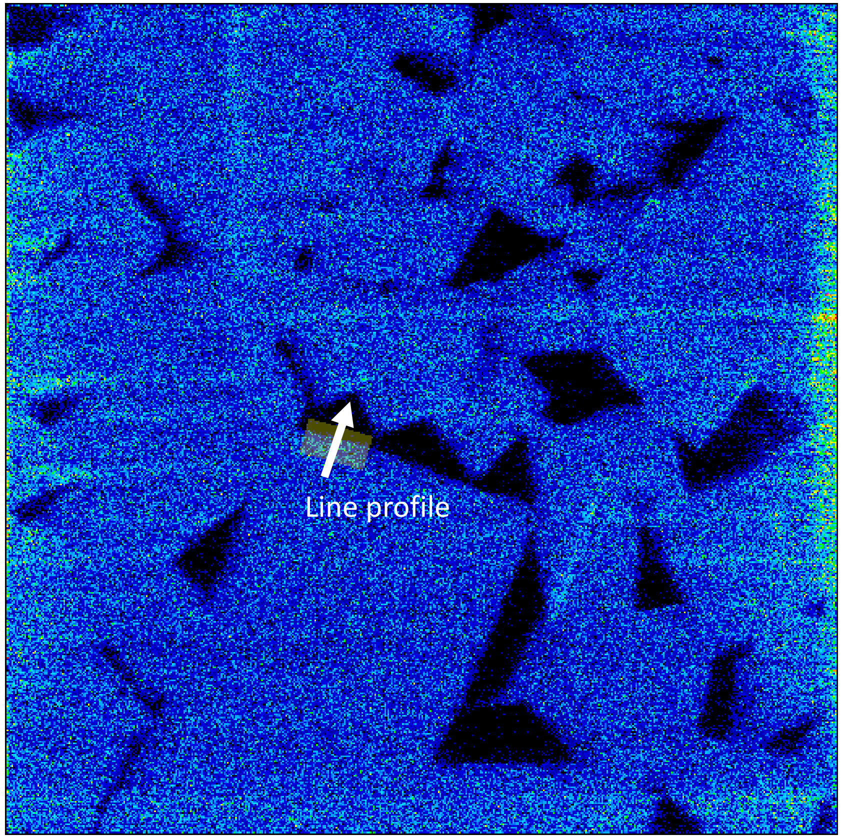
SIMS Mode (SIMS Extraction Optics Inserted)

- Highest spatial resolution SIMS imaging
  - $\sigma = 6$ nm demonstrated
- Mass resolution $M/\Delta M = 400$
- Mass range up to 300 amu
- High secondary ion throughput (~40% simulated)
- 4-Channel Detector Standard (Continuous Focal Plane Detector available)

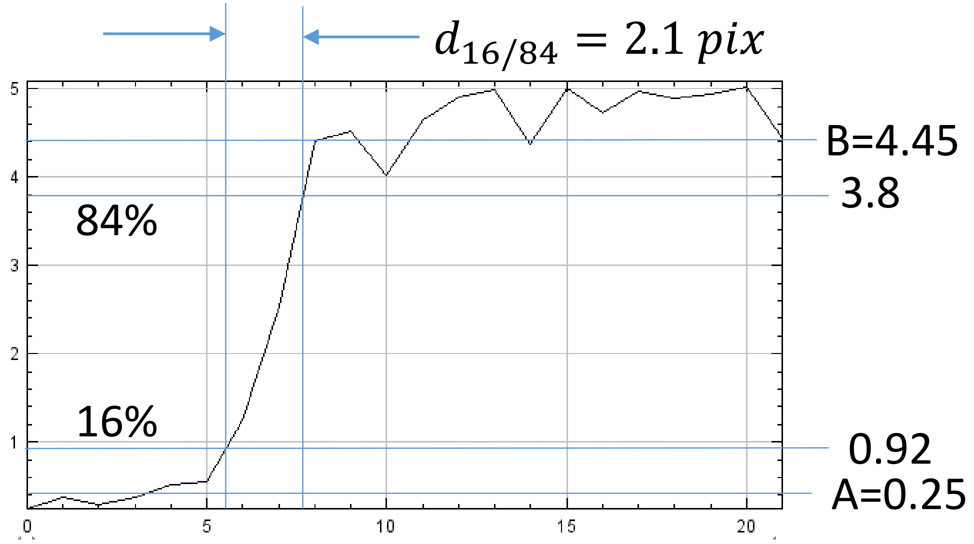
SIMS:ZERO Resolution

Tungsten Carbide

- **SIMS:ZERO can provide higher resolution SIMS scans than any other instrument**
- SIMS resolution is a function of abundance, yield, and spot size
- SIMS:ZERO has a focused ion beam with <3 nm spot size, and since it's Cs^+ we achieve high yields for many materials
- In samples with high abundances, resolution at near the physical limits of SIMS can be achieved (see right)



Multi_WC_2105121624015_CH1.TIF



$$d_{16/84} = 2.97\ \mu m * \frac{2.1}{512} = 12.2\ nm$$

$$\boldsymbol{\sigma = 6.1nm}\ \textbf{(!)}$$

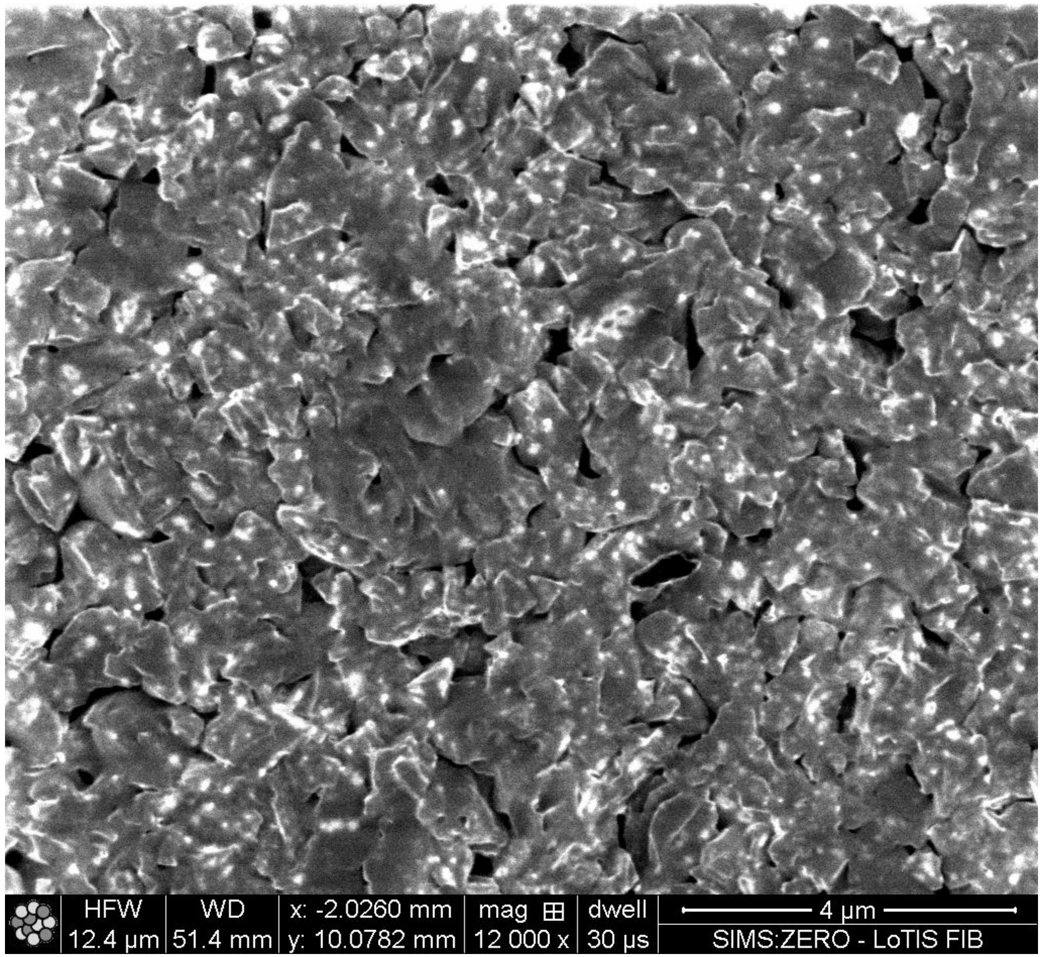
Working Distance = 51.6mm
272s acquisition time.

Negative Ions

Date	05/12/2021
Sample	WC (184 amu)
FOV (um)	2.97um
I (pA)	2.5
U (kV)	16

SIMS Analysis Example

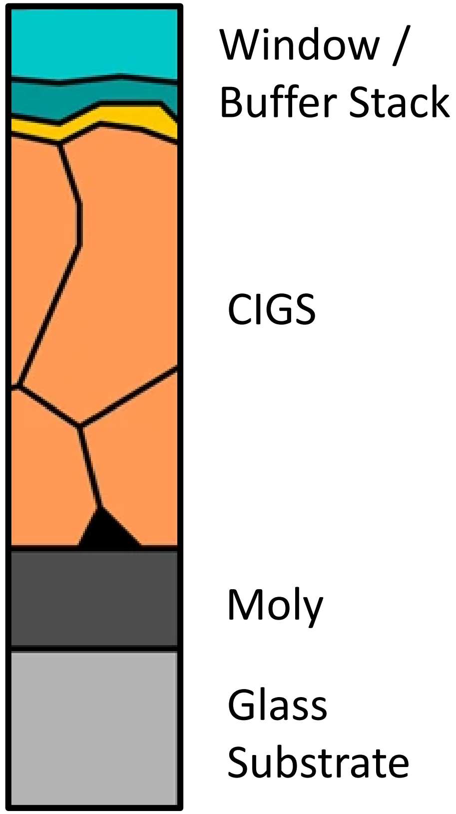
CIGS Cu(In,Ga)Se_2 – Rb doped



SE Image Cs+, 16keV, 10pA, 51.6mm WD

Summary

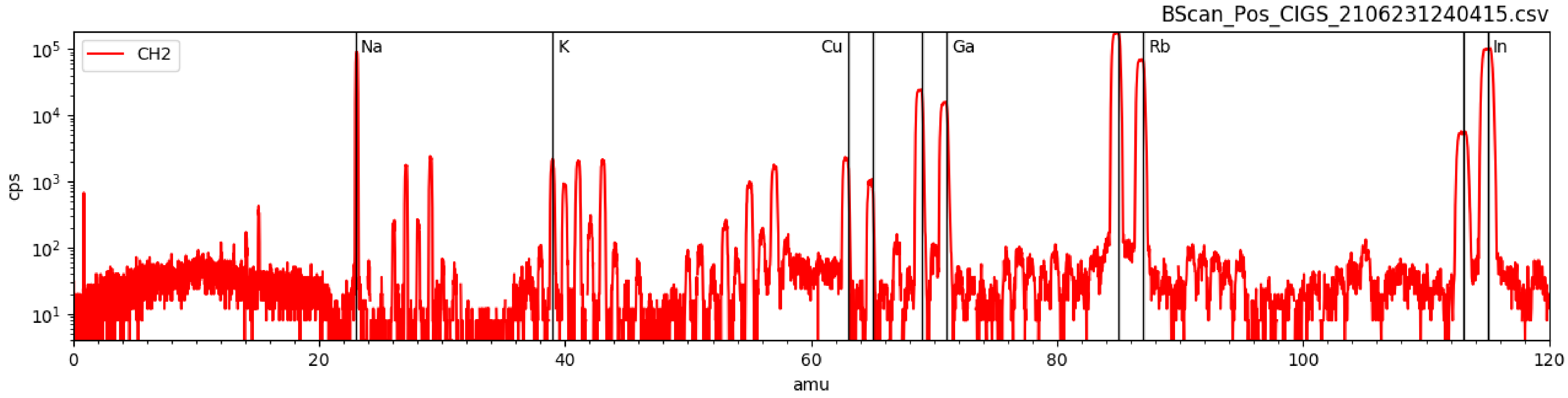
- CIGS is a solar cell absorber material
  - Rubidium doping increases conversion efficiency
- SIMS spectra clearly show all CIGS elements:
  - Cu, In, Ga, Rb in Positive Mode
  - Se, S in Negative Mode
- Secondary ion imaging channels show distribution of elements in sample, eg Rb dopants concentrated in grain boundaries
- Secondary electron images provide complementary information at high resolution
- Section view technique provides superior SIMS data

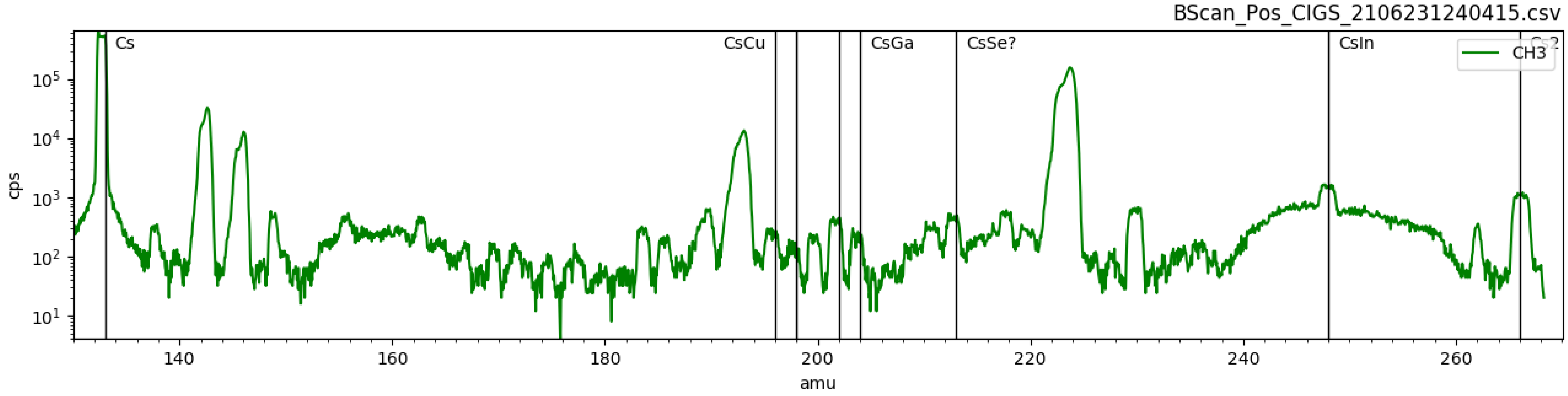


Werner, et al. *Scientific Reports* **volume 10**, 7530 (2020)

CIGS Cu(In,Ga)Se_2 – Rb doped

Mass Spectra – Positive Ions



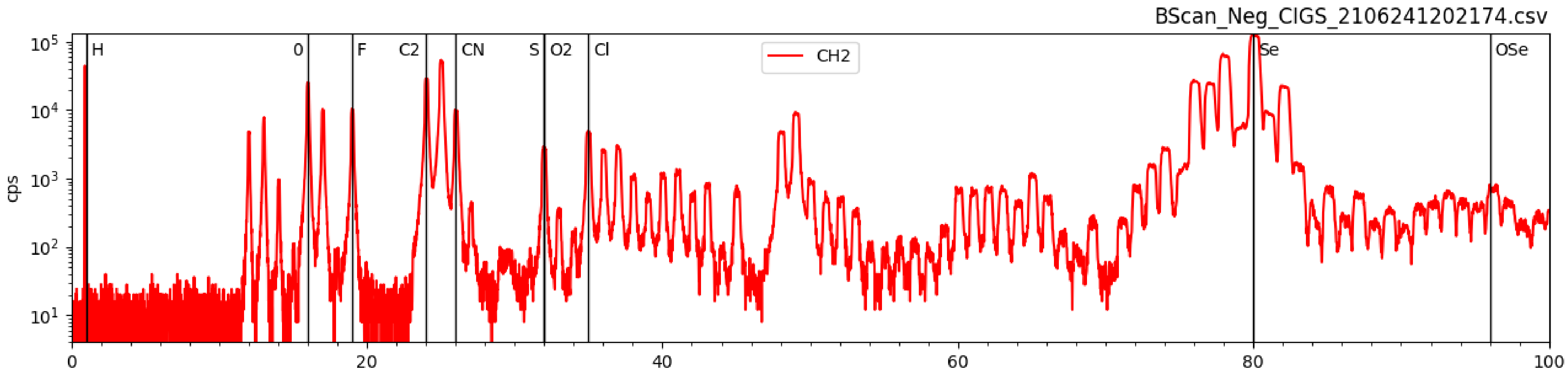


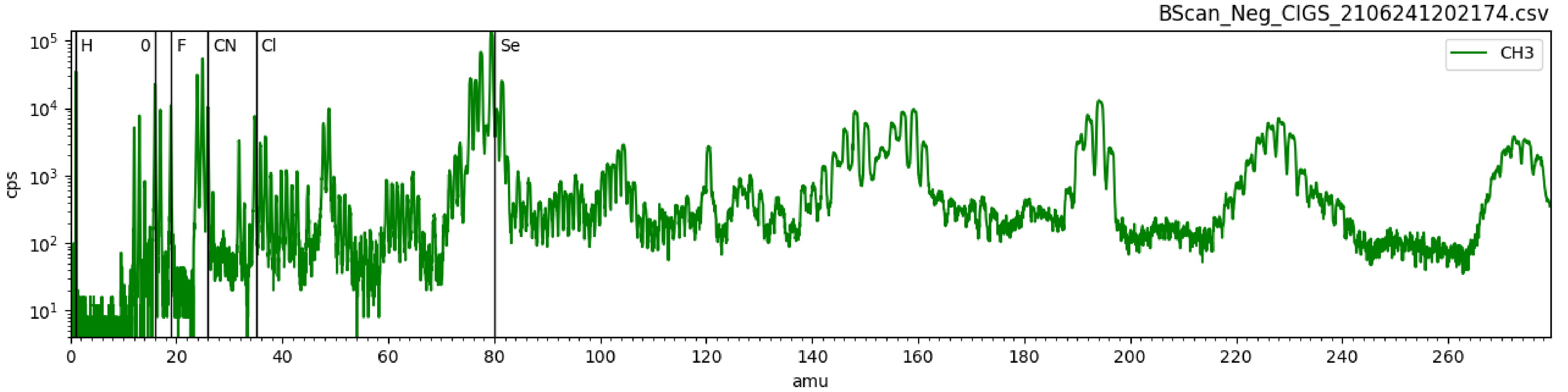
Start (mT) : 30.000000
Stop (mT) : 700.000000
Delta (mT) : 0.100000
Sampling rate (ms) : 250.000000
Waiting time (s) : 0.250000
Period of beam acq : 0
Pos CH1 : 100.000675
Pos CH2 : 200.000362
Pos CH3 : 299.999717
Pos CH4 : 390.000000

Date	06/23/2021
Sample	CIGS
Aperture Slit	100um
FOV (um)	43
I (pA)	10
U (kV)	16

CIGS $Cu(In,Ga)Se_2$ – Rb doped

Mass Spectra – Negative Ions





Start (mT) : 30.000000
Stop (mT) : 700.000000
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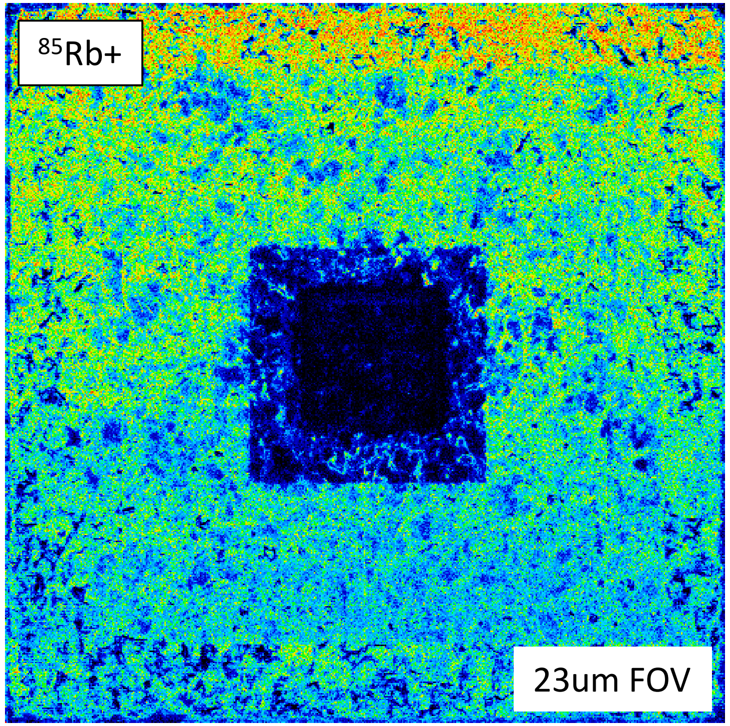
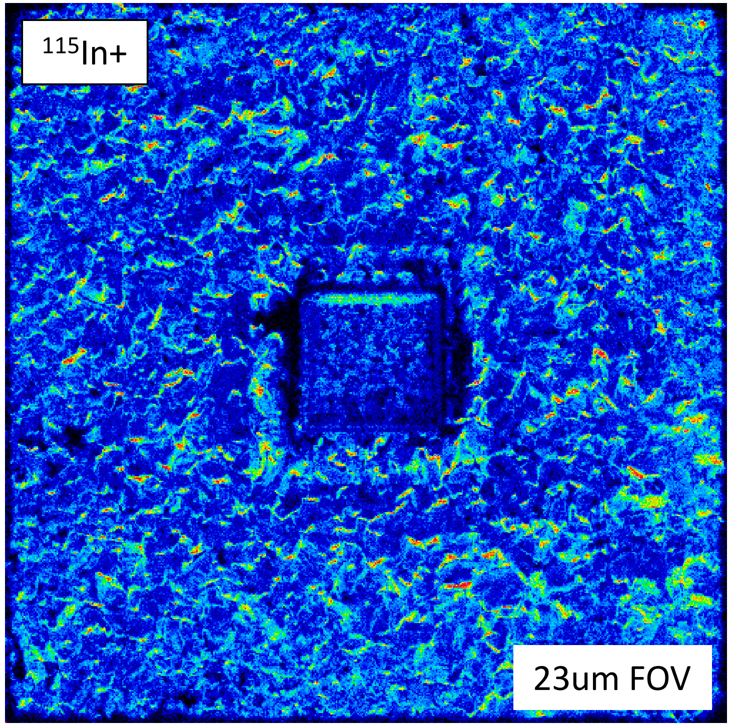
Date	06/24/2021
Sample	CIGS
Aperture Slit	100um
FOV (um)	43
I (pA)	10
U (kV)	16

CIGS $Cu(In,Ga)Se_2$ – Rb doped

Secondary Ion Image - Large FOV





Rb, In is everywhere on surface (window/buffer stack layer).

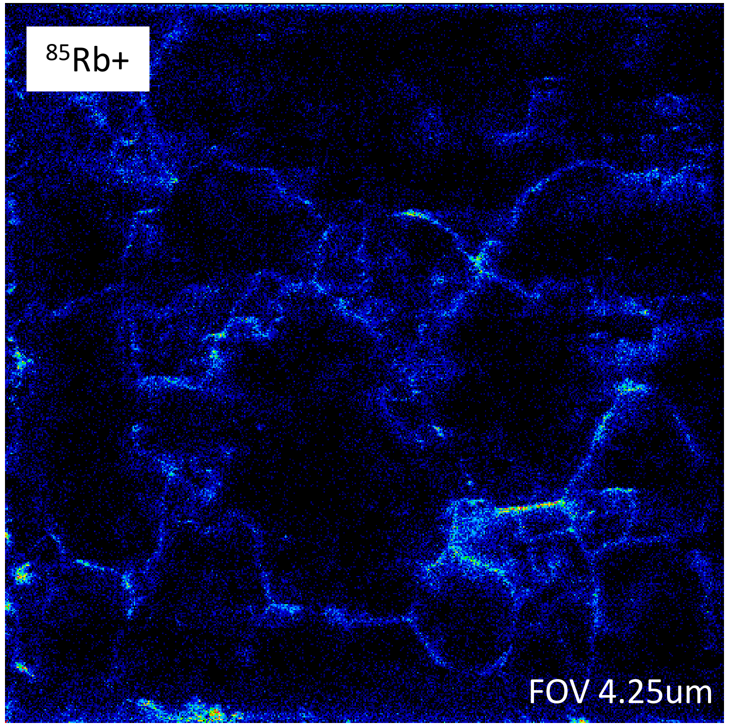
Signal variation largely due to topography

We have milled a crater to see subsurface structure, e.g. where Rb is confined to CIGS grain boundaries (see next slide).

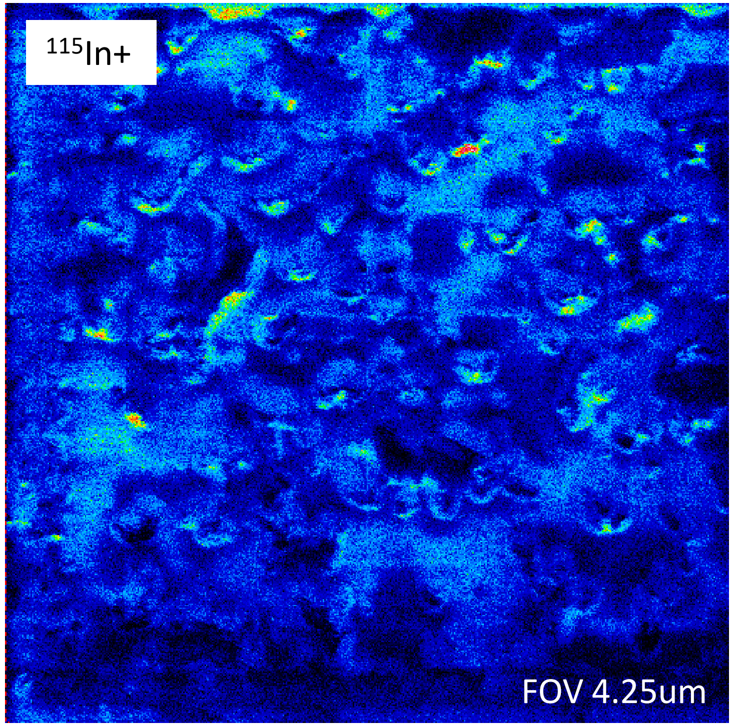
Cs+, 16keV, 10pA
1ms dwell, 4.5min acquisition time
CIGS_Pos_2107081255037.csv

CIGS $Cu(In,Ga)Se_2$ – Rb doped

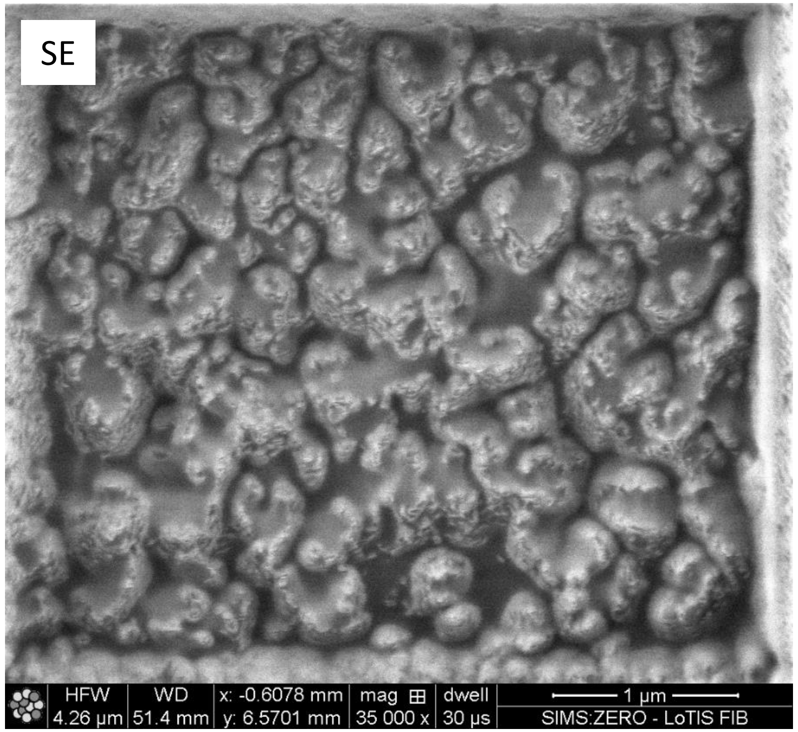
Secondary Ion Image - Smaller FOV - Crater



Rubidium dopants are found primarily along grain boundaries



Indium signal determined primarily by topography not spatial distribution



Secondary electron image

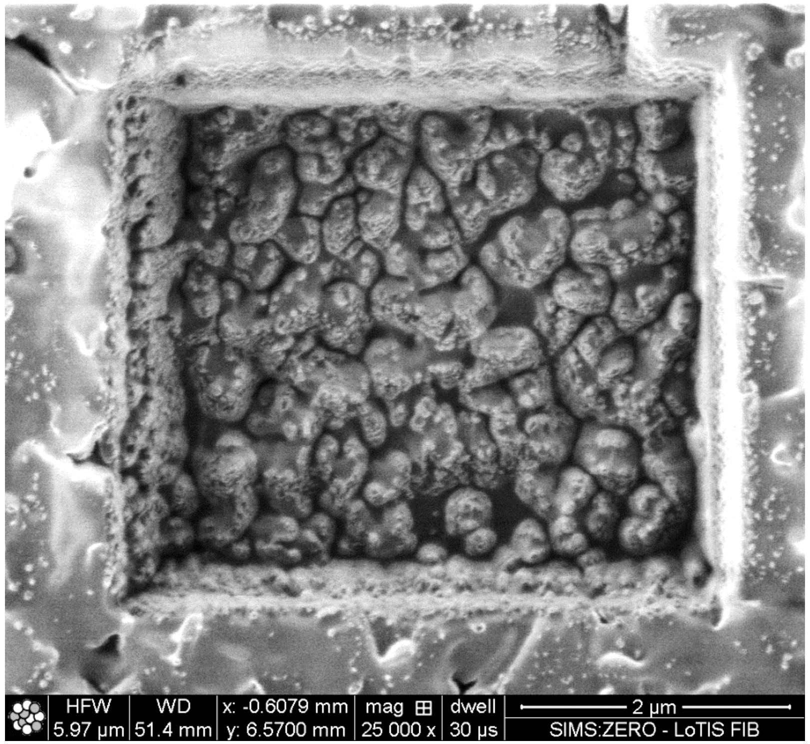
(NOTE: somewhat deeper than where SIMS image was acquired)

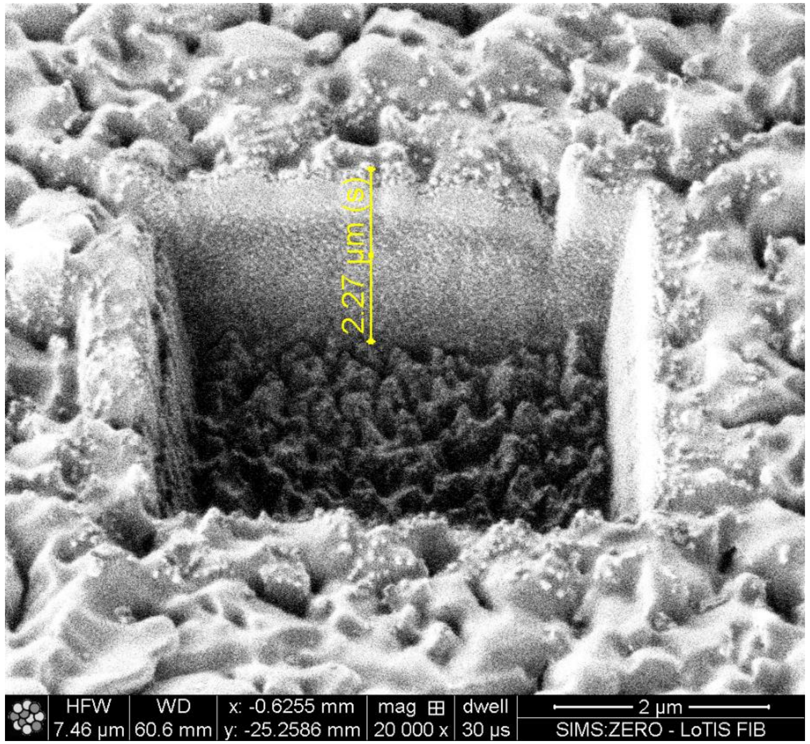
Cs+ 16keV, 2.5pA, 51.6mm WD
1ms dwell, 4.5min acquisition time
CIGS_Pos_2107081226114.csv

CIGS $Cu(In,Ga)Se_2$ – Rb doped

SE Images

Crater Geometry





Very rough, pointy surface topography develops while milling the crater

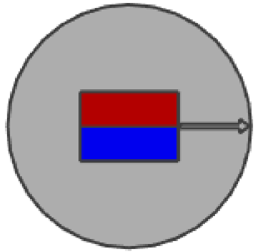
This kind of topography is reflected in the SIMS images, obscuring elemental contrast (Slide 9)

With proper sample sectioning techniques, we obtain more and better SIMS data (Slides 11-18)

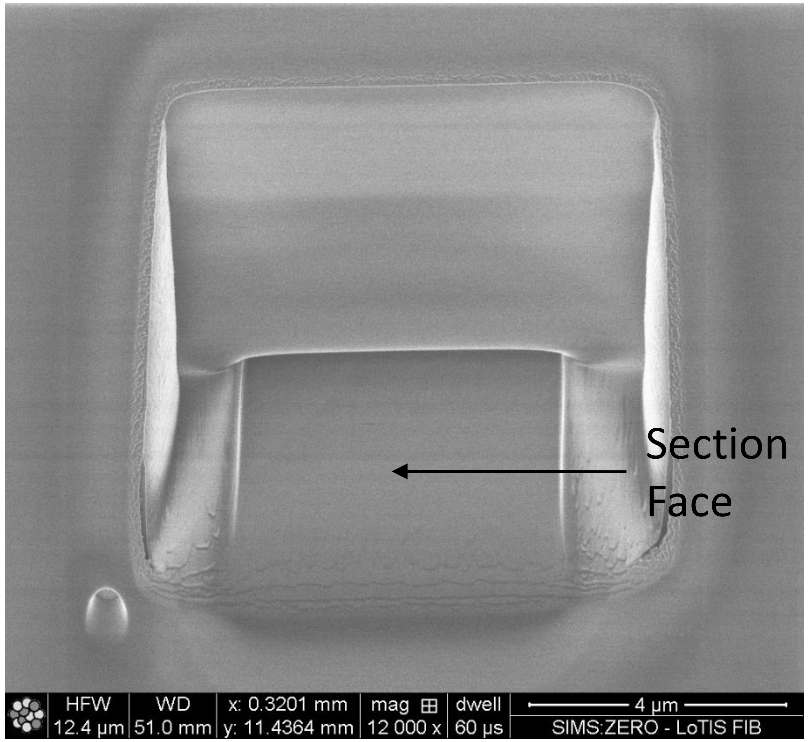
Cs+, 16keV, 10pA, 51.6mm WD

SIMS-Compatible Section View

45° Angle Cut - Example



View with Sample Normal to Beam; Ready for SIMS on Section



For many samples, working with a section view is a sensible choice

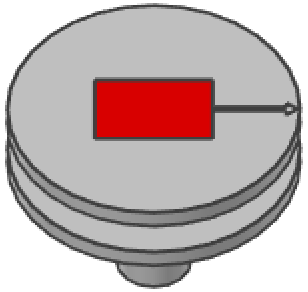
1. Reveal sub-surface structure
2. Obtain depth profile data without accumulated topography from uneven sputtering
3. Polish rough samples to isolate elemental from topographical contrast
4. Build 3D tomographic reconstructions through serial sectioning/polishing

In SIMS:ZERO, sample must be normal to ion beam in SIMS Mode, so section face is cut at 45° to sample surface

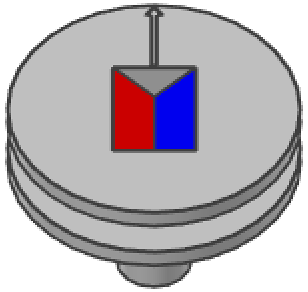
This sectioning is done in FIB mode. Switching between FIB and SIMS mode takes about 2 min

SIMS-Compatible Section View

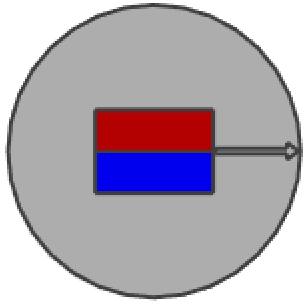
45° Angle Cut – Sample Prep Example



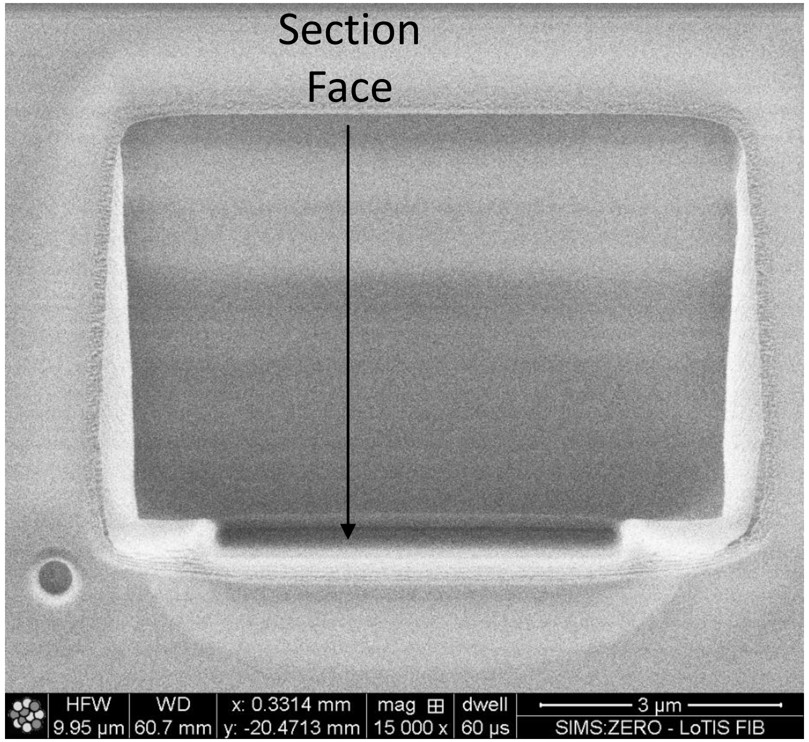
Section Cut with Sample Tilted at 45°

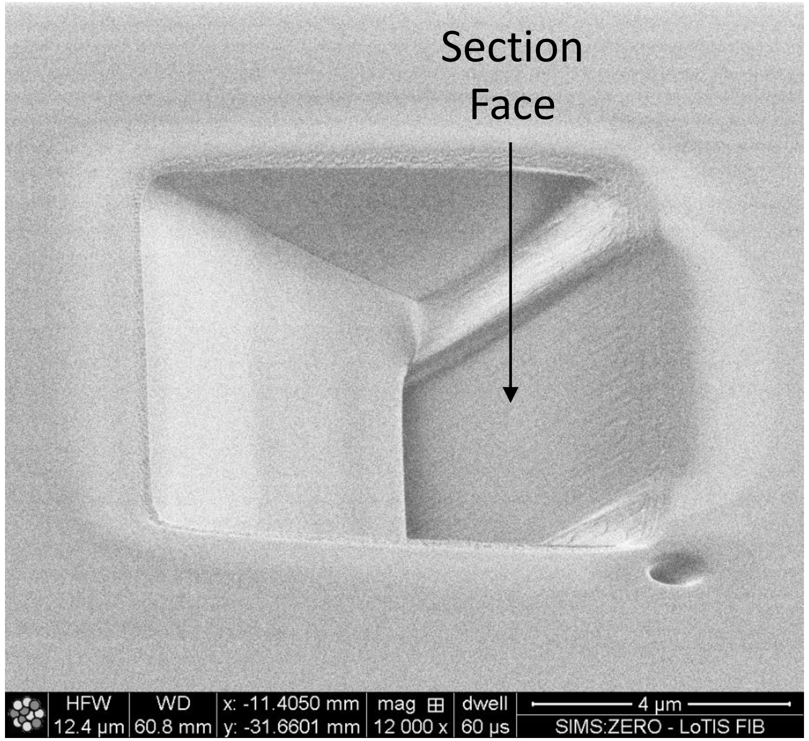


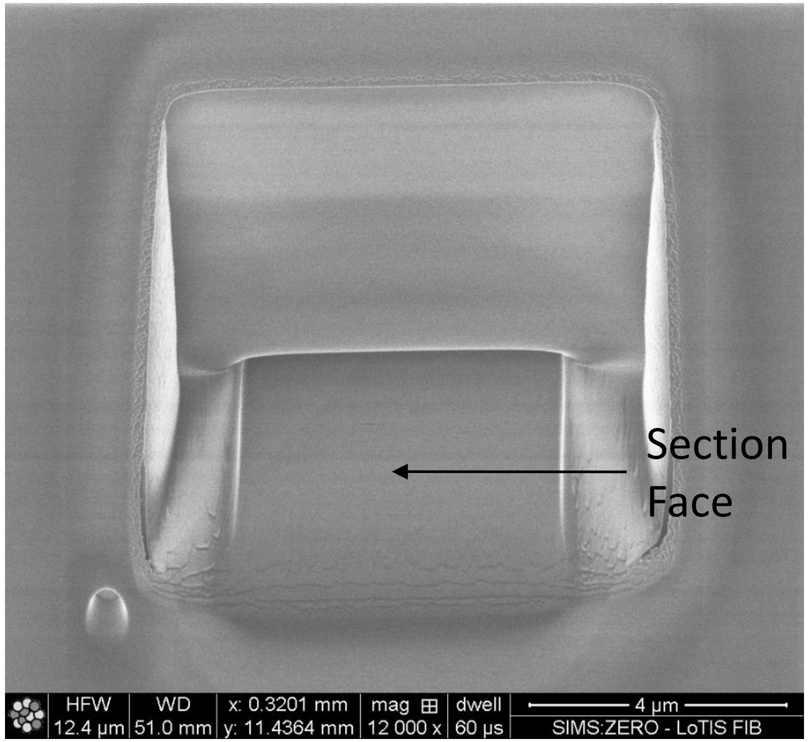
View with Sample Tilted at 45° & Rotated 90°



View with Sample Normal to Beam; Ready for SIMS on Section



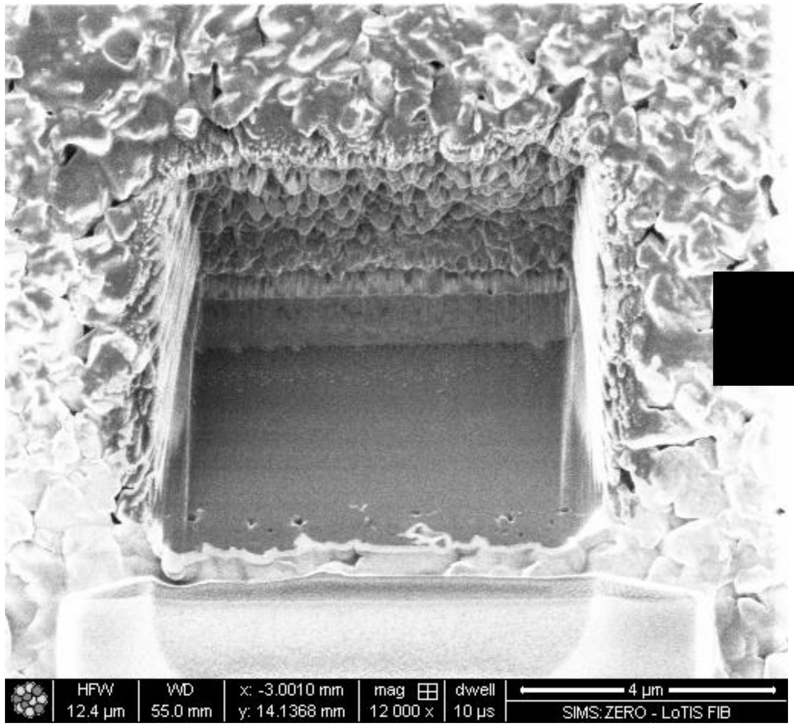




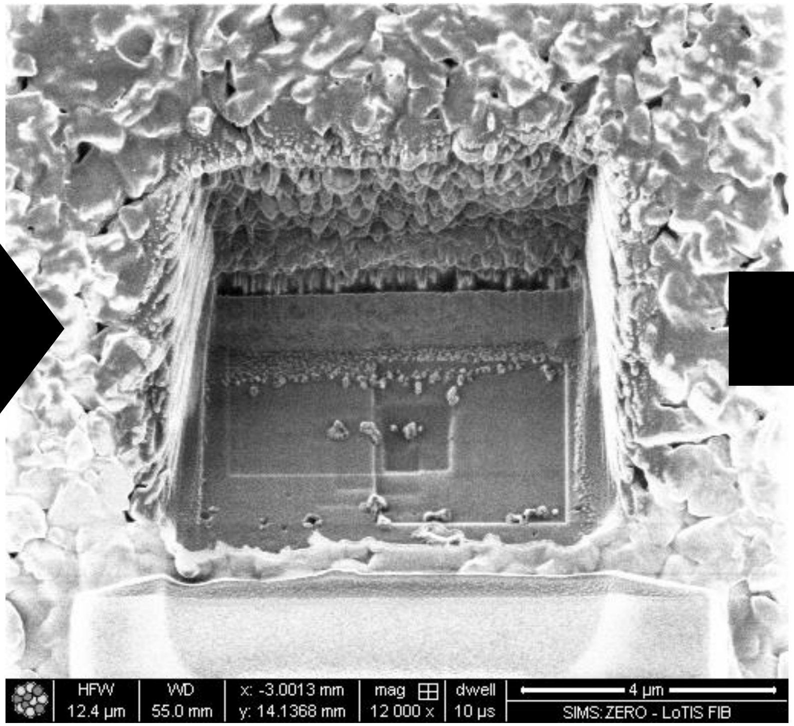
CIGS $Cu(In,Ga)Se_2$ – Rb doped

Serial Sectioning / Imaging / Polishing Work-Flow

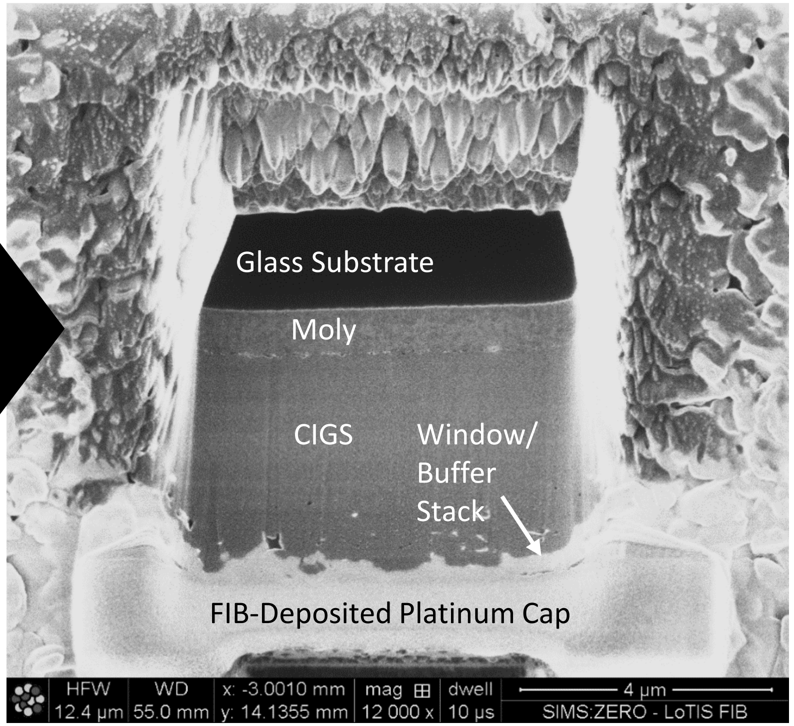
SE Images



SIMS section, prepared with low surface topography, reveals layer structure (glass, moly, CIGS, Window/Buffer Stack)



After SIMS Imaging, section face develops topography which obscures elemental contrast / distribution information



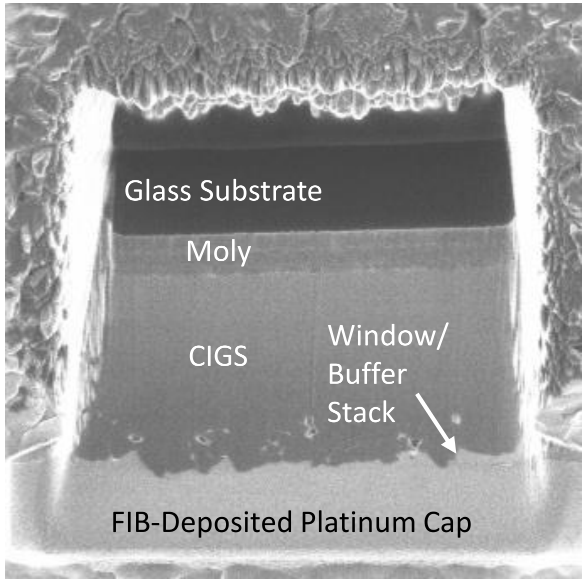
Section face after cleanup mill. Ready for SIMS on next layer

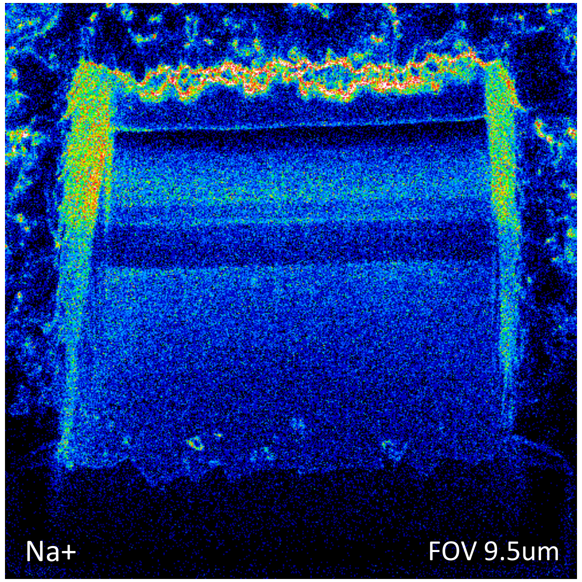
Cs+, 16keV, 10pA, 51.6mm WD

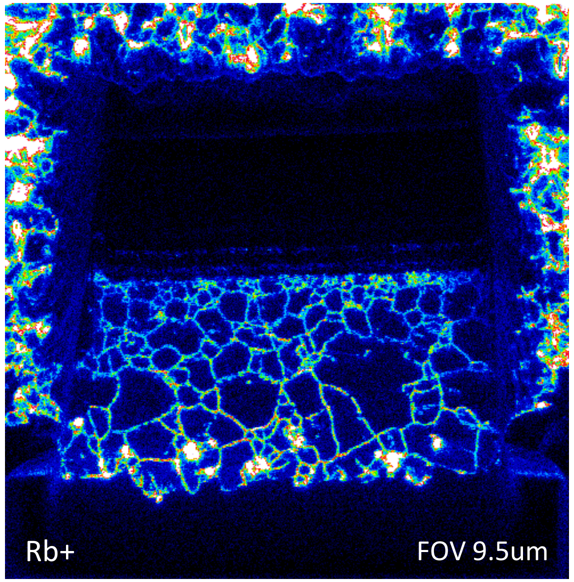
CIGS $Cu(In,Ga)Se_2$ – Rb doped

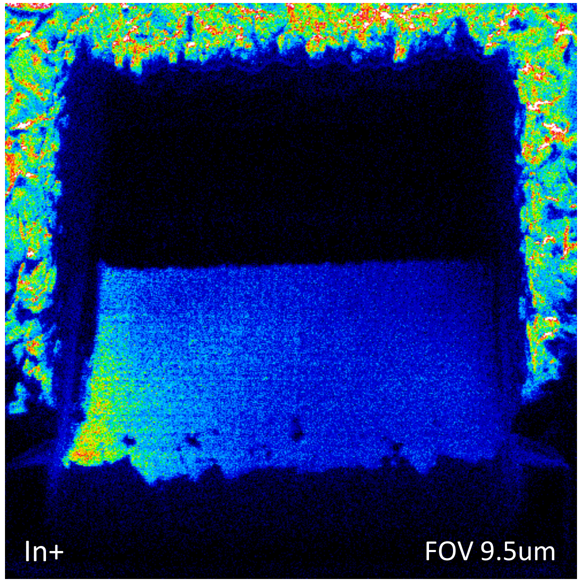
Section View – Positive Ions

SE Image – Pre-SIMS









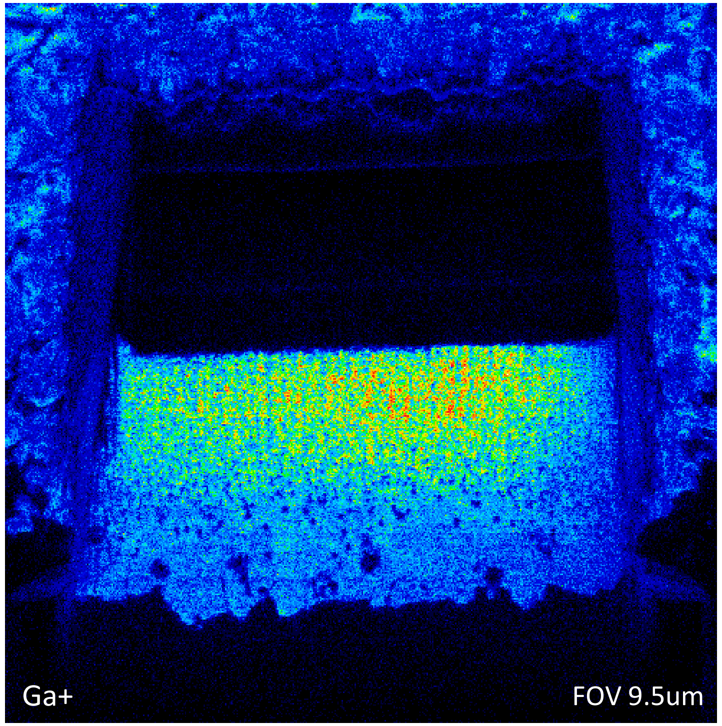
- Rb confined to grain boundaries
- Grains are smaller near the interfaces

Cs+, 16keV, 3.5pA, 51.6mm WD
CIGS_Pos_2107161606287.csv
CIGS_Pos_2107161613425.csv

CIGS Cu(In,Ga)Se_2 – Rb doped

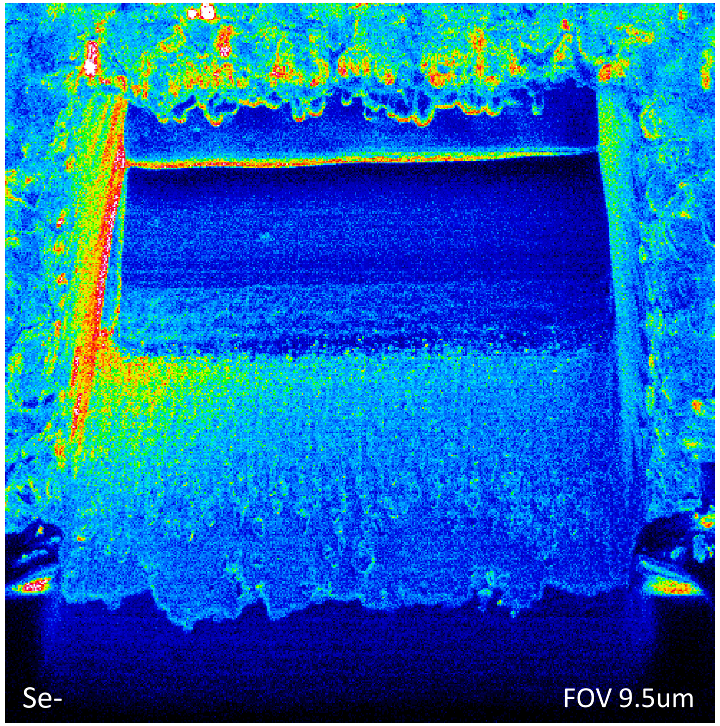
Section View – Positive Ions / Negative Ions / SE

Positive Mode



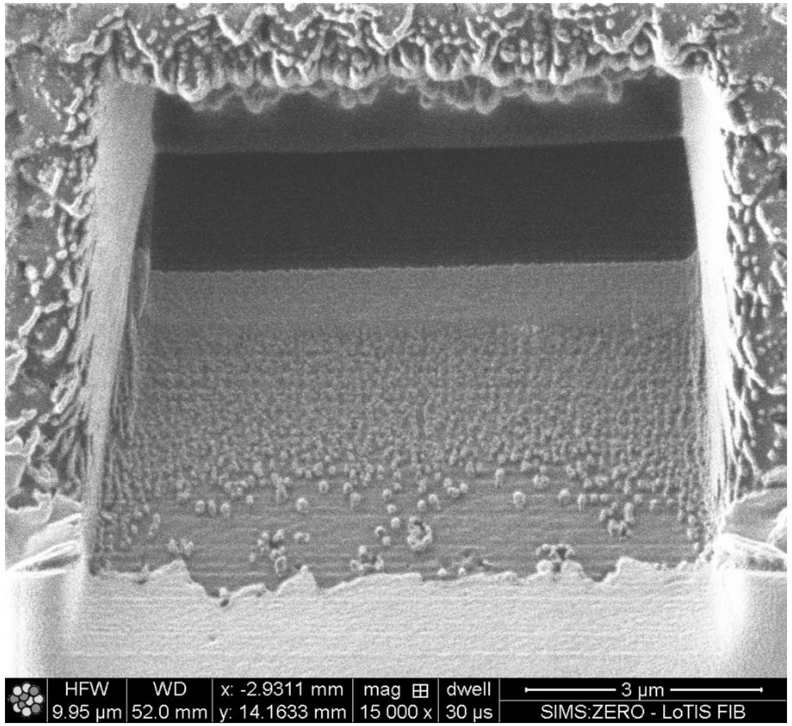
- Ga concentration gradient ↑
- Dark spots appear on image

Negative Mode



- Spherical drops containing Se develop on CIGS region after repeated imaging

SE Image – Post SIMS

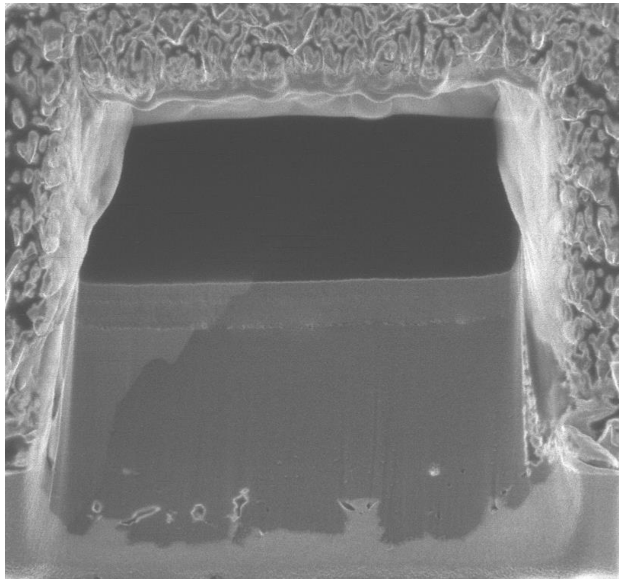


- Unwanted topography can be cleaned up by polishing in FIB mode

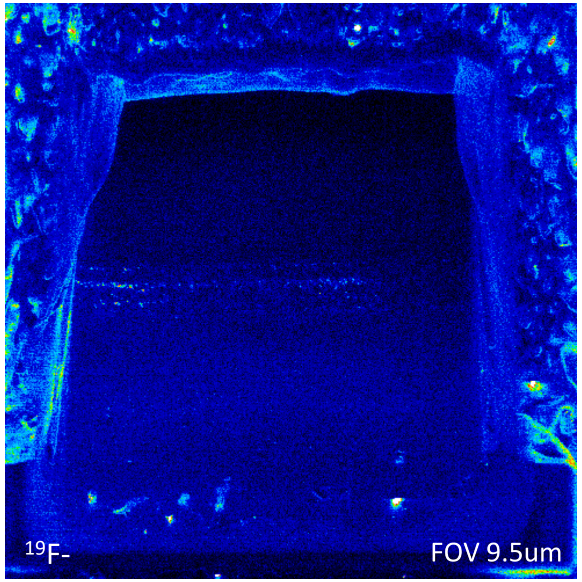
Cs+, 16keV, 3.5pA, 51.6mm WD
CIGS_Pos_2107161613425.csv
CIGS_Neg_2107161719423.csv

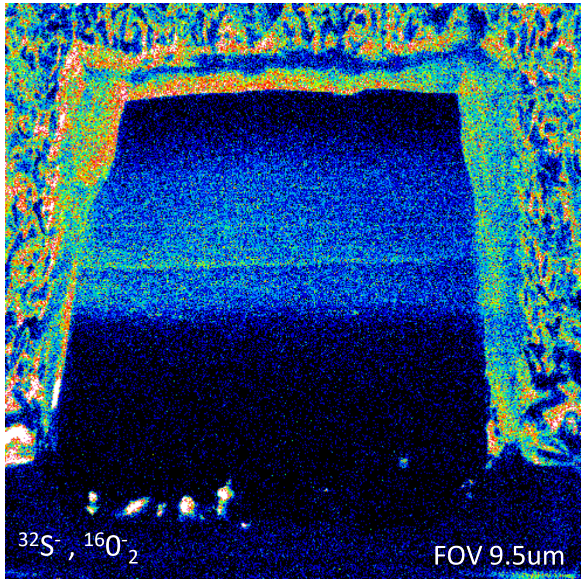
CIGS $Cu(In,Ga)Se_2$ – Rb doped

Section View – Negative Ions – Post 2nd Polish

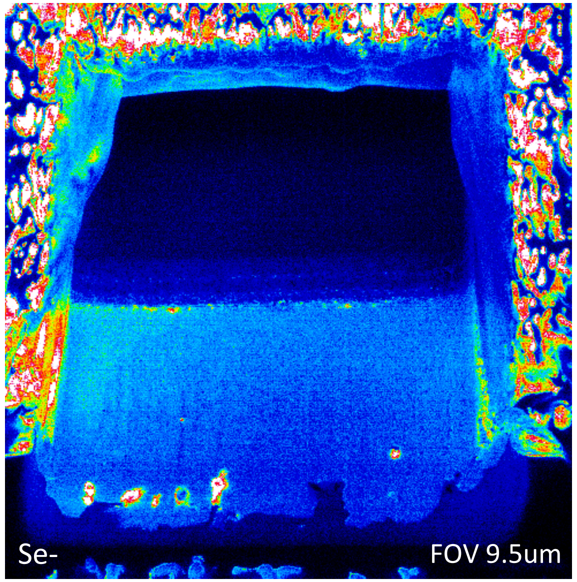


SE Image – Post Polish
Low topography restored





Signal band in CIGS layer near moly may be sulfur, commonly used in CIGS fabrication process; inclusions near surface

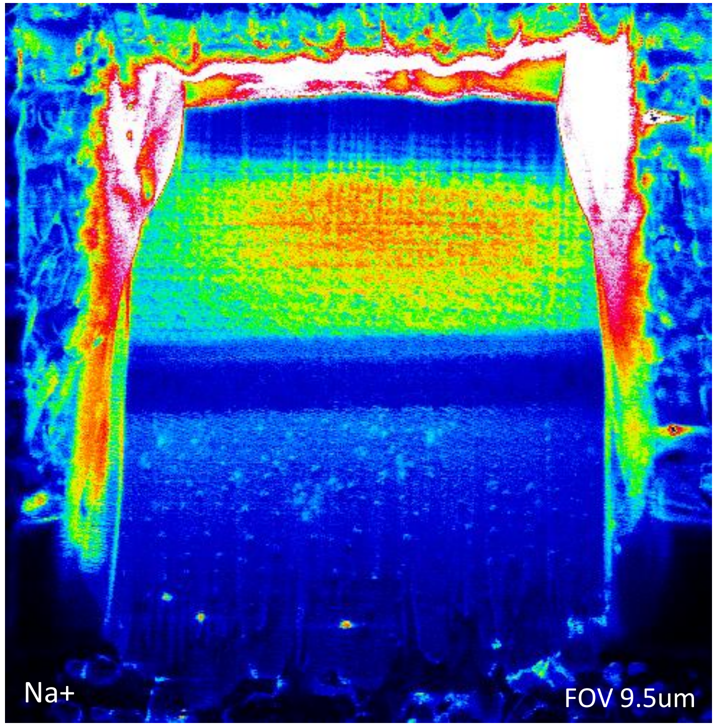


Se is more uniformly distributed in CIGS layer; droplets at moly interface, a few inclusion near surface

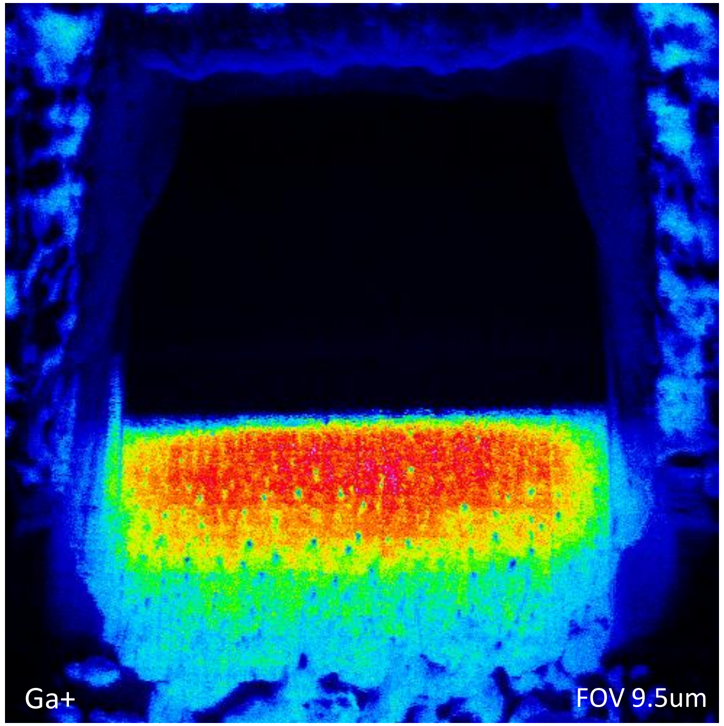
Cs+, 16keV, 10pA, 51.6mm WD
CIGS_Neg_2107201513310.csv

CIGS Cu(In,Ga)Se_2 – Rb doped

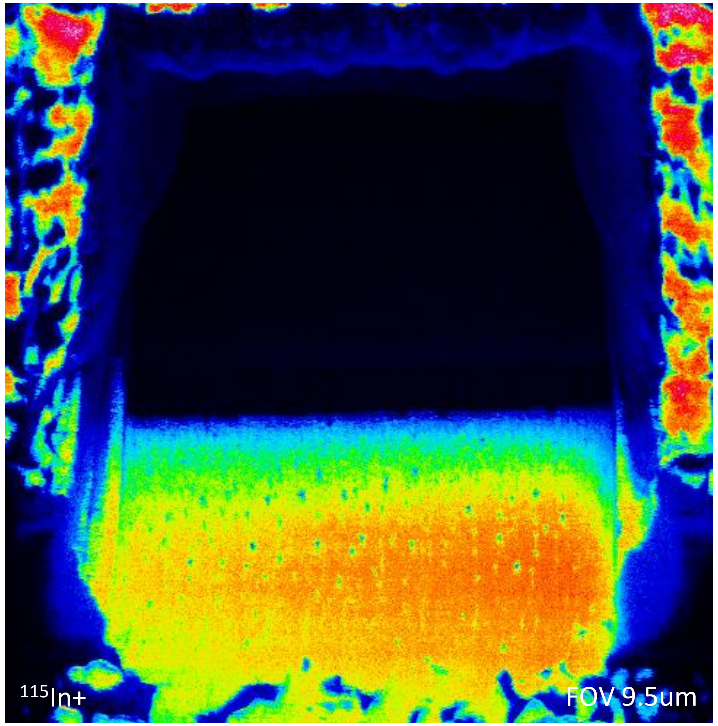
Section View – Positive Ions – Post 3rd Polish



Na – Soda Lime Glass



Ga concentration gradient ↑

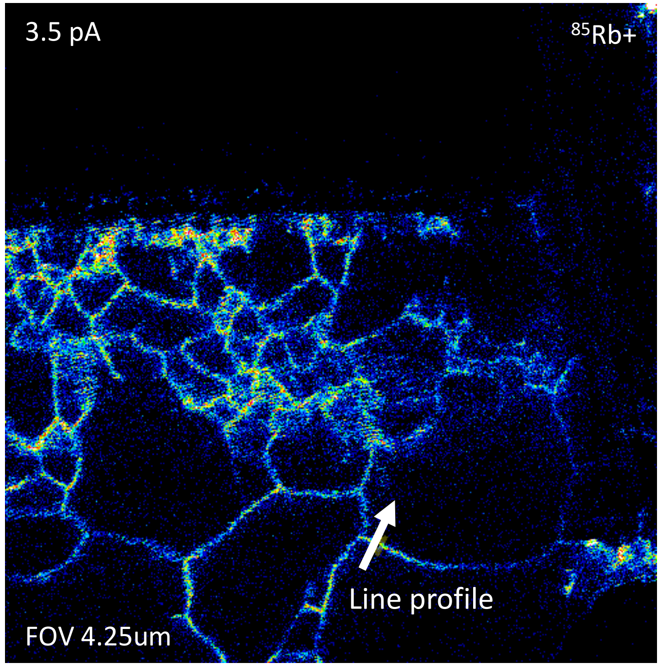


In concentration gradient ↓

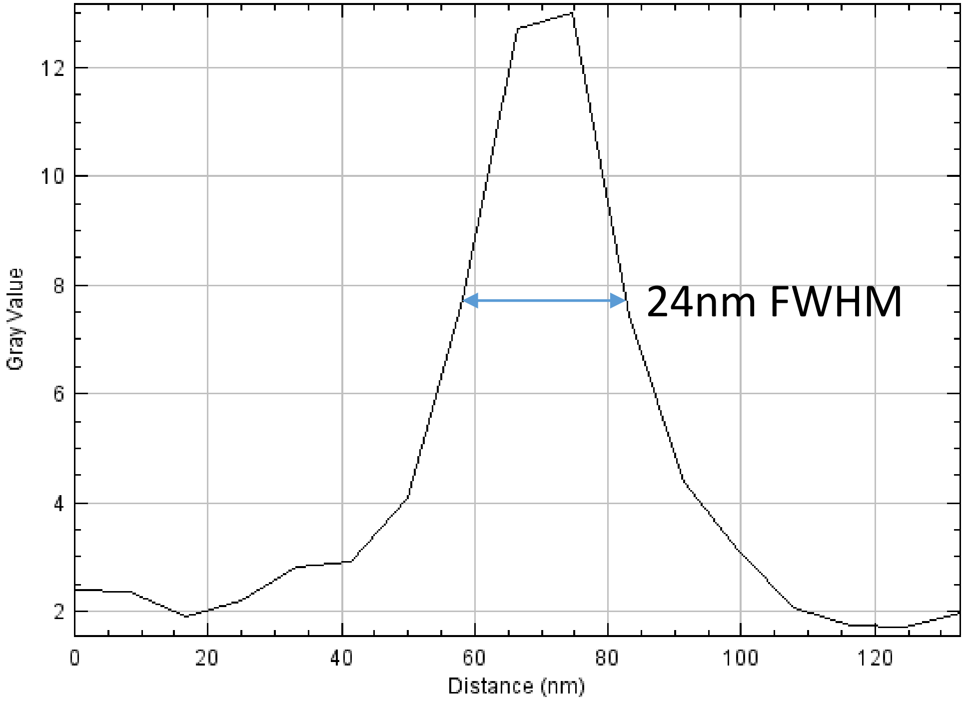
Cs+, 16keV, 10pA, 51.6mm WD
CIGS_Pos_2107201626359.csv

CIGS $Cu(In,Ga)Se_2$ – Rb doped

Section View – Positive Ions



Apparent width of Rubidium signal between grains

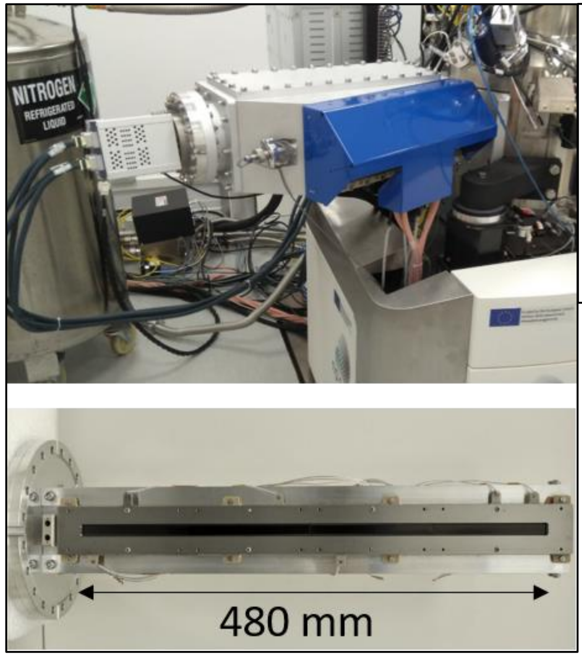


Cs+, 16keV, 3.5pA, 51.6mm WD
CIGS_Pos_2107151409368.csv

Continuous Detector

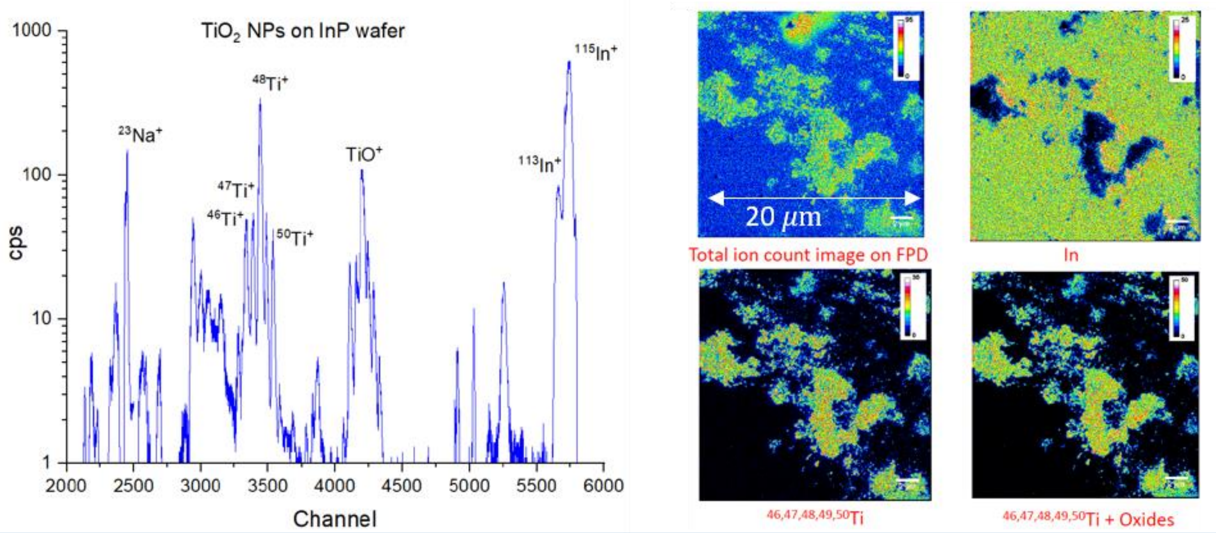
A SIMS:ZERO Option

- SIMS signals for a given element are split into many lines (e.g. Ti, TiO etc..) .
- In discrete-detector systems this leads to a loss of information and lower SNR.
- With continuous detector technology we can sample the entire mass spectrum at once.
- Now we can collect the entire spectrum as in TOF systems, but without painfully long acquisition times.



(Top) Photo of SIMS spectrometer (at LIST) and the continuous focal plane detector mounted to a vacuum flange.

(Bottom) A 480mm micro-channel plate that spans the focal plane of the spectrometer.



Data from by a continuous focal plane detector. Mass spectrum (Left) and surface compositional maps (Right). The sample under interrogation was titanium oxide nanoparticles on an indium phosphide substrate.