COVALENT METROLOGY

# Welcome

COVALENT METROLOGY

# MODERNIZING MICROSCOPY METHODS: CAPABILITIES AND APPLICATIONS OF TEM/STEM SYSTEMS

SPEAKER:

**Dr. Jan Ringnalda**
Principal Scientist, Materials and Structural Analysis
Thermo Fisher Scientific

November 11, 2021 | 11am PT

ThermoFisher SCIENTIFIC

COVALENT METROLOGY



# COVALENT METROLOGY

**Silicon Valley-based analytical labs and platform delivering quality data and expert analysis for advanced materials and device innovation**



## Comprehensive Solutions Stack

*50+ cutting-edge instruments, offering 100+ Techniques*

*Analytical Services*

*Advanced Modeling*

*Method Development*

*Temp. Staffing Solutions*



## Affordable and Fast

*Fast Turnaround Times, No Expedite Fees*

*Volume Savings*

*Instant Access to Data and Reports in Secure Portal*



## Flexible Business Model

*Custom Consulting Solutions and Certified Onsite Support*

*Training and Certification on Instrumentation*

*Co-op and Tool-Share Opportunities*

*Laboratory Audits*




## Rich Network of Partnerships

*Partner to World's Leading Instrument Manufacturers and Labs*

*Expanding Instrumentation, Lab Connections and Learning*



## Who We Are, Who We Serve

*500+ Clients, 40-60 Added / Quarter*

*50+ People, 14 PhDs*

*Cutting-edge Analytical Capabilities*

*Lab Location: Sunnyvale, CA*

# Covalent Technical Groups and Organization

COVALENT METROLOGY



## PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis

- DPA / Mechanical Cross-section
- Dye & Pry Test
- EBIC / OBIC failure analysis
- Hot Spot Detection
- IR Imaging / Emission Microscopy
- NIR Imaging
- Root-Cause Failure Analysis

## Electron Microscopy and Scanning Probe Microscopy

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM)
- Scanning Acoustic Microscopy (SAM)
- SEM (+ EDS)
- FIB-SEM ( + EDS)
- S/TEM ( + EDS / + EELS )
- Nano-indent / Nano-scratch

## Optical Microscopy & Spectroscopy

- Chromatic Aberration
- Digital Optical Microscopy
- FTIR and ATR-FTIR
- Laser Scanning Confocal Microscopy
- Spectral Ellipsometry
- UV-Vis-NIR Spectroscopy
- White Light Interferometry

## X-Ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micron-spot ED-XRF
- WDXRF
- Micro-computed X-ray Tomography (Micro-CT)
- 2D X-ray Inspection & X-ray Radiography

## Elemental / Chemical Composition Analysis

- EPMA
- GD-OES
- GC-MS
- ICP-MS and LA-ICP-MS
- Raman Microscopy & Spectroscopy
- NMR (1D or 2D; solid / liquid)

## Particle Analysis

- Dynamic Light Scattering (DLS)
- Laser Diffraction Particle Size Analysis (PSA)
- Particle Zeta Potential

## Material Property Characterization

- DSC
- DMA & TMA
- Rheometry
- TGA
- Surface Zeta Potential
- Porometry / Porosity
- Gas Adsorption
- Gas Pycnometry
- Foam Density
- Tap Density

## Surface Spectroscopy Analysis

- Dynamic-SIMS
- ToF-SIMS (Static-SIMS)
- Ion Scattering Spectroscopy (ISS)
- Ultraviolet Photoelectron Spectroscopy (UPS)
- X-ray Photoelectron Spectroscopy (XPS)

# Covalent Partners



COVALENT METROLOGY

ThermoFisher SCIENTIFIC

Cutting-edge Thermo Fisher Scientific Instruments installed at Covalent include:

- **Talos ™ F200 G2 (Scanning) Transmission Electron Microscope (TEM)** delivers fast, precise, quantitative imaging and elemental composition analysis on an angstrom scale with powerful electron optics and a high-sensitivity detector array
- **Helios 5 ™ DualBeam ™ Microscope (FIB-SEM)** incorporates the most advanced electron optics, detectors, and software technologies available for materials science to deliver unprecedented imaging performance with sub-nm resolution
- **Nexsa ™ X-ray Photoelectron Spectrometer (XPS)** produces high-throughput, high-quality results across XPS, ISS, UPS, REELS, and Raman spectroscopy with fully automated multi-technique workflows that allow true correlative analysis

## Other Covalent Partners

Rigaku

HORIBA Scientific

J.A. Woollam

KEYENCE

Anton Paar

PVA TePla

Asylum Research an Oxford Instruments company

TA Instruments

Digital Surf

TELEDYNE CETAC TECHNOLOGIES Everywhereyoulook™

# Dr. Jan Ringnalda

**Principal Scientist, Materials and Structural Analysis**

Thermo Fisher Scientific

- PhD From Liverpool University in 1993
- Postdoctoral research at Ohio State University
- Involved with Transmission Electron Microscopy work since 1984 = over 35 years of experience
- Background includes failure analysis, materials characterization using EDS , EELS and imaging using TEM and STEM techniques
- Worked with the product design group developing the Titan TEM platform
- In his present position with Thermo fisher Scientific, he provides technical sales support, presents scientific results at conferences and still participates in research with students at The Ohio State University



# Modernizing Microscopy Methods: Capabilities and Applications of TEM/STEM Systems

Jan Ringnalda PhD

MSD Materials Science

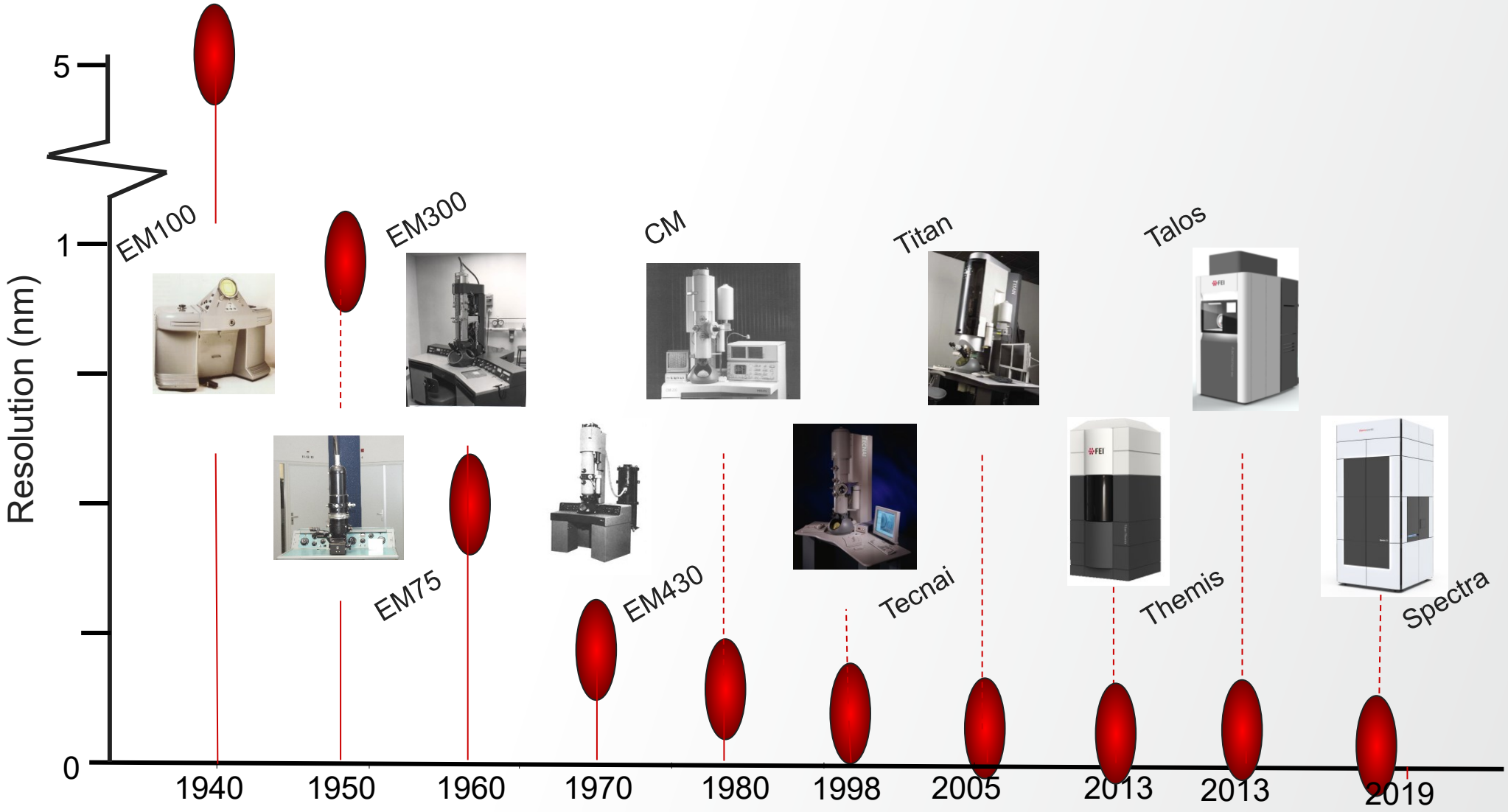



The world leader in serving science

# Agenda

- TEM Introduction
- Different Techniques, BF-TEM, DF-TEM, STEM HAADF and iDPC
- Analytical capabilities: EDS and quantification
- Efficient imaging for modern samples
- Nanoprobe diffraction; CBED
- Imaging at lower kV’s to enhance contrast
- Inert sample transfer
- 4D-STEM

# …Decades of TEM Revolution & Evolution



# Talos F200X – highest sensitivity / cleanliness in EDS

## **Smart Box**/Enclosure

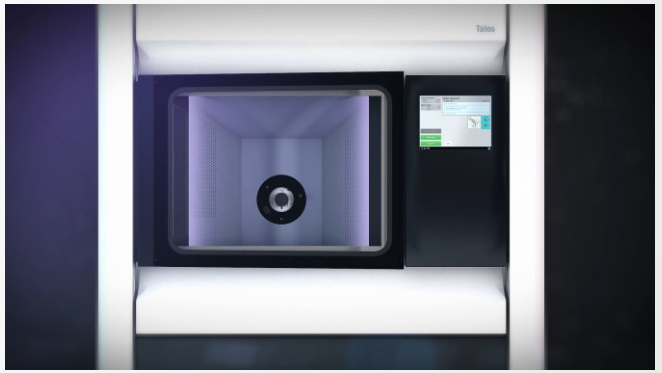
- Reduces environmental sensitivity
- Touch-screen info panel built-in

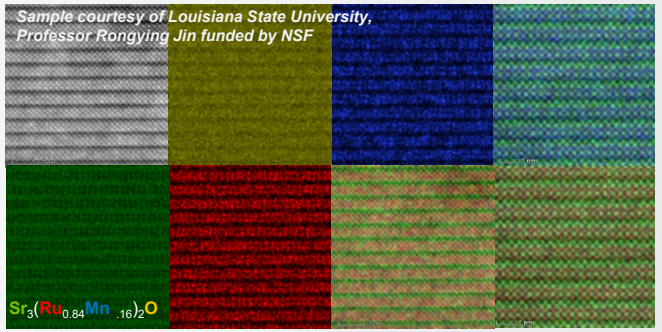
## **Highest Brightness** (X-FEG)

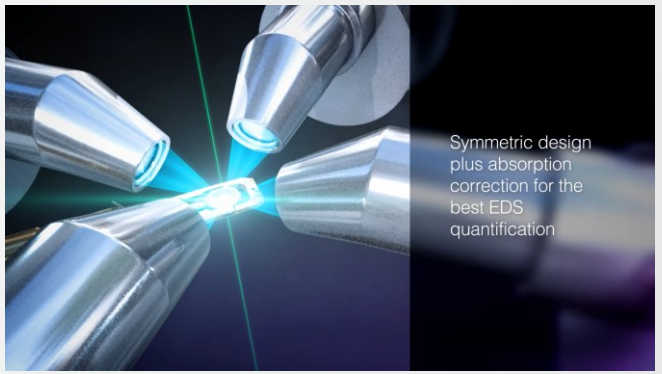
- More electrons in small spots with small convergence angle.
  - Better S/N in HRSTEM images
  - Cleaner analytical footprint in thicker samples – will explain
  - More X-rays gives higher sensitivity

## **Cleanest EDS** - Highest Peak/Background$_{Fiori}$

- Super-X G2 detector with 4 independent symmetrical SDD's
- Enables clean EDS tomography for 3D chemical info
- Unique absorption correction for the most accurate quantification
  - No matter what your sample orientation is





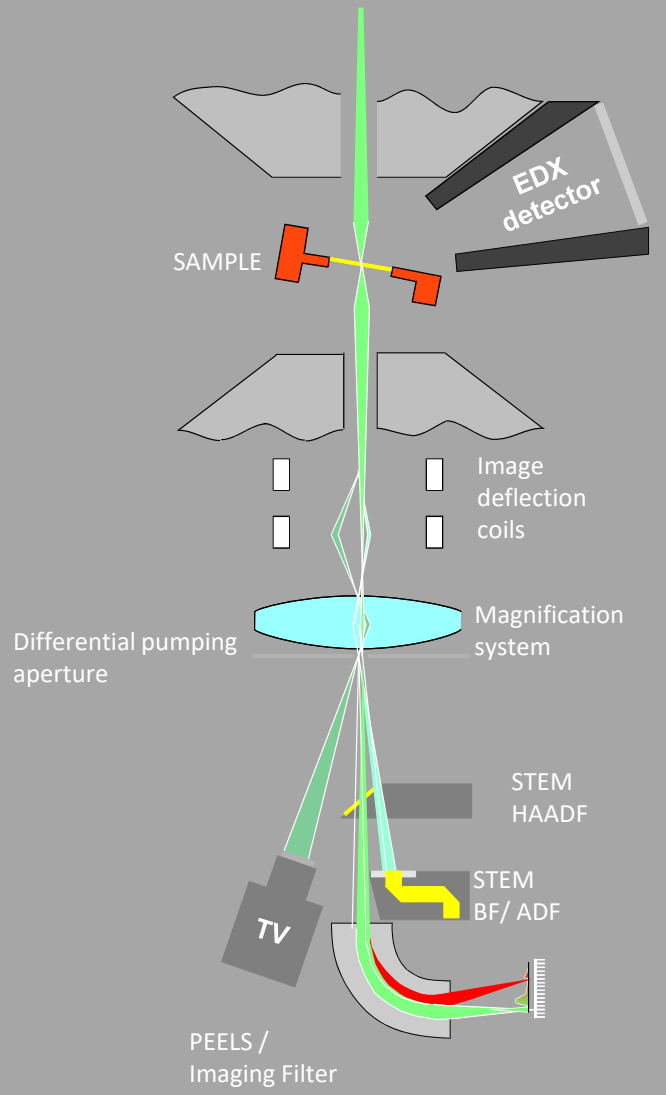
# Detector placement in the (S)TEM

TEM

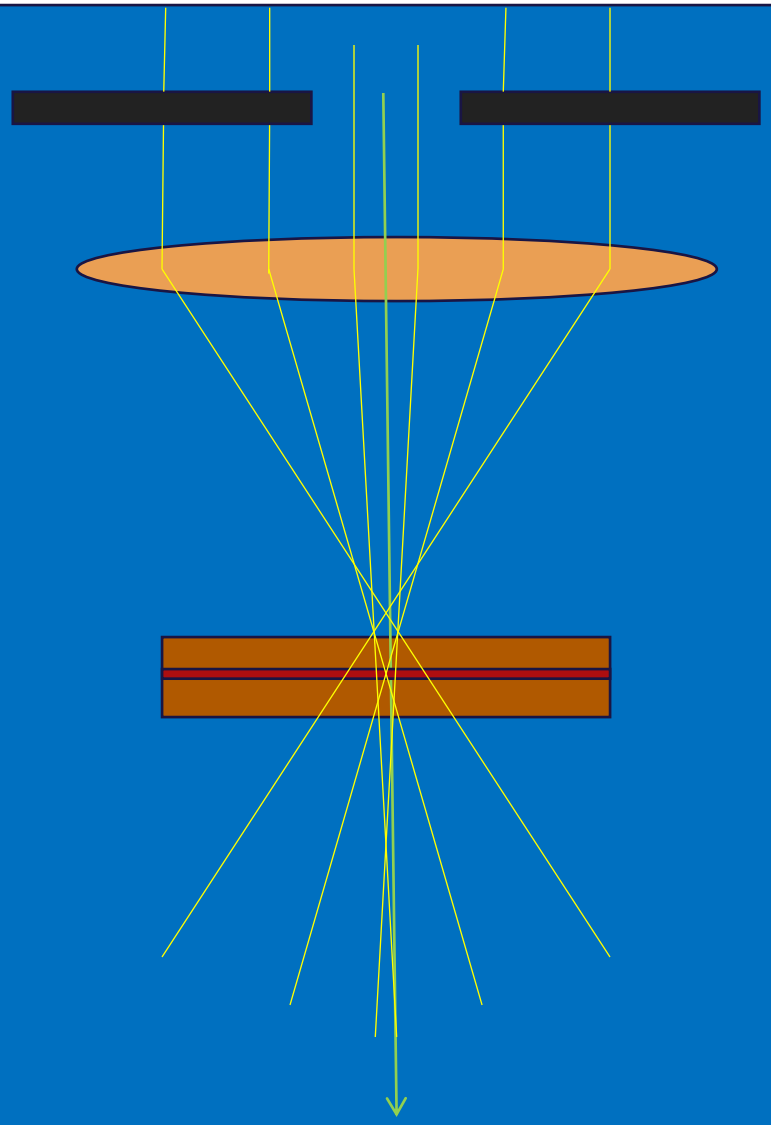
- Energy Filter
- TV / SMART camera
- CMOS camera

STEM

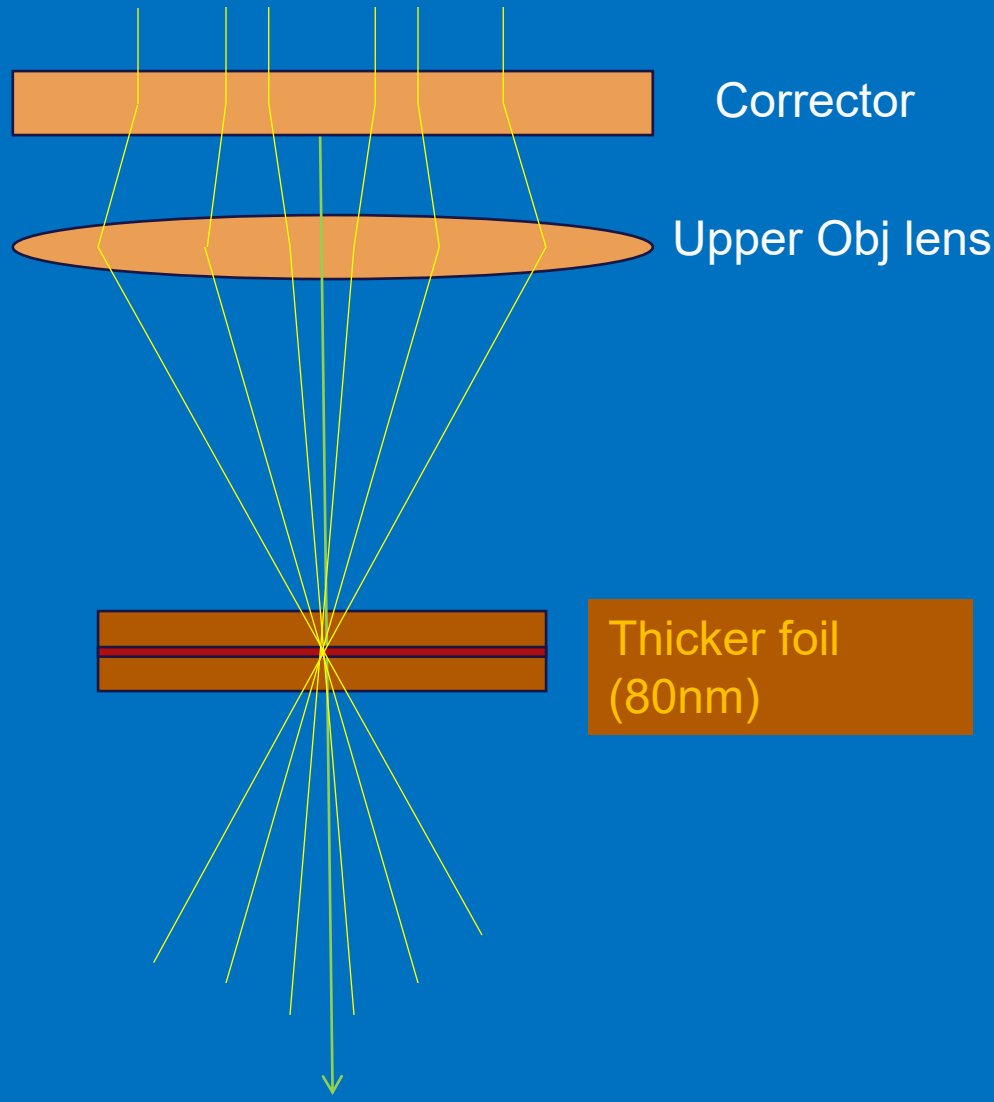
- BF / DF
- HAADF
- 4D STEM
- EDX and PEELS Spectrum Imaging



# Probe Corrector: Layman's view

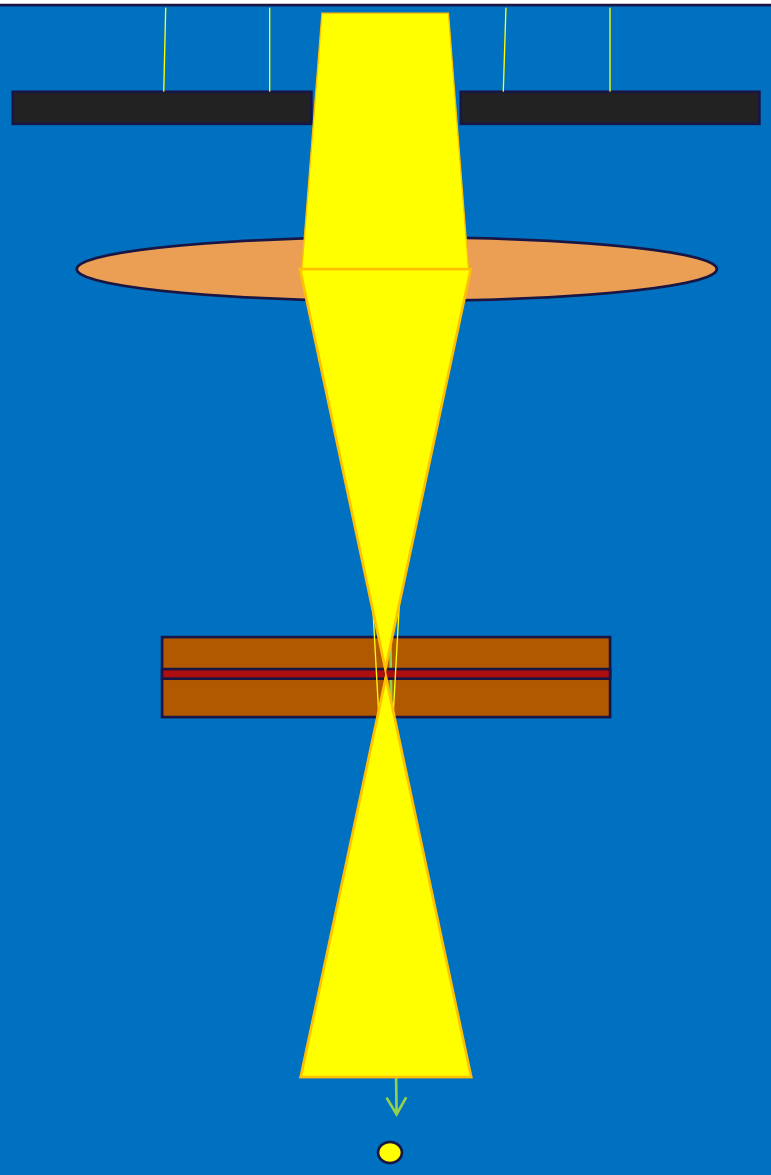



Non-Corrected



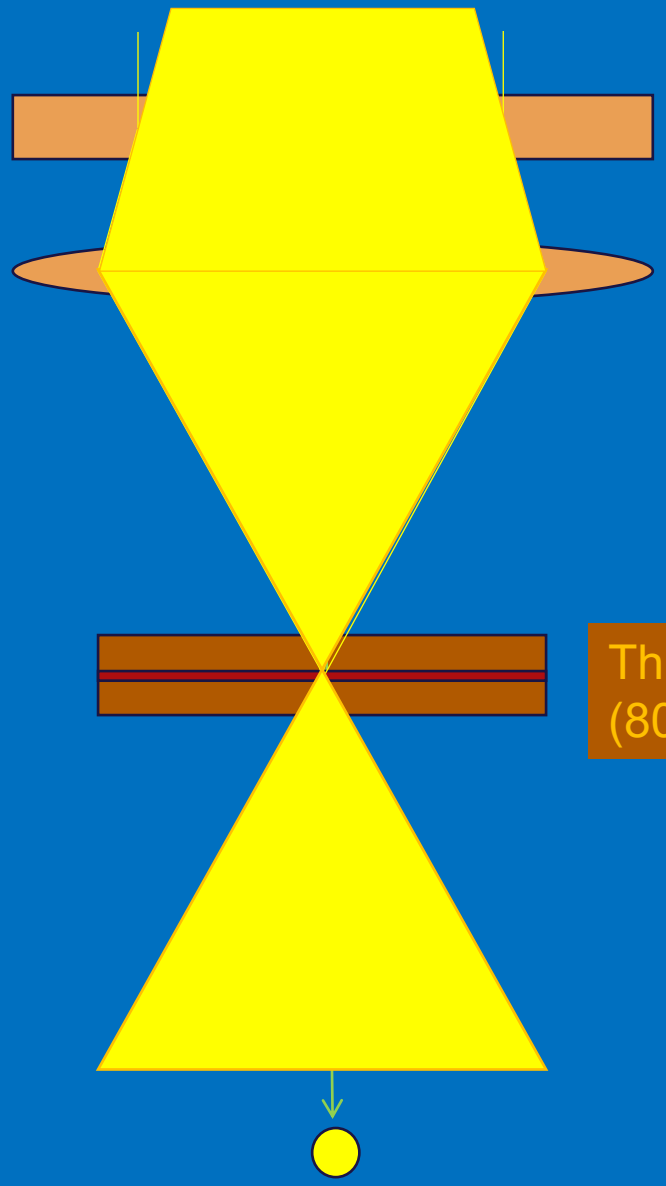

Corrected

# Probe Corrector: Layman's view



Condenser Aperture

Non-Corrected



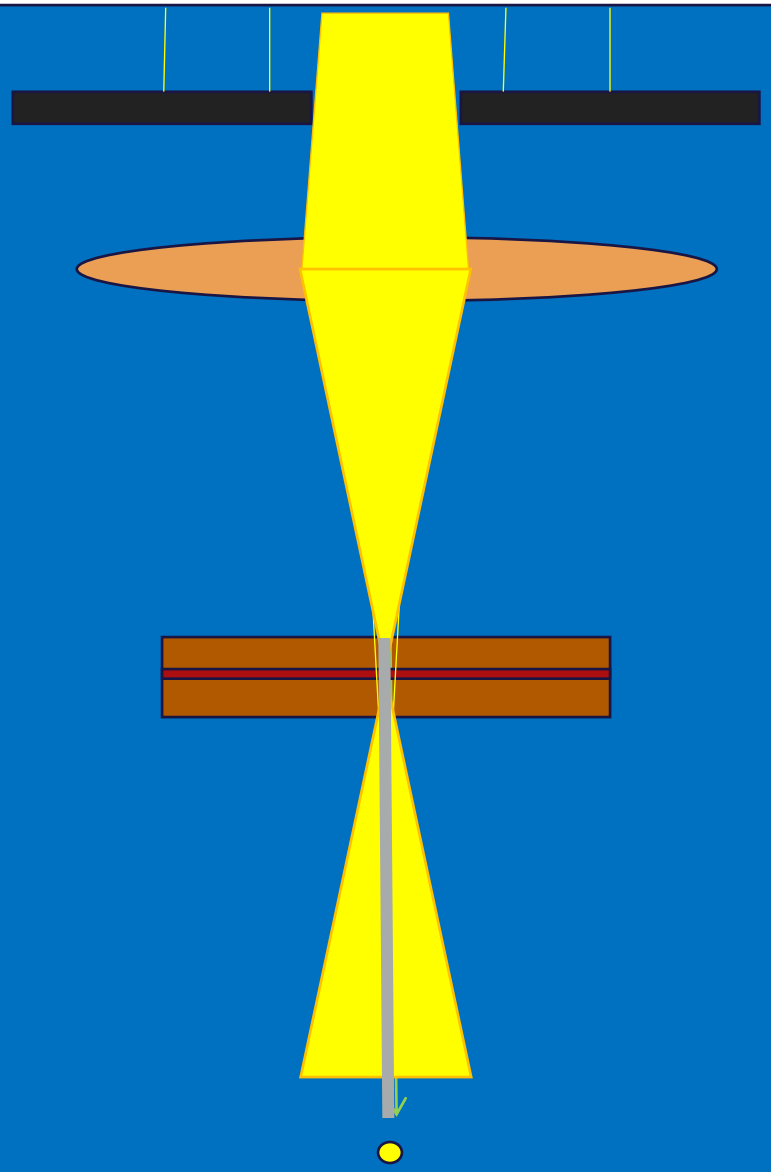
Corrector

Upper Obj lens

Thicker foil (80nm)

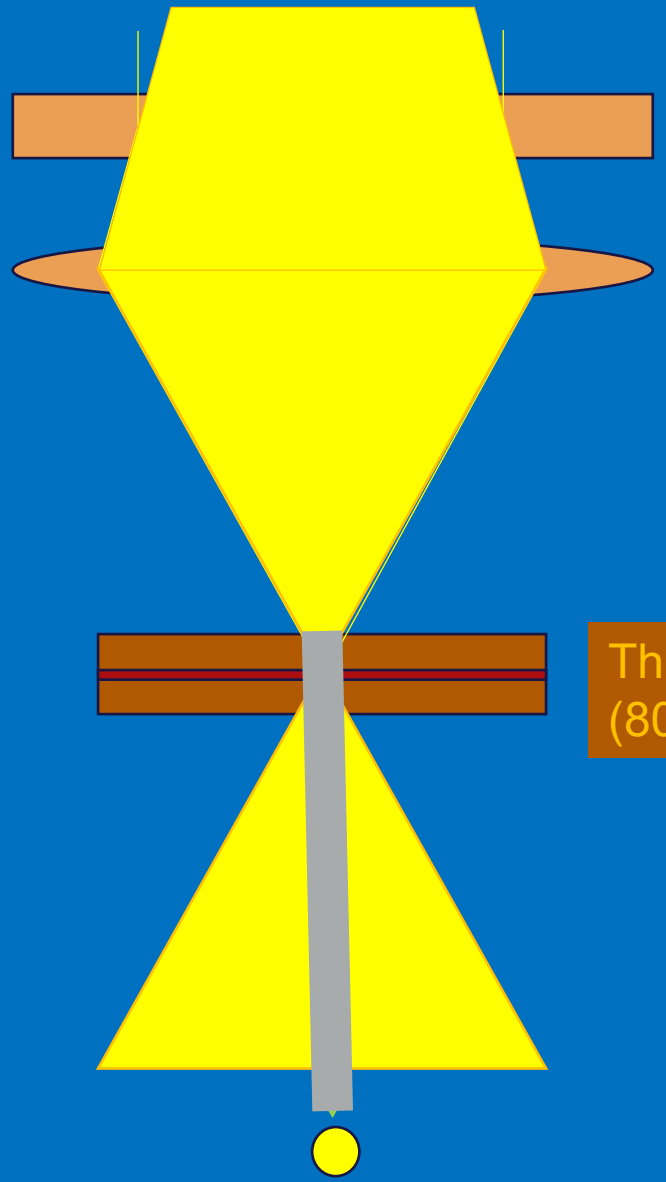
Corrected

# Probe Corrector: Layman's view



Condenser Aperture

Aberration Correction is complex, and ONLY works on very thin samples



Corrector

Upper Obj lens

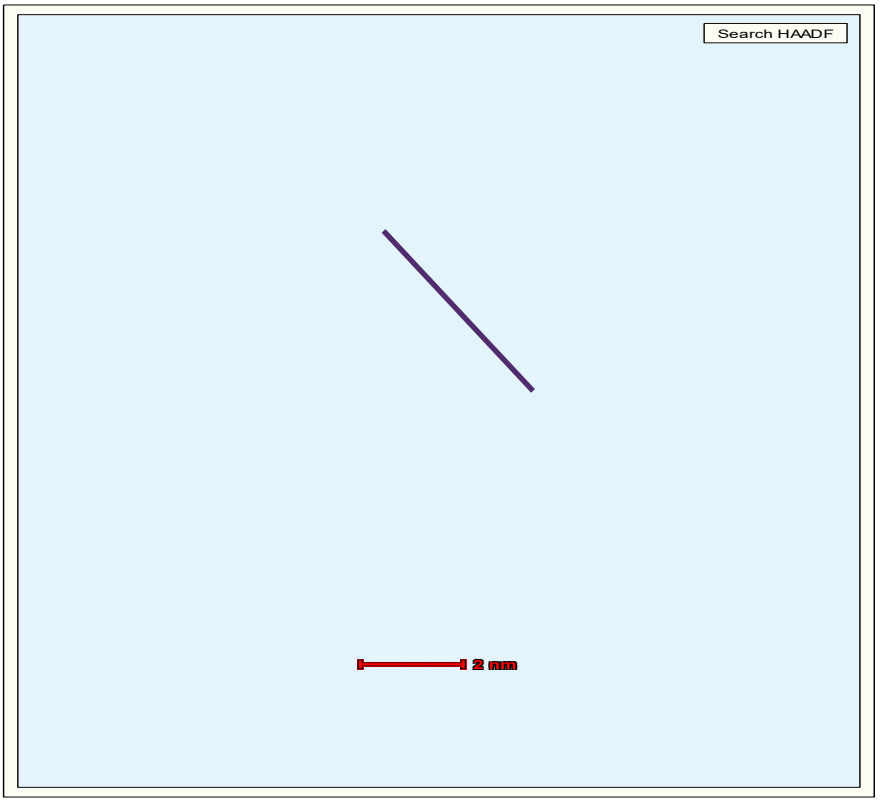
Thicker foil (80nm)

**Non-Corrected**

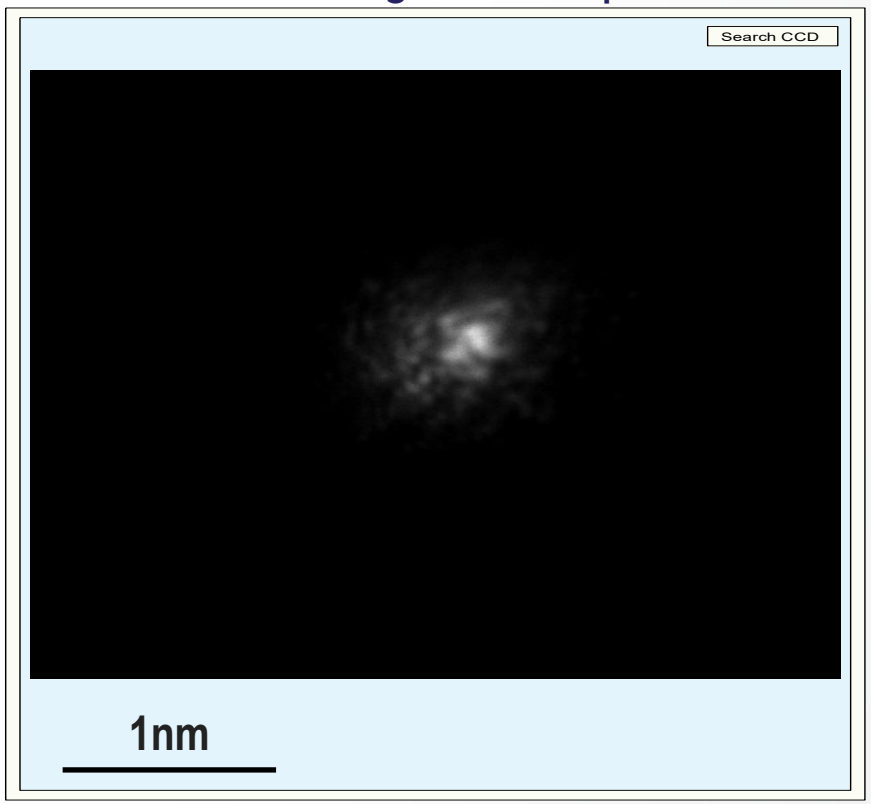
**Corrected**

# Imaging the Probe (Channeling/de-channeling) in $SrTiO_3$

HAADF STEM image



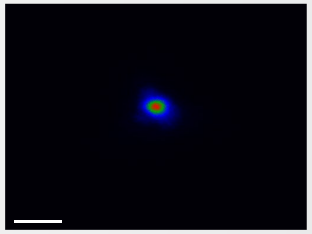

Probe image after sample

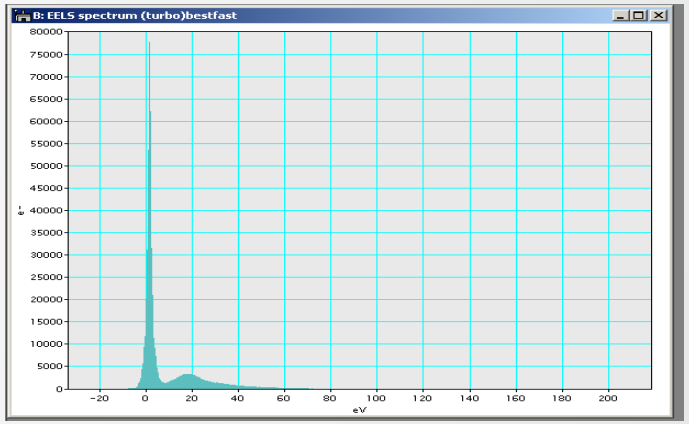



300kV

$\alpha$ = 10mrad

Image Cs-corrected






**Thickness ~0.38MFP**

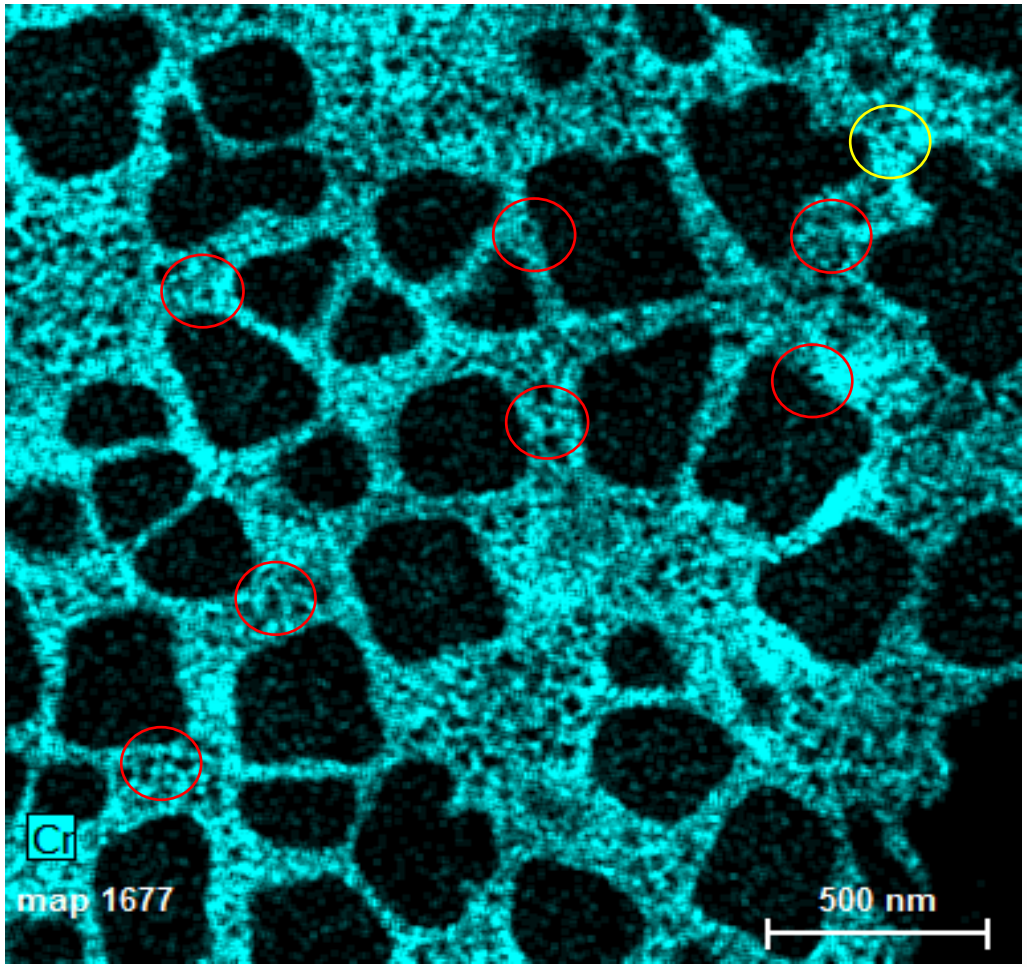
*B.Freitag, C.Mitterbauer, FEI*

**Image of the probe as it EXITS $SrTiO_3$**

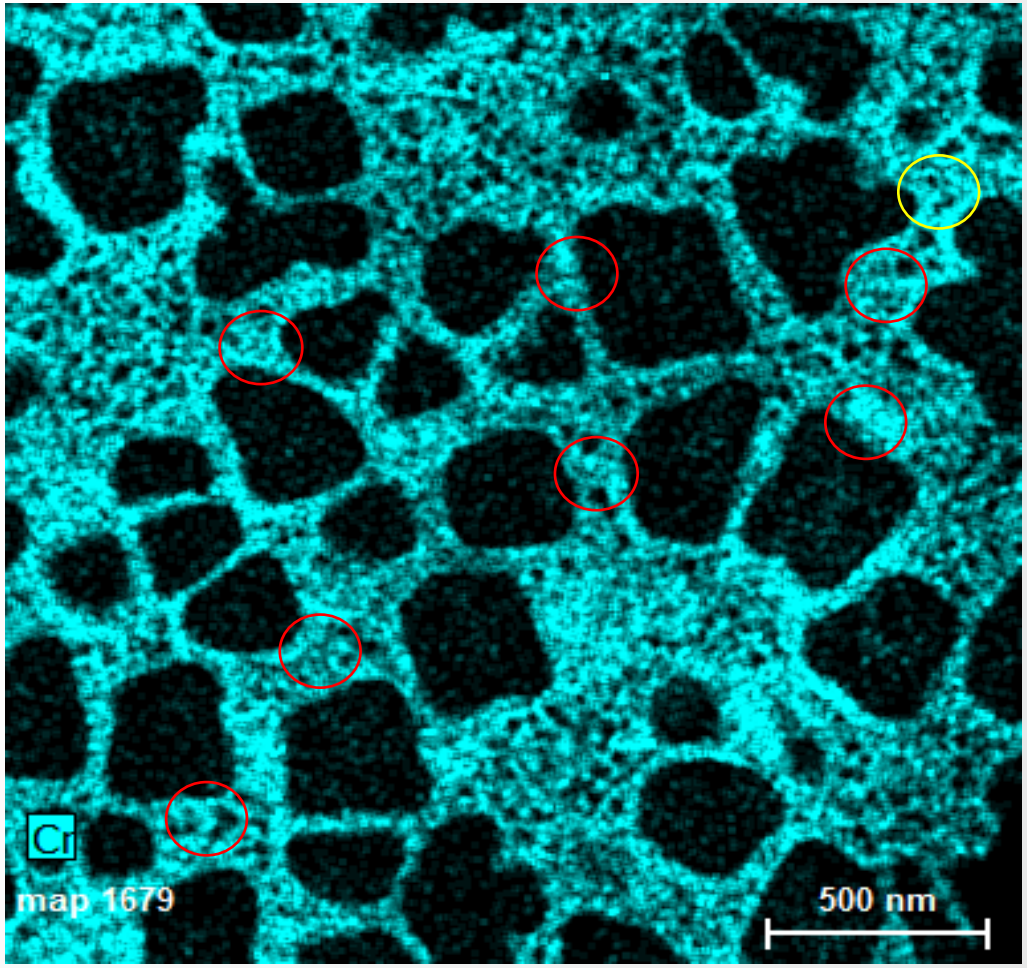
**BE CAREFUL: Sample messes up the resolution.**

**Channeling helps you...**

# Comparison of Analytical ‘Cleanliness’




Semi convergence angle : 10 mrad
DOF : ~ 20nm

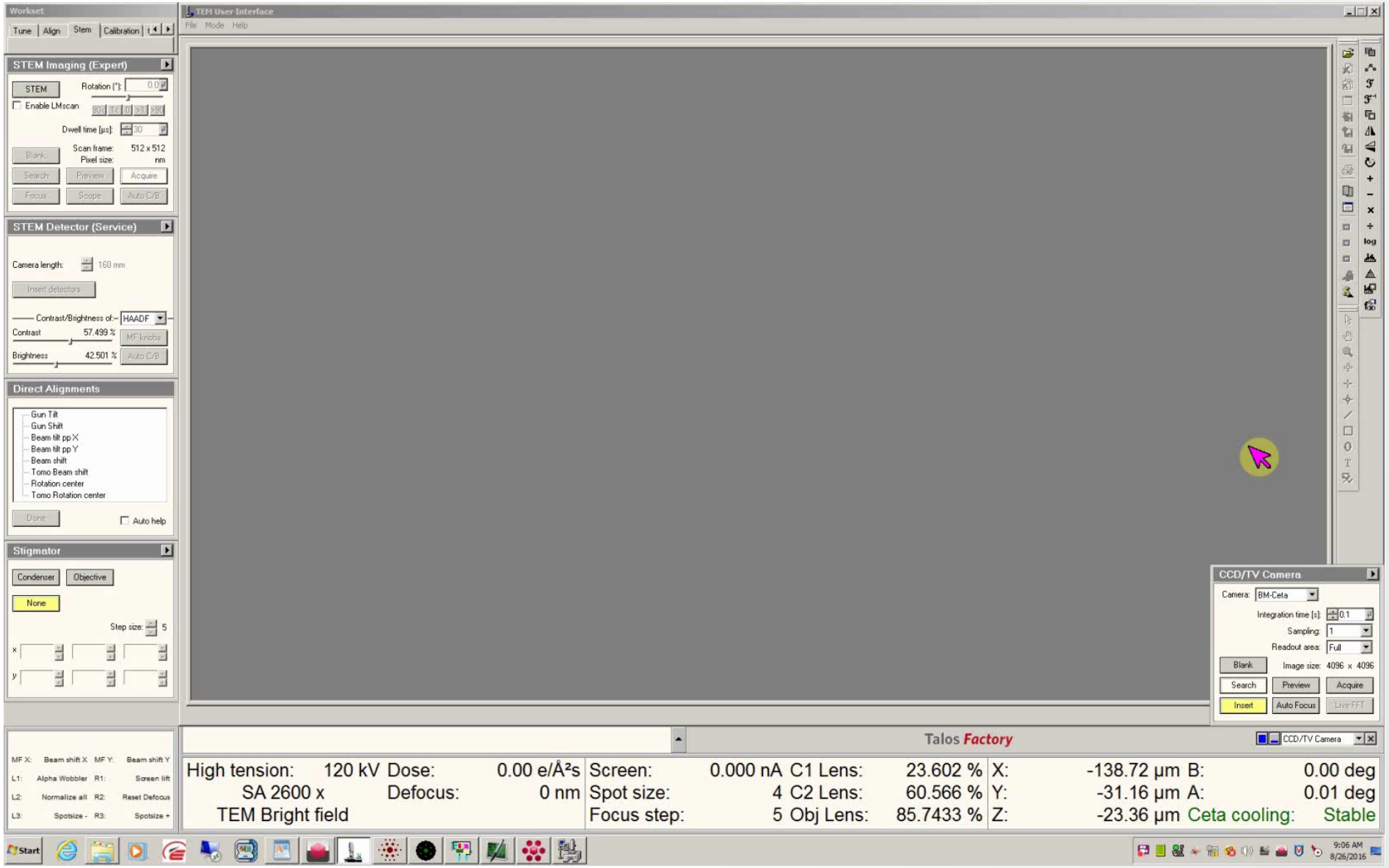



Semi convergence angle : 21 mrad
DOF : ~5.1 nm

**Superalloy**

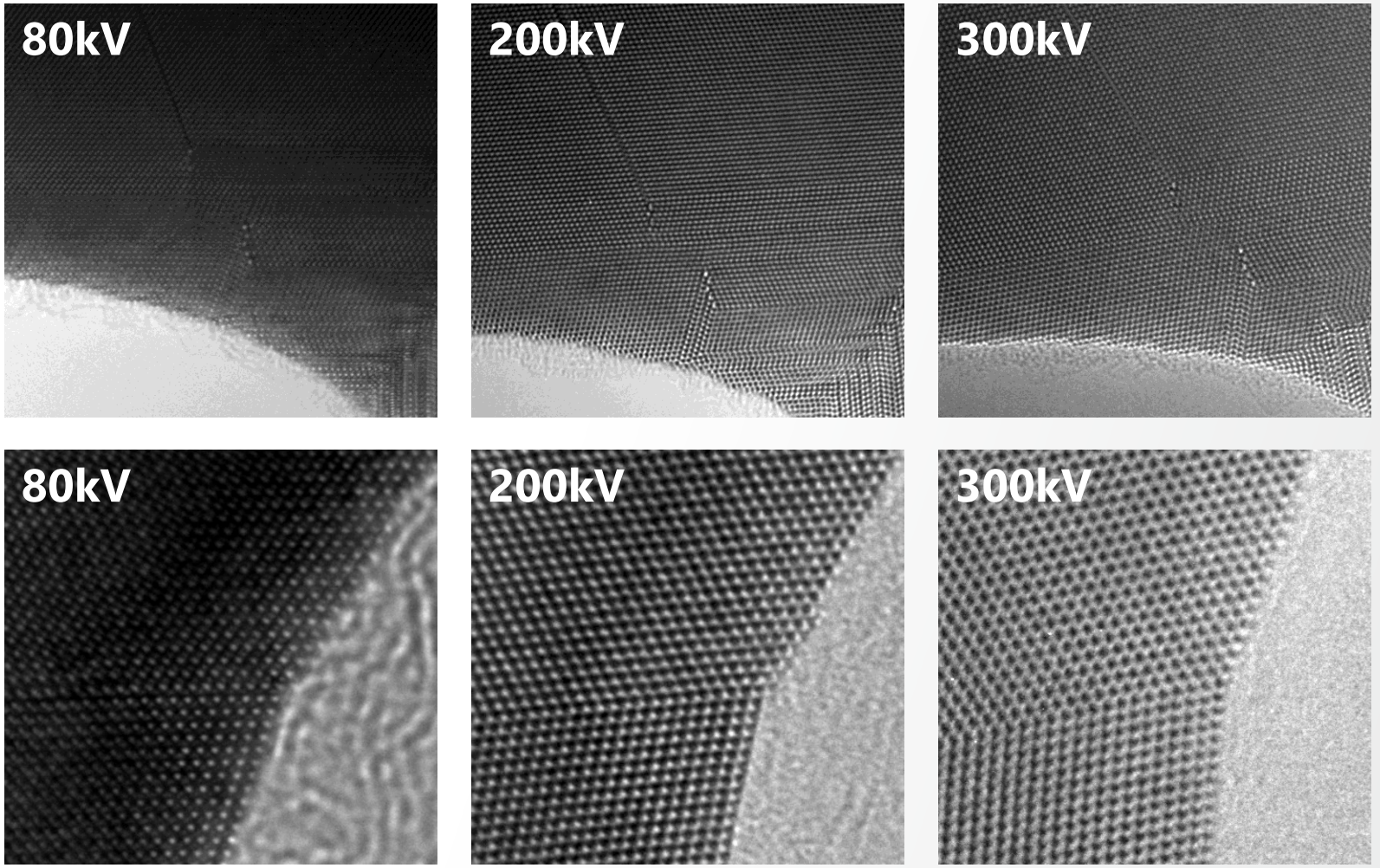
Both maps:
Beam current : 0.4nA
Accelerating voltage: 200 kV
Beam size: 0.2nm

# Swift TEM-STEM switches




Real time TEM image acquisition with Ceta 16M, TEM-STEM switch & STEM image acquisition

# Changing kV for contrast/visibility




Lowering kV enhances contrast; however, makes sample preparation more challenging.

# Velox Software - Mission

Provide users with the fastest and easiest way
to acquire and analyze multimodal data

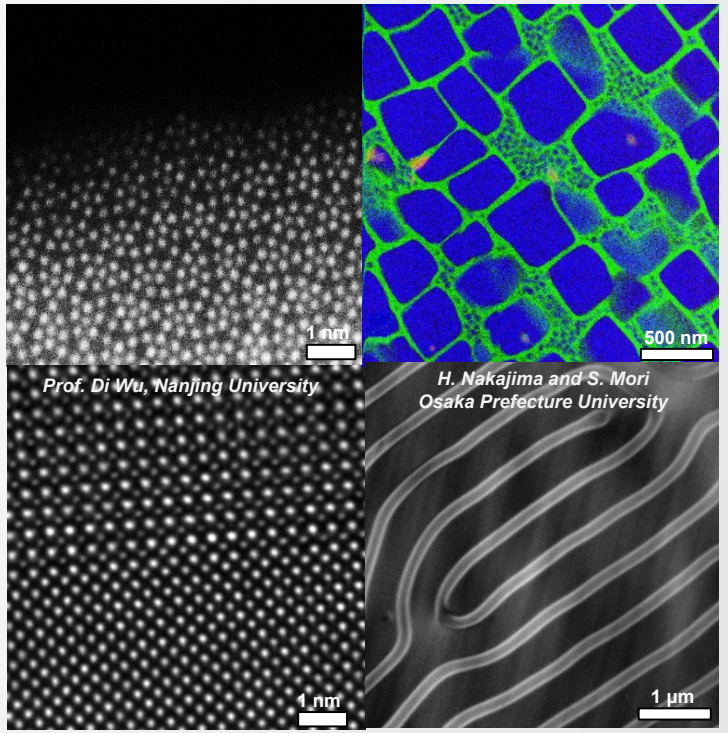
## (HR)TEM and (HR)STEM imaging

- All conventional bright and dark field applications
- Magnetic and electrical field imaging.
- Simultaneous imaging of light and heavy elements

## Spectral data

- EDS spectra and EDS spectrum images
- Simultaneous EDS and EELS

## Drift correction available for all acquisition modes

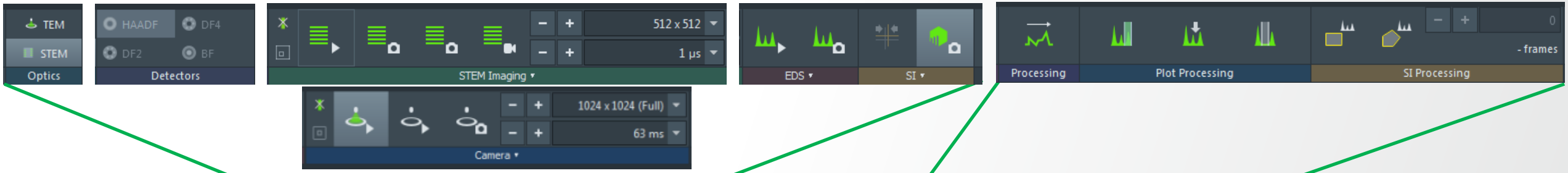


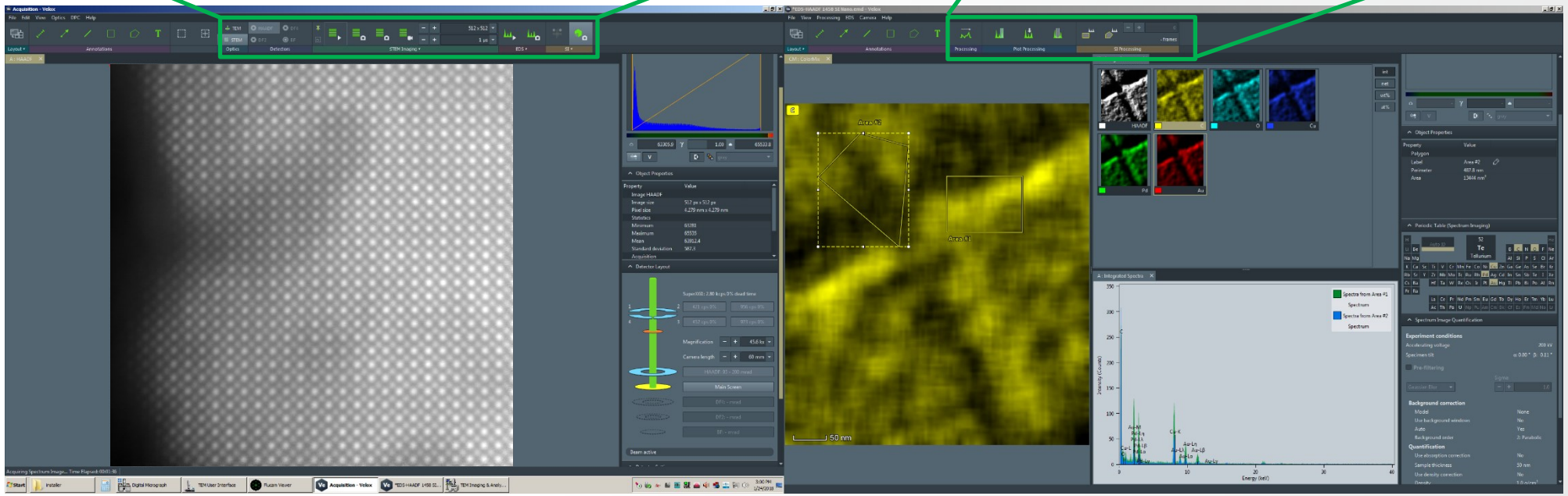
# Multimodal Acquisition Engine: Workflow Based Operation

ThermoFisher SCIENTIFIC

## Pushbutton graphical UI for easy workflow

S/TEM → Detectors → S/TEM Acquisition + Analytics → Processing

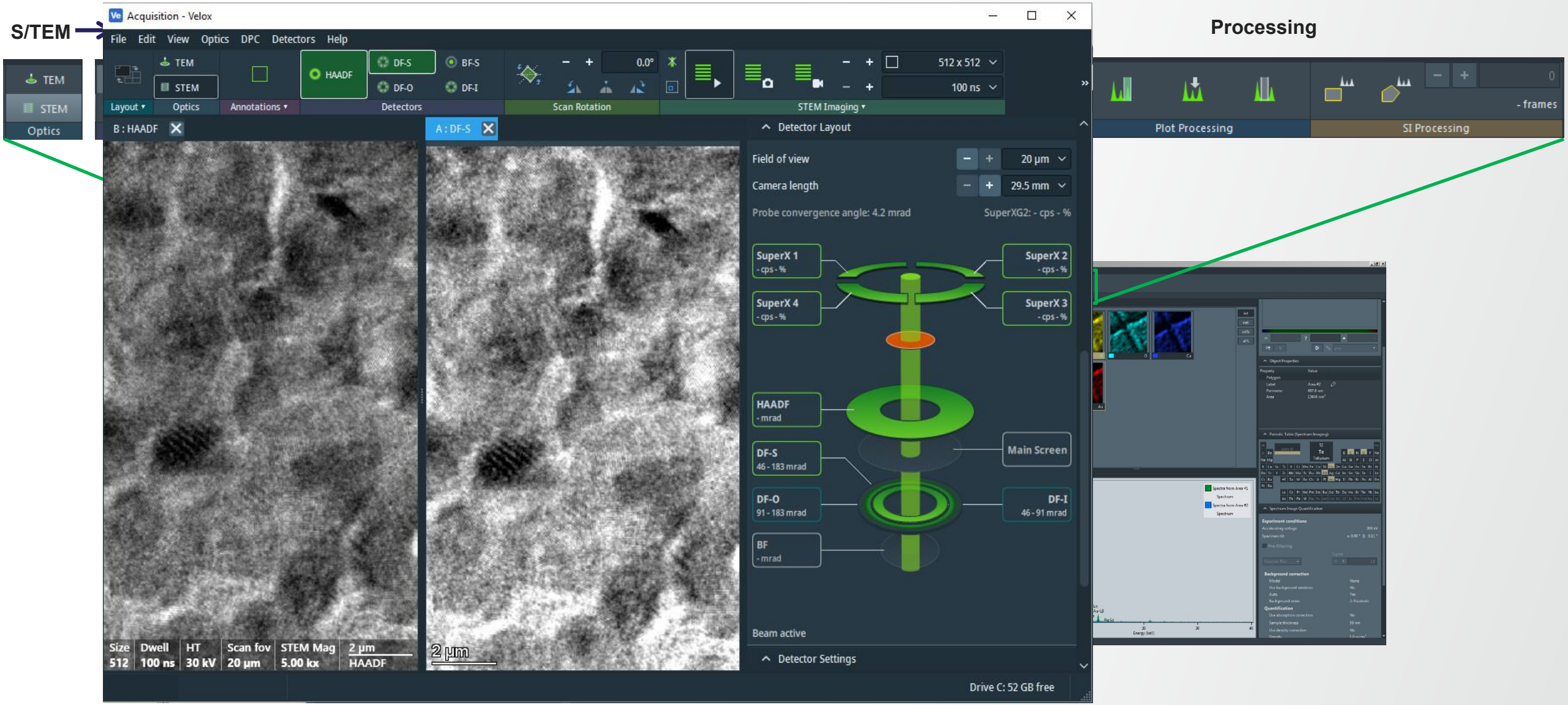


# Multimodal Acquisition Engine: Workflow Based Operation

ThermoFisher SCIENTIFIC

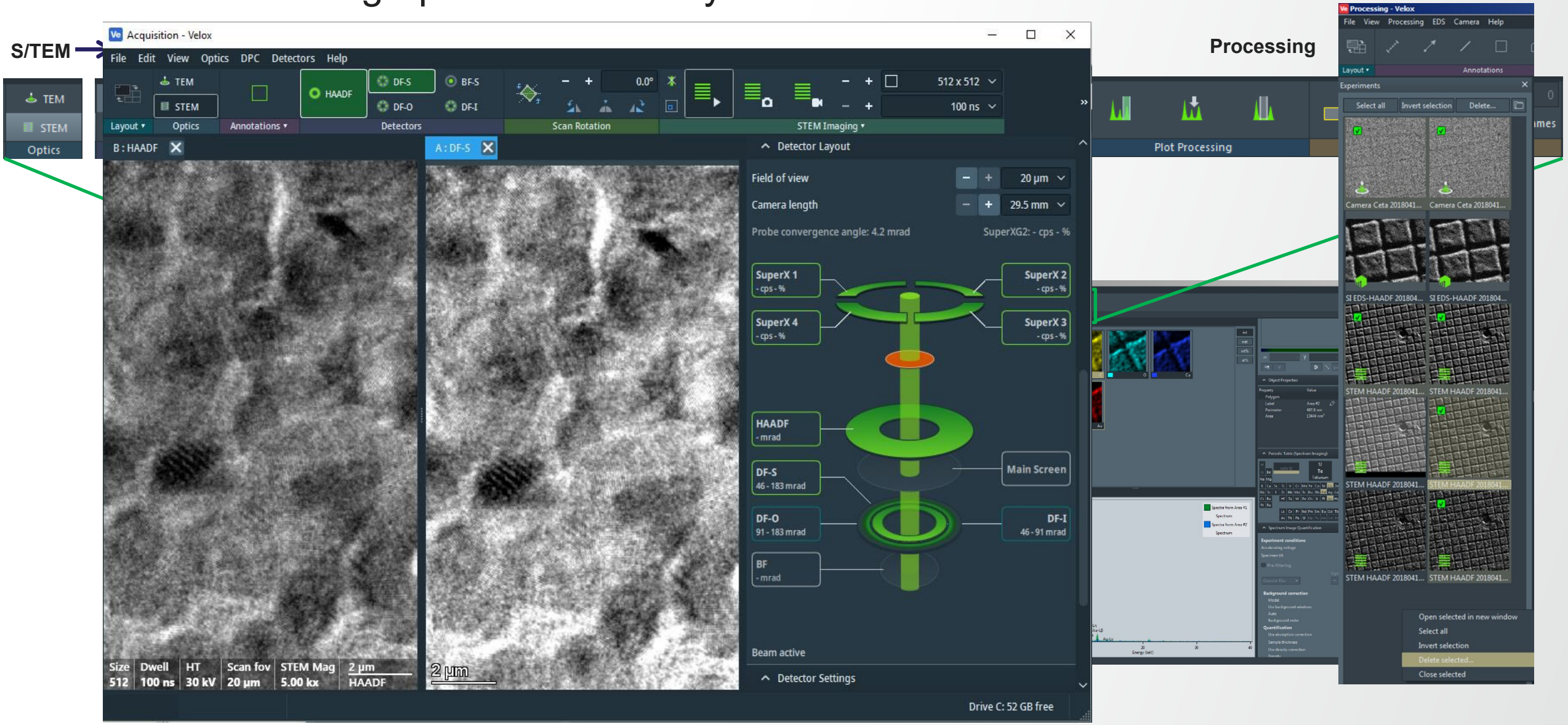
## Pushbutton graphical UI for easy workflow



# Multimodal Acquisition Engine: Workflow Based Operation

ThermoFisher SCIENTIFIC

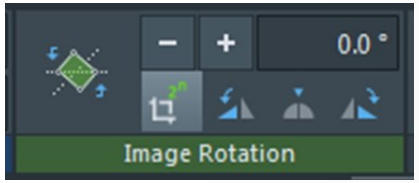
## Pushbutton graphical UI for easy workflow

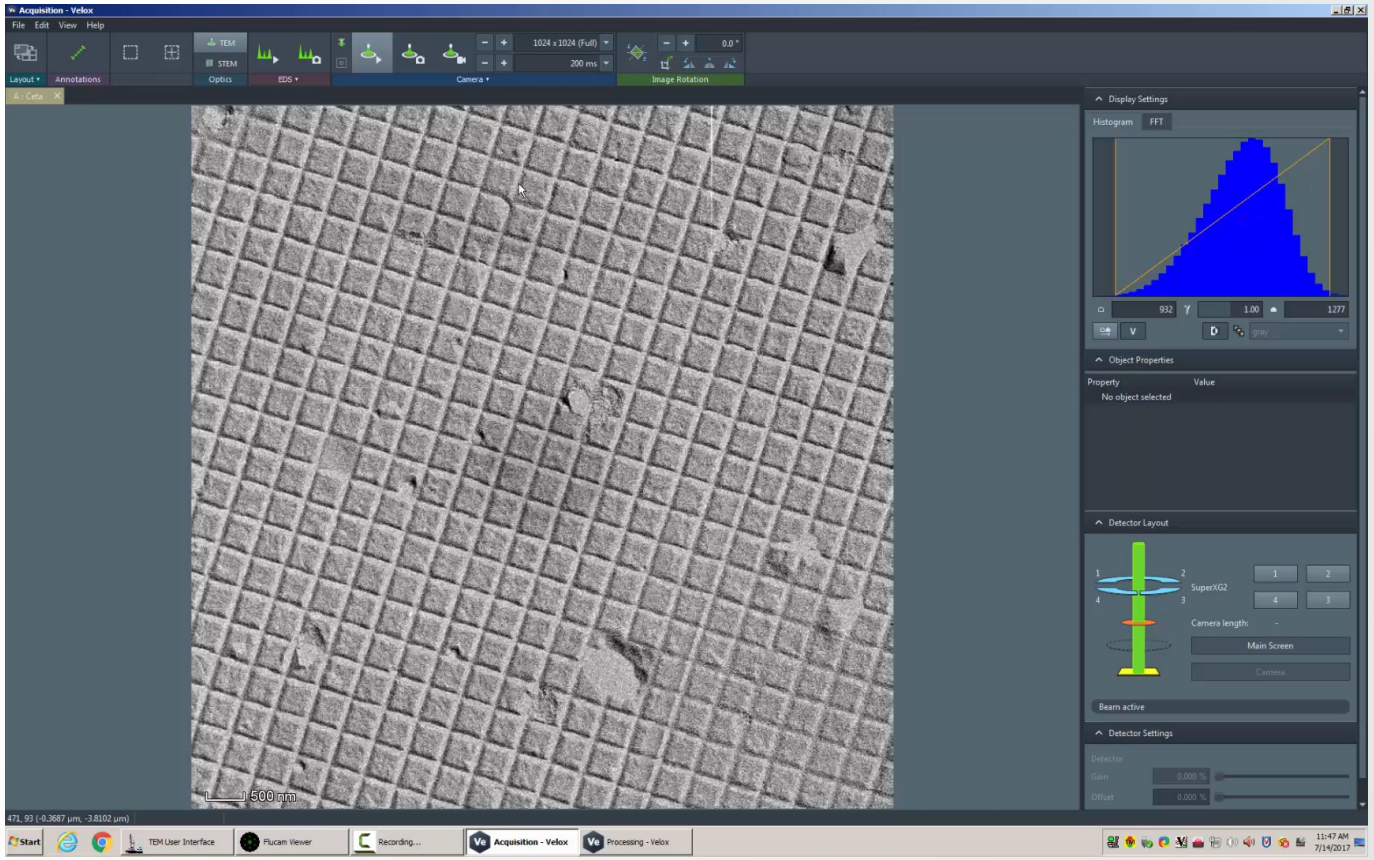


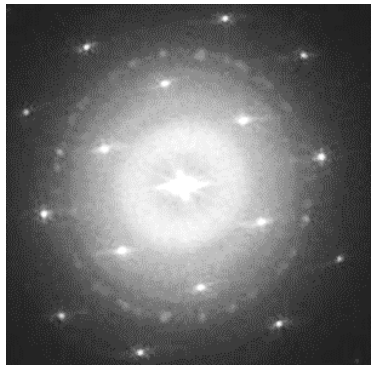
# TEM Live Image Rotation

## Ceta 16M Camera

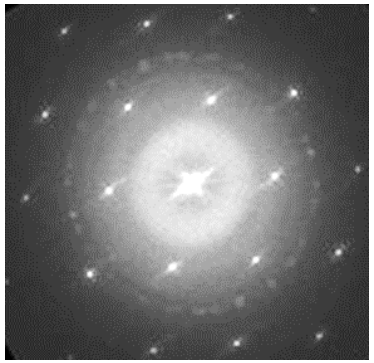
- Fast and easy to use
- Automatic crop of corners (power of 2)
- Does not affect raw data
- **Automatic stage adjustment**
- Does not have artifacts in FFT



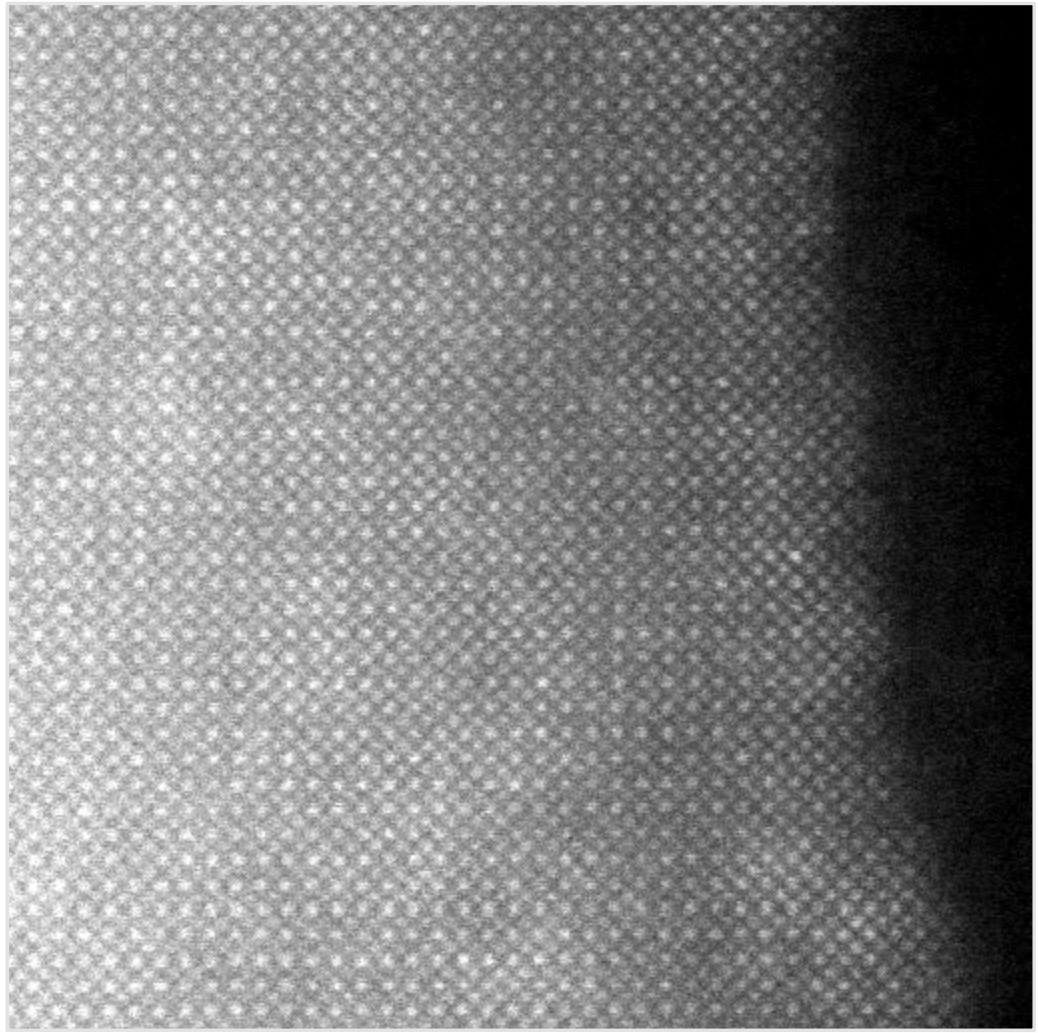



FFT from original image

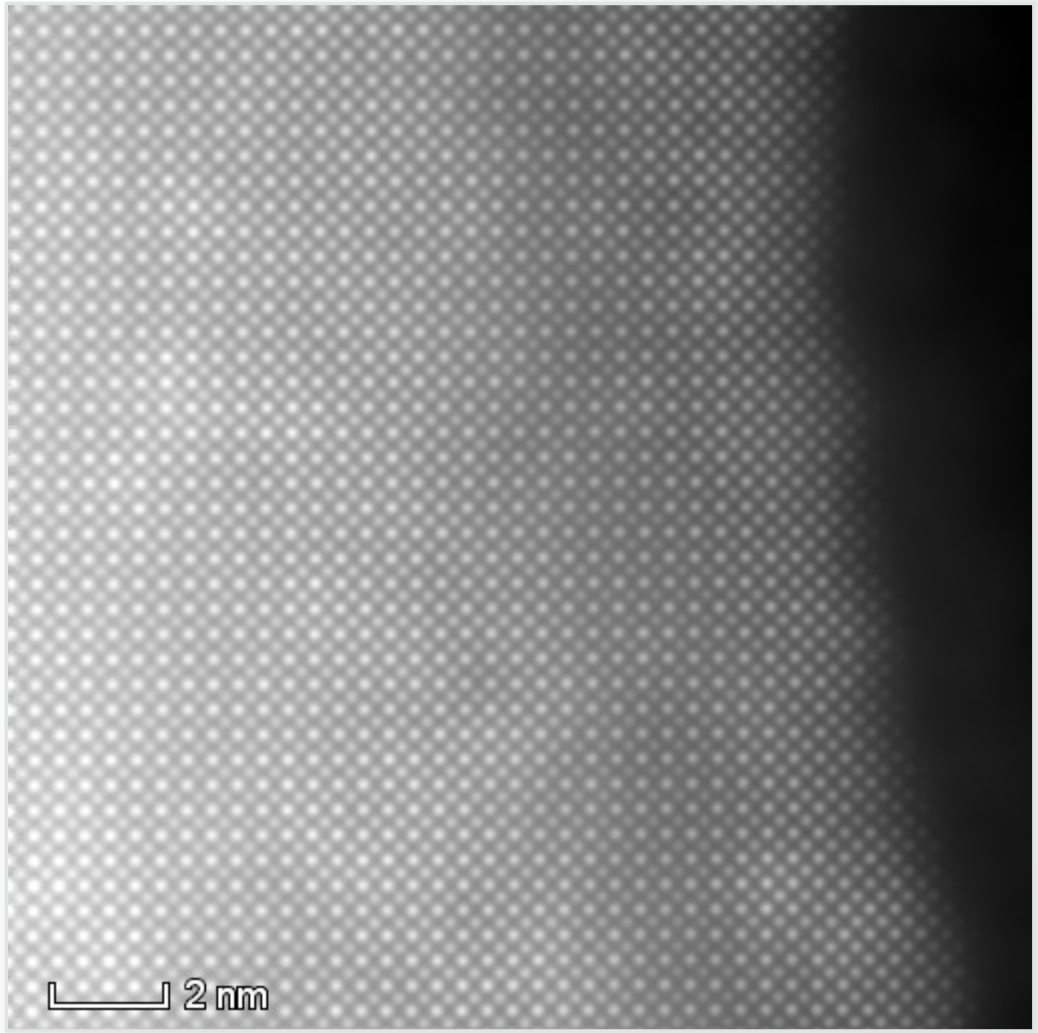


FFT of rotated image

# Intelligent scanning and camera imaging



HRSTEM series 600 frames (>10 minutes)

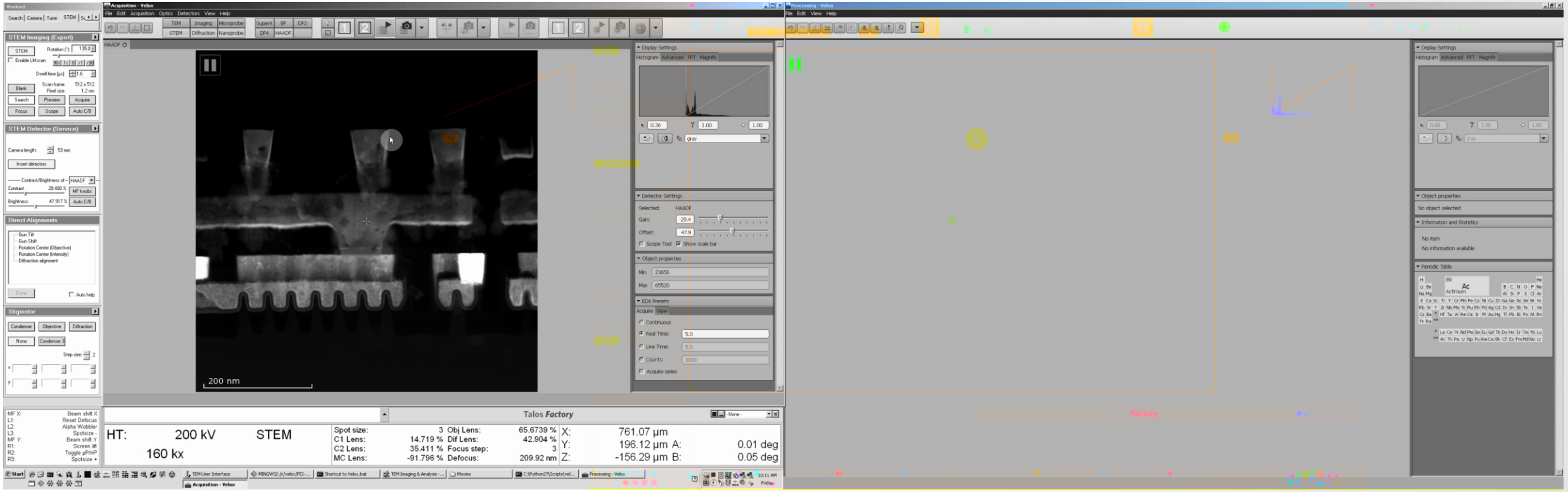



HRSTEM DCFI 600

# Fast EDS quantification with Velox™ analytical SW

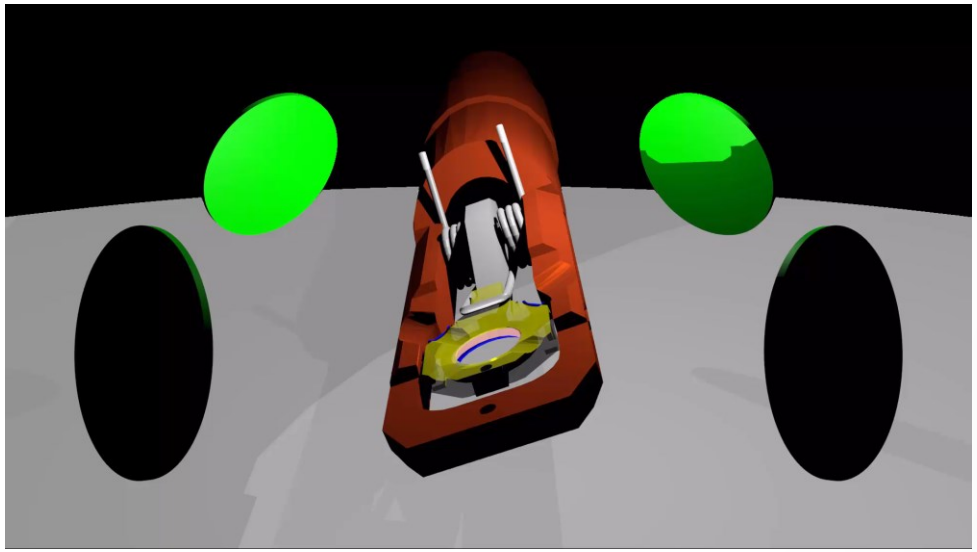
Example of overcoming the Si-W overlap in quantification by peak fitting.

More accurate quantification made possible through automated absorption correction, holder shadowing etc. through intelligent TEM/STEM specific SW.

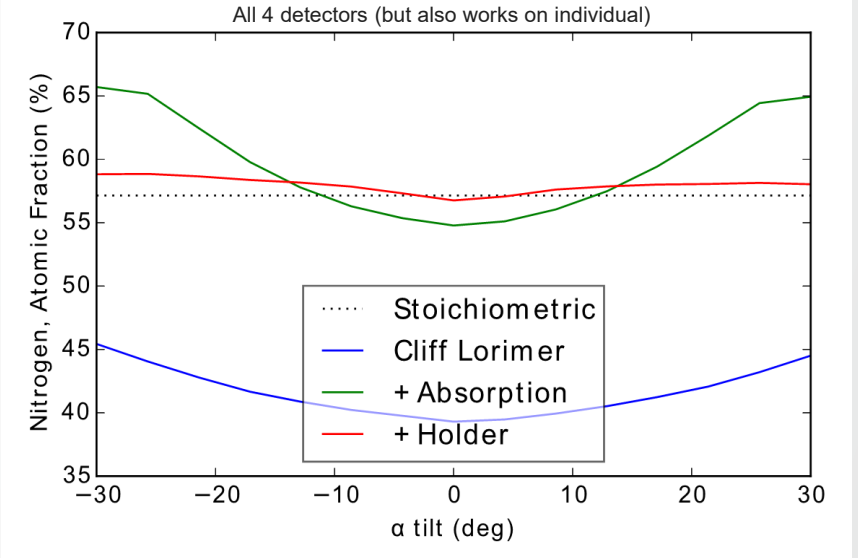


# EDS Analysis – Absorption Correction

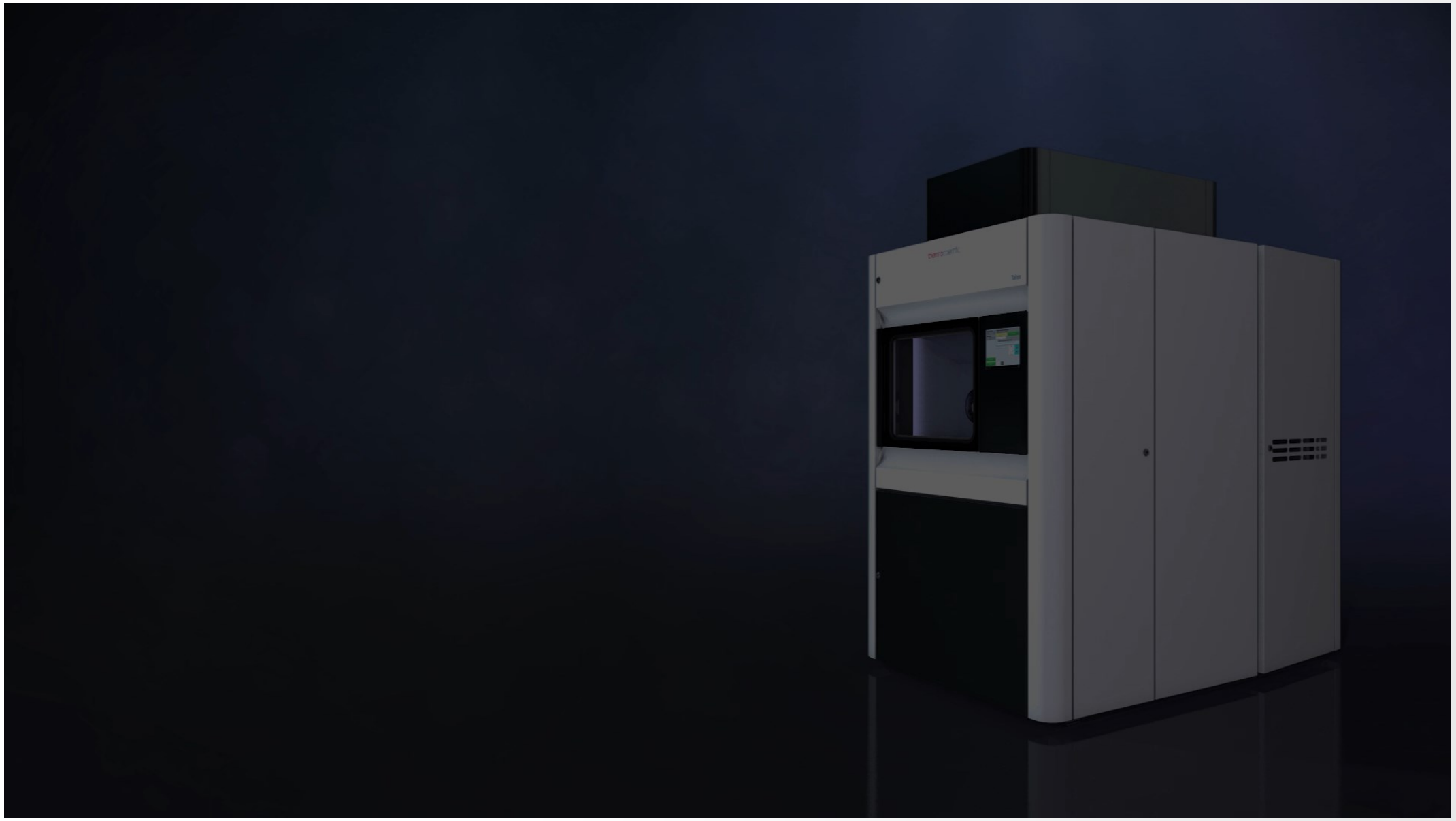
- Velox absorption correction scheme takes into account:
  - The Super-X Detector geometry; the quad-sensor configuration
  - The holder geometry



- Sample: Polycrystalline $Si_3N_4$ (42.9/57.1 at%)
  - 180 nm -> extreme absorption
- Chemical composition is independent of tilt

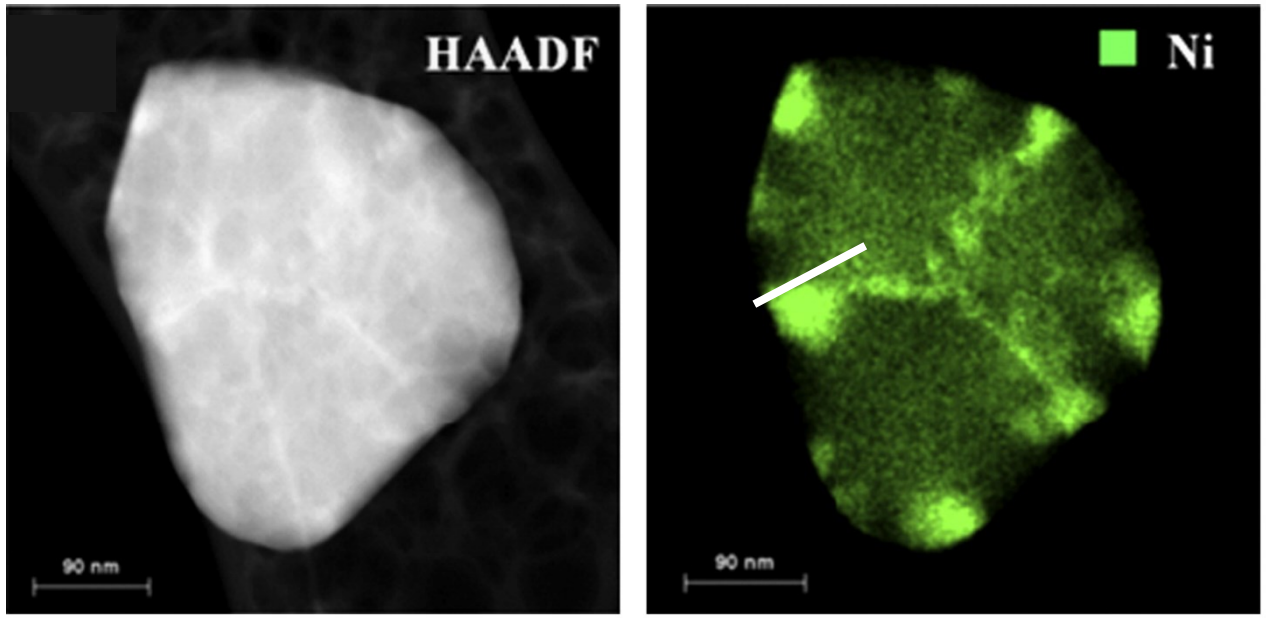


# Automated 3D EDS



# 2-D elemental mapping

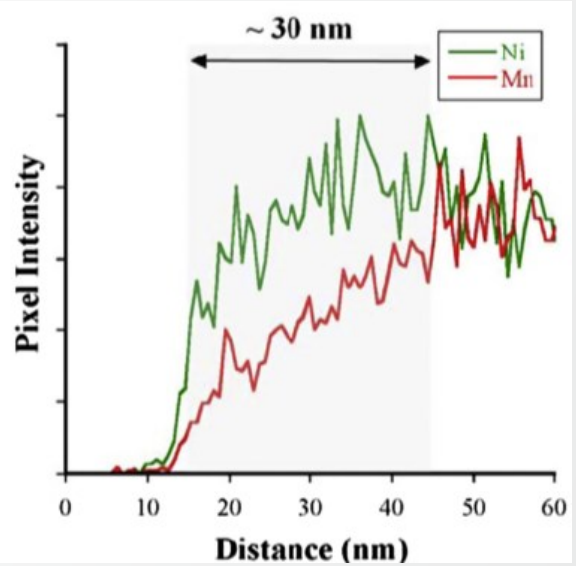
**Study cathode material in Lithium (Li) ion batteries.**




2-D imaging & 2-D elemental maps

2D analysis

Line profile analysis of 2-D elemental map

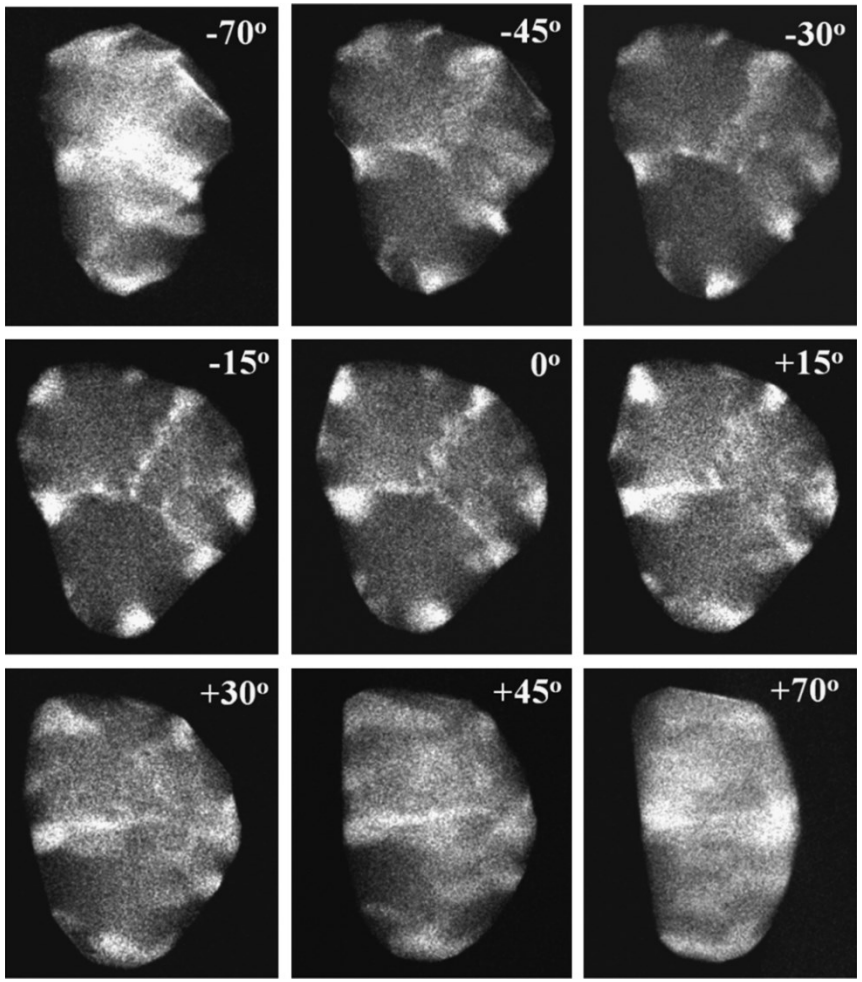


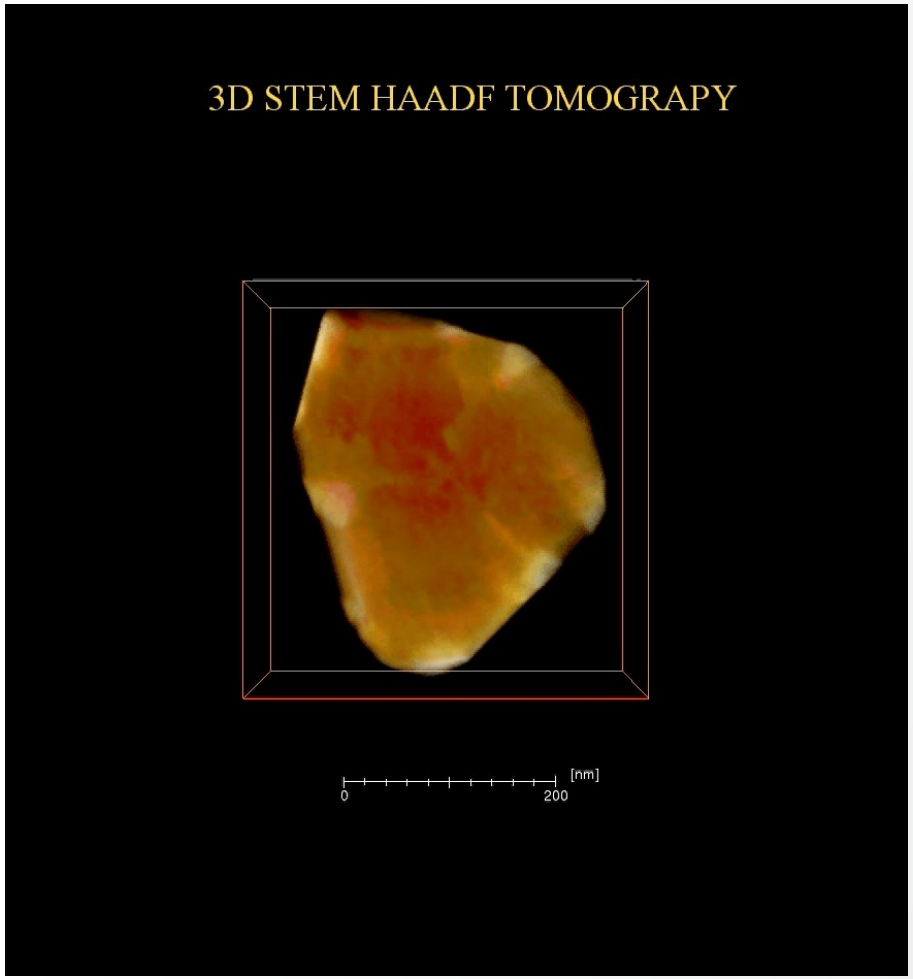

**Ni segregation?**
**Distance from surface?**

M. Gu, et al. Nano Lett. 12, 5186-5191 (2012)
A. Genc, et al., Ultramicroscopy 131, 24-32 (2013)
M. Gu, et al., Chem. Mater. 25 (11), 2319-2326 (2013)

# 3-D elemental mapping

## Study cathode material in Lithium (Li) ion batteries.

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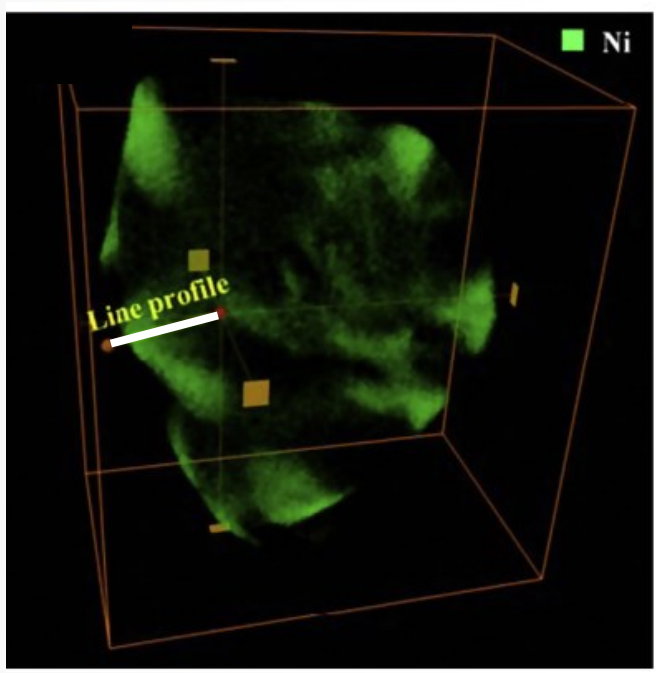
M. Gu, et al., Chem. Mater. 25 (11), 2319-2326 (2013)

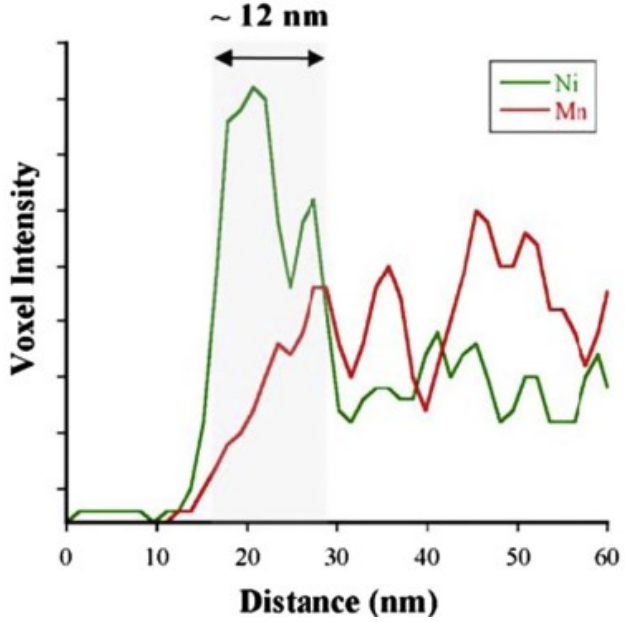
# 3-D elemental mapping: more accurate measurement

**Study cathode material in Lithium (Li) ion batteries.**




3D analysis

Line profile analysis of 3-D elemental map




**Ni segregation is on surface of the LNMO battery cathode.**

**2-D map suffers from projection problems: 30nm vs. 12nm**

M. Gu, et al. Nano Lett. 12, 5186-5191 (2012)
A. Genc, et al., Ultramicroscopy 131, 24-32 (2013)
M. Gu, et al., Chem. Mater. 25 (11), 2319-2326 (2013)

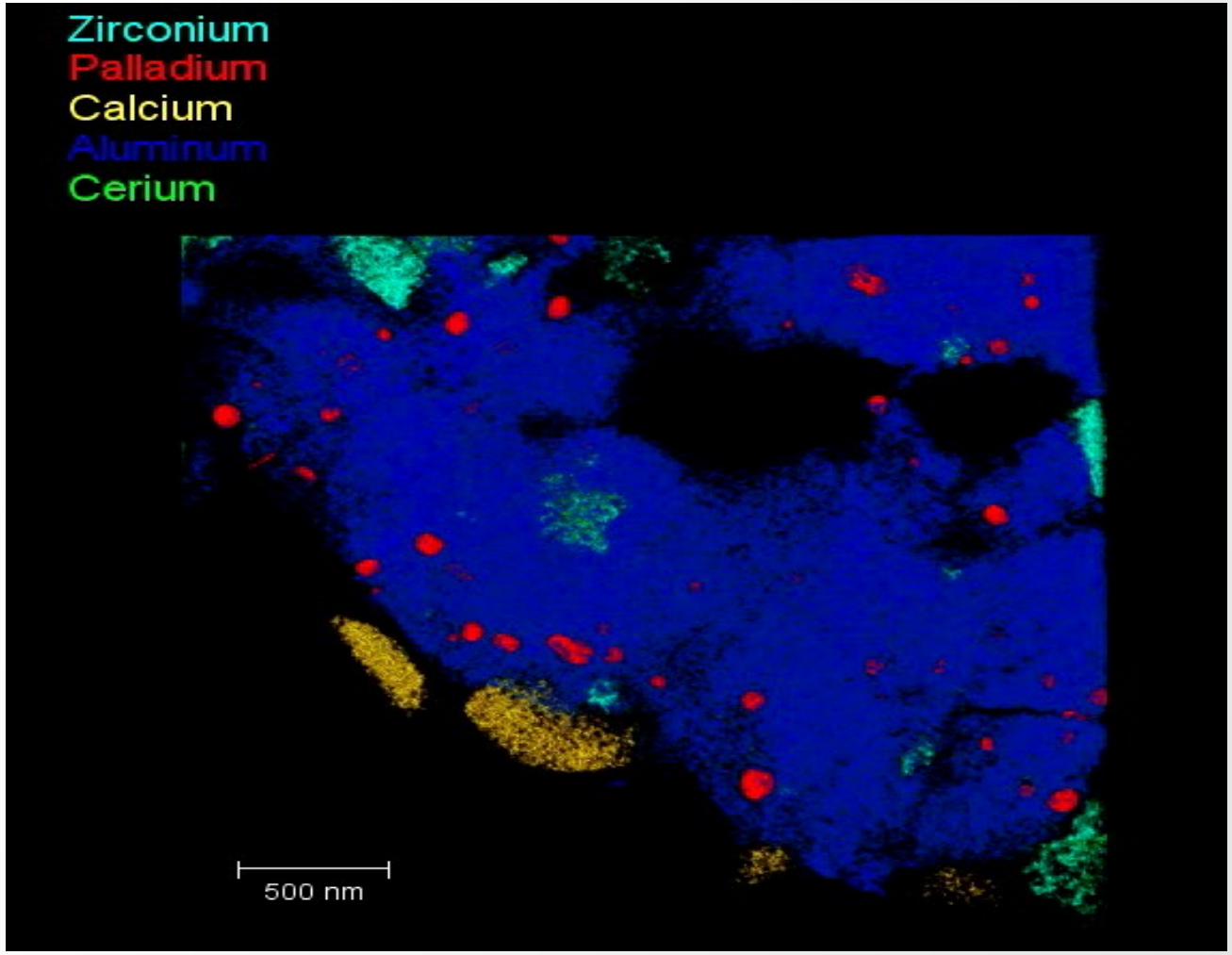
# Statistically Valid EDS

SW features: (enabling batch/overnight unattended acquisition 6.5 hrs)

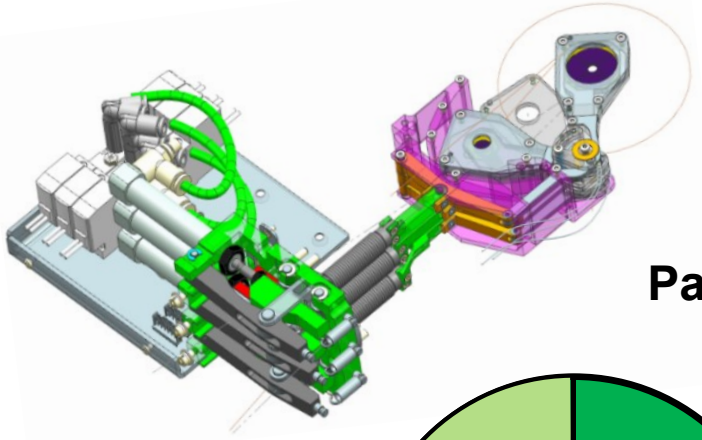
- Up to several hundreds  2D EDX maps of pre-defined ROI's
- Fully automated 3D EDX tomography
- Large field of view, statistically more valid.

-60 to 60° with 2° steps
**6.5h** (unattended, overnight)
Beam current: 0.3 nA

Vehicle-aged automotive catalyst

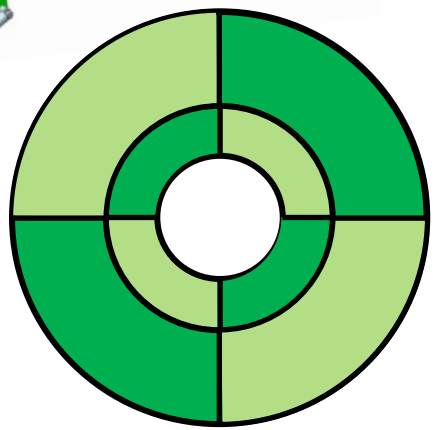


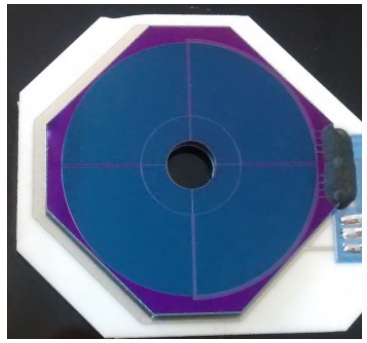
# Panther STEM Detection System



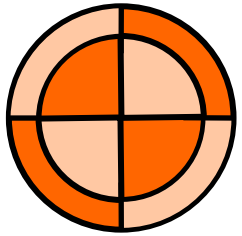
**Panther STEM Detectors**

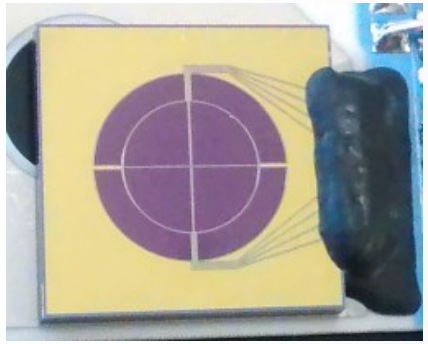
Ring





Disk





**Main improvements:**

**New Multi-segment, Solid State BF/DF**

300kV radiation hard

Optimised detector geometry for STEM/EELS, iDPC collection

Easier mechanical alignment of the BF/DF module

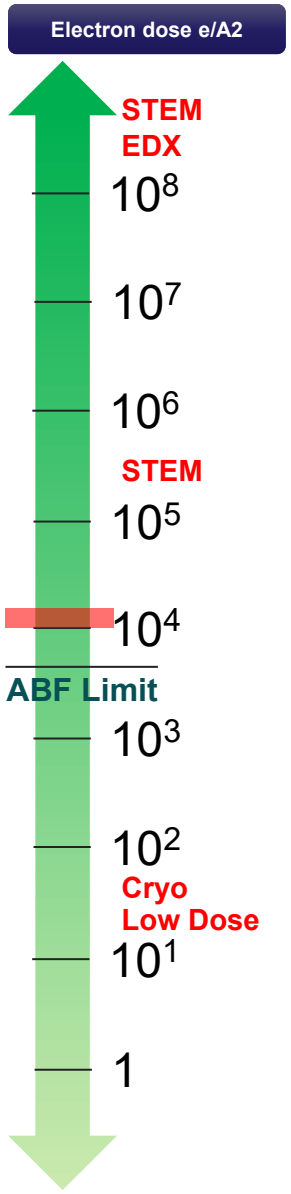
**New amplifiers with improved SNR**

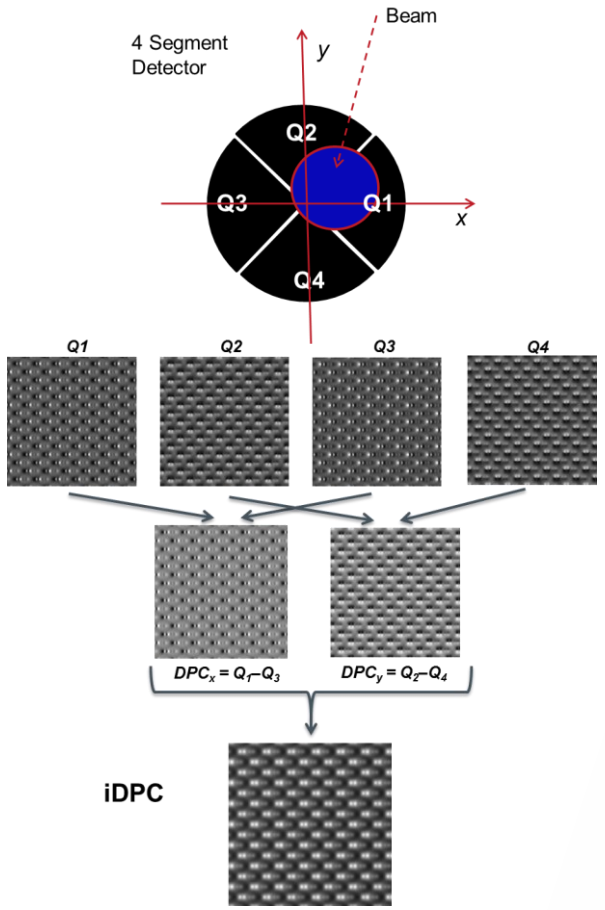
Single electron sensitivity up to 1.25nA (at 300kV)

Over 100x more gain than with PIA

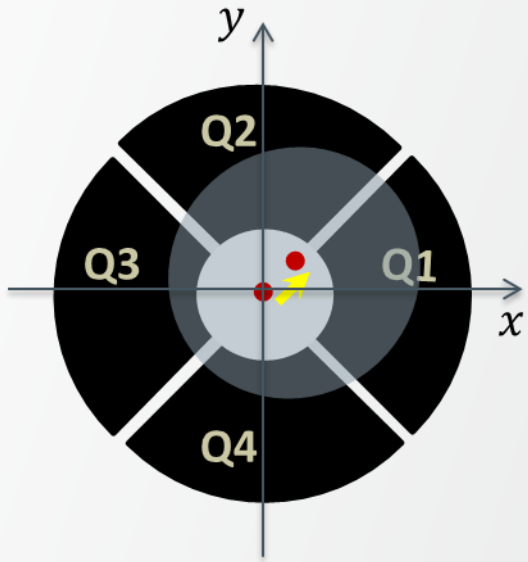
Noise floor dramatically reduced;
Improved low dose imaging capability

# Panther STEM – Improved low dose imaging, iDPC capability



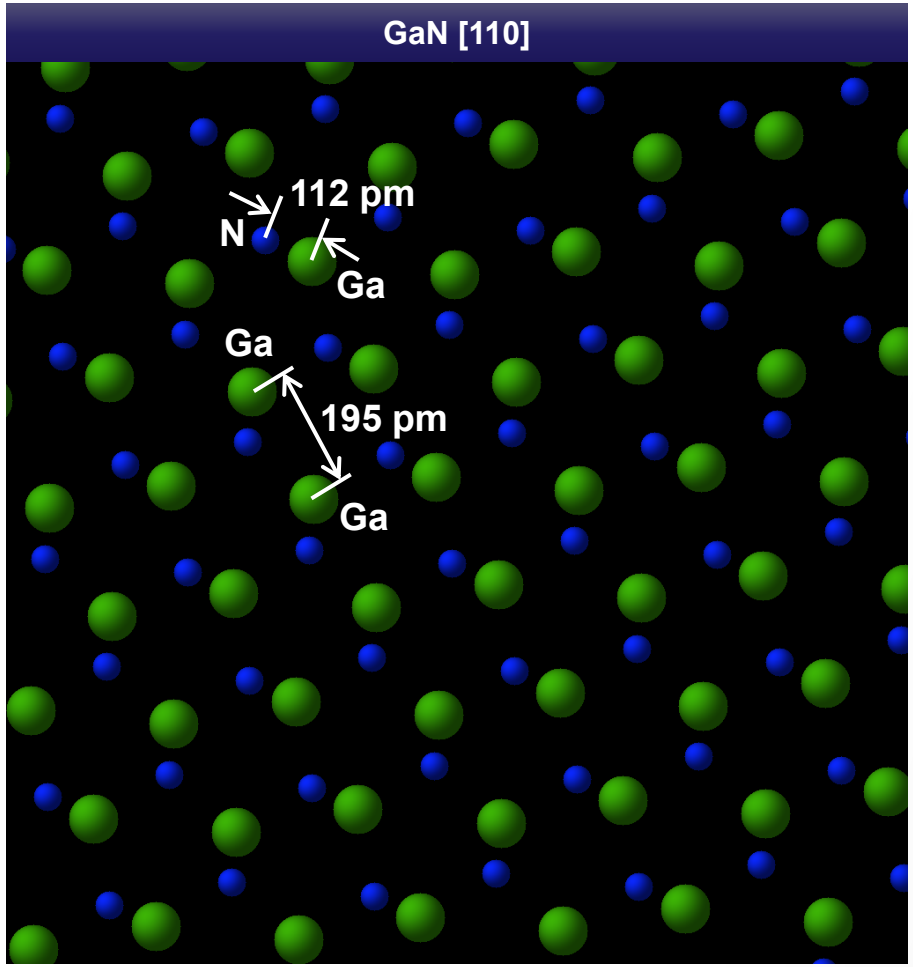



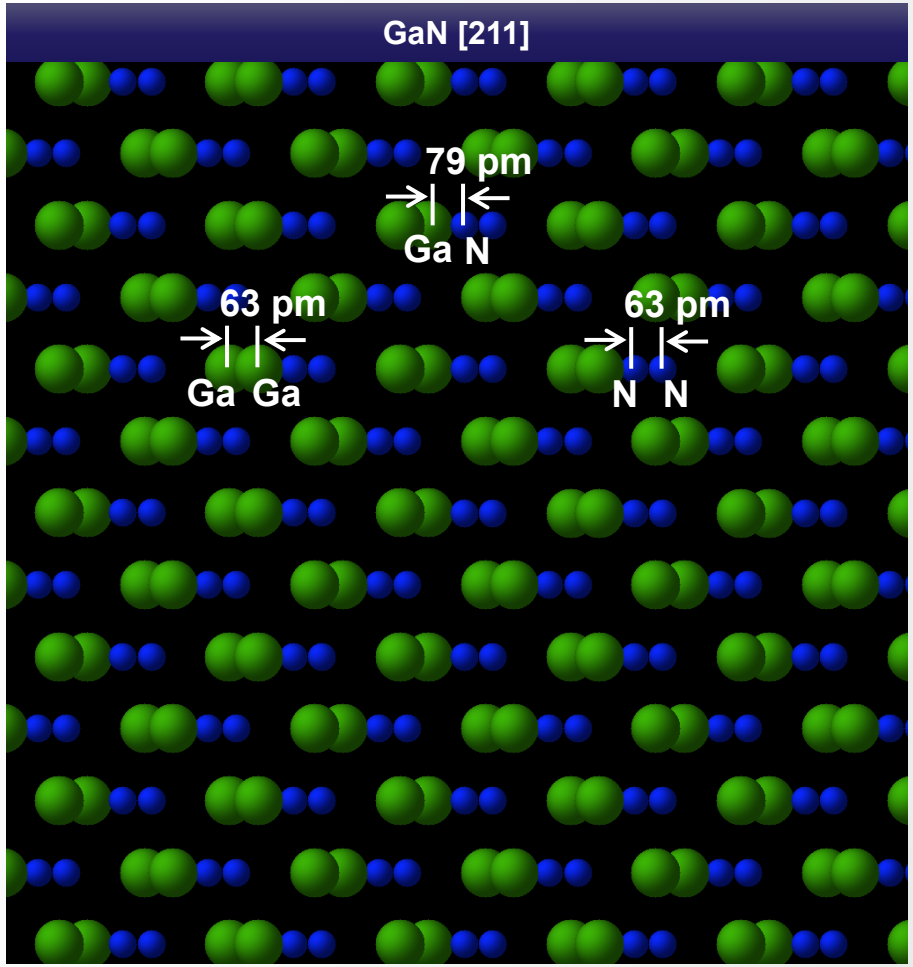

Quadrants of the detector are used to reconstruct the final iDPC image



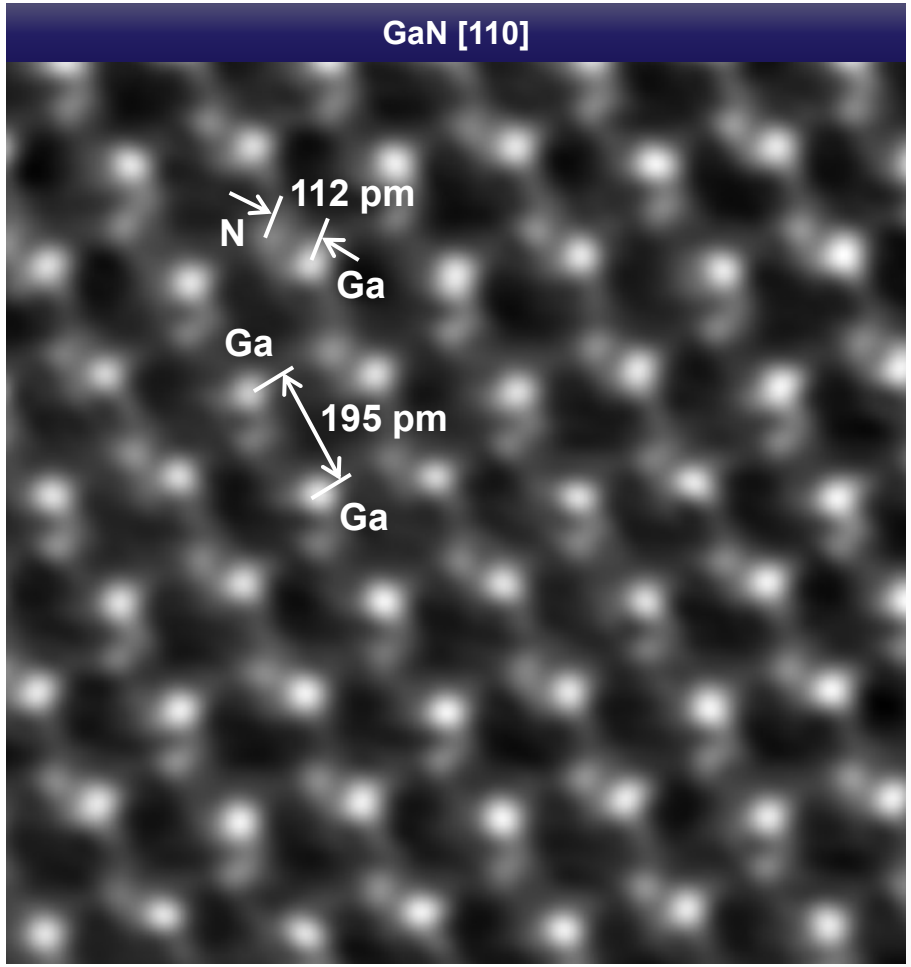

i-DPC is not new, but the ability to display the i-DPC image live in the user interface is. It is a much improved way to see light elements in STEM mode.

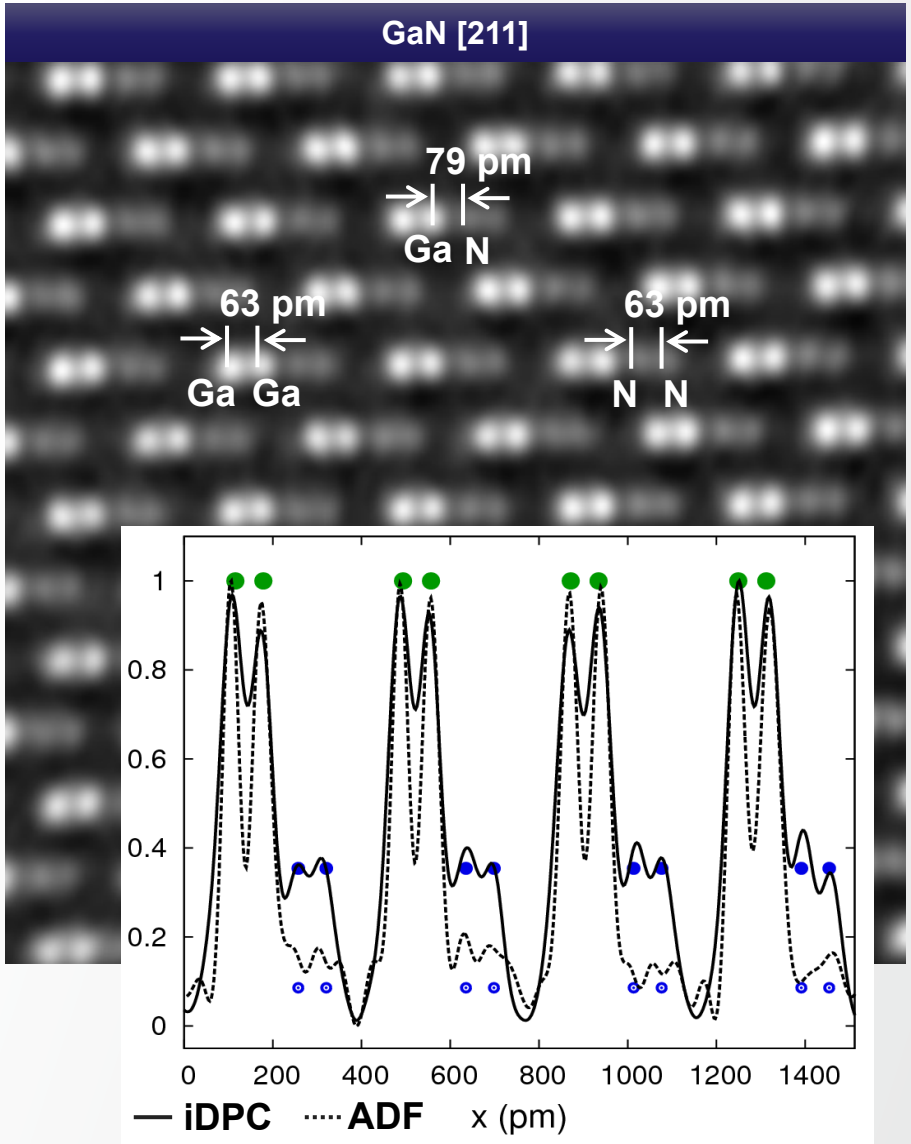
# Non-centrosymmetric structures (GaN) i-DPC imaging



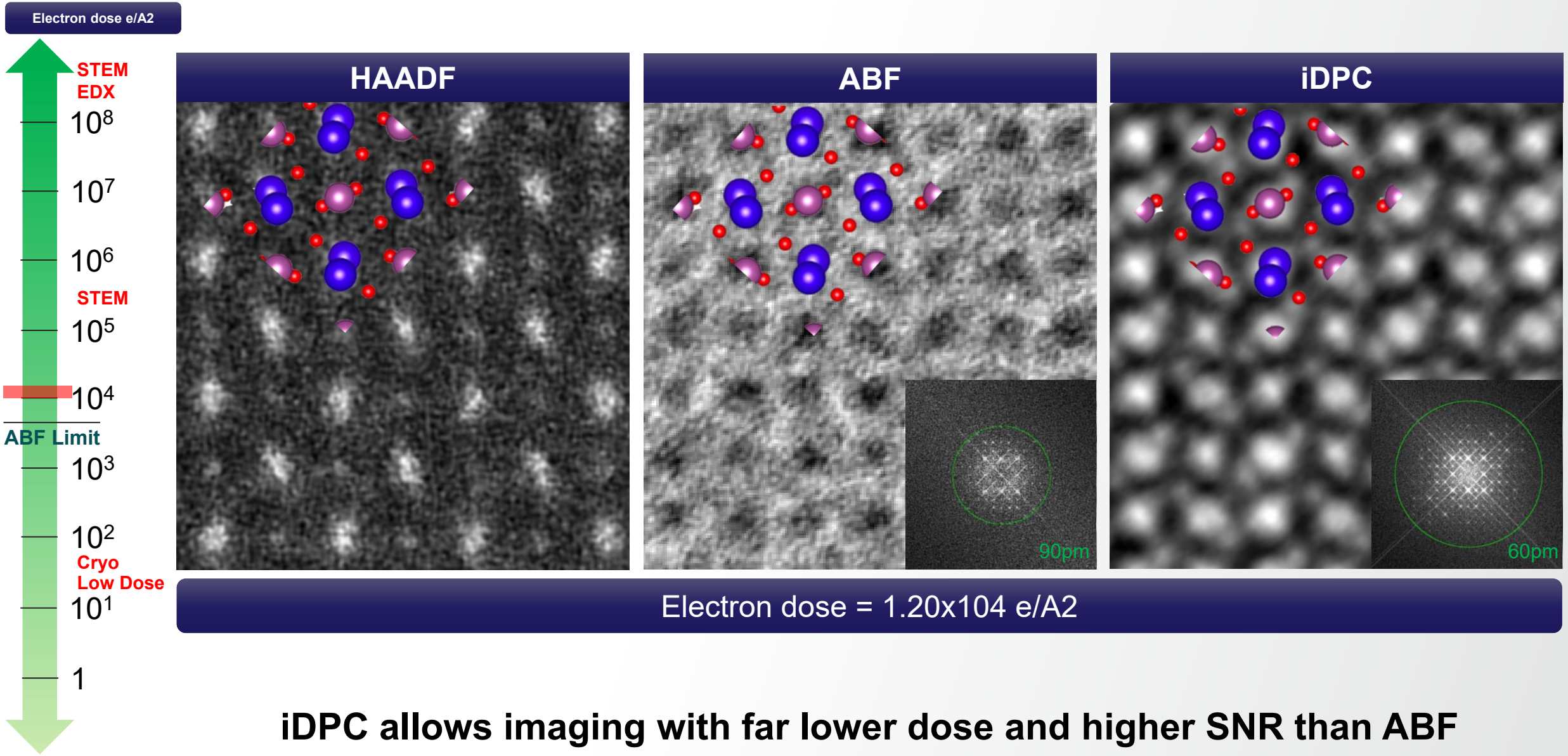



# Non-centrosymmetric structures (GaN) i-DPC imaging



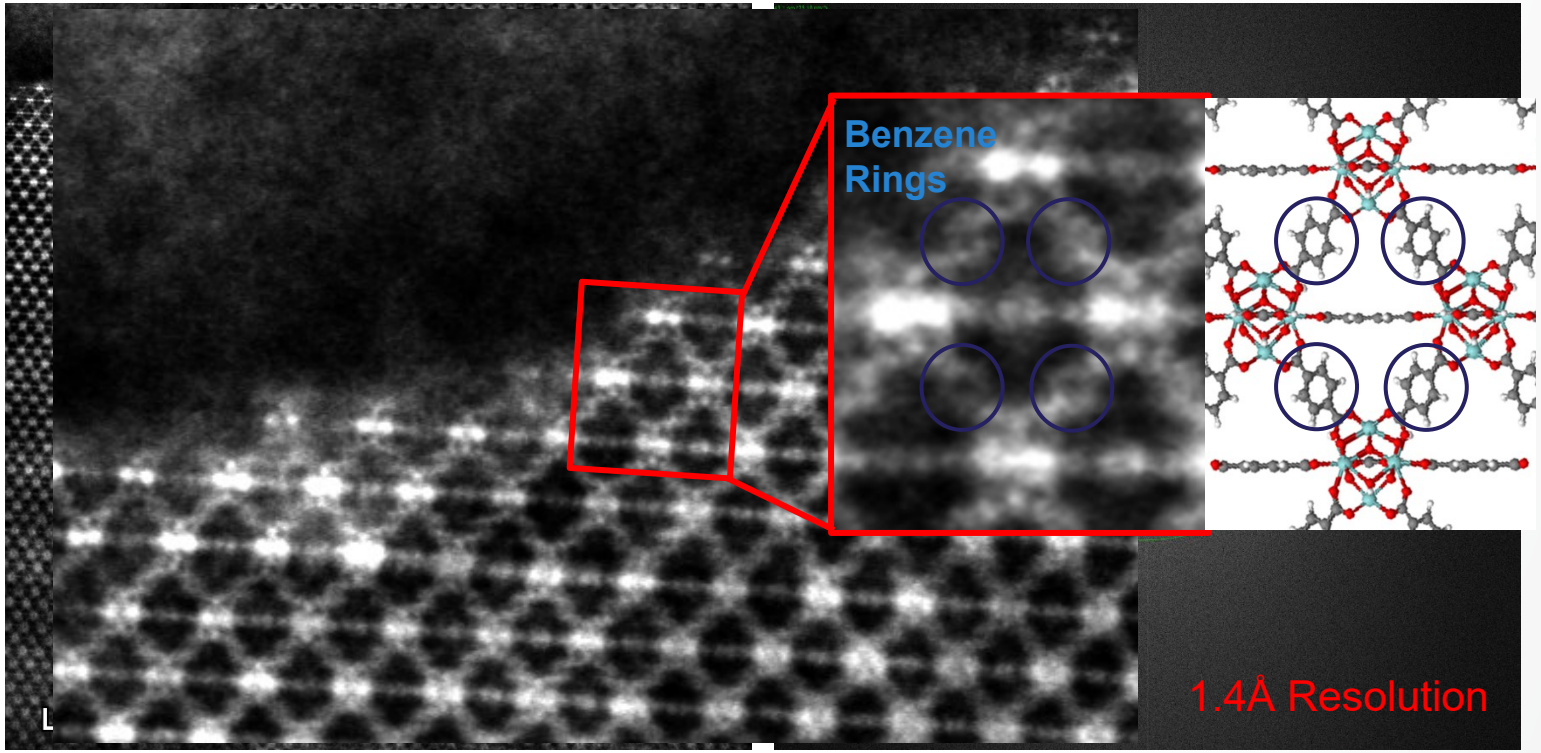



# Comparing HAADF, ABF and iDPC for signal to noise.




**iDPC allows imaging with far lower dose and higher SNR than ABF**

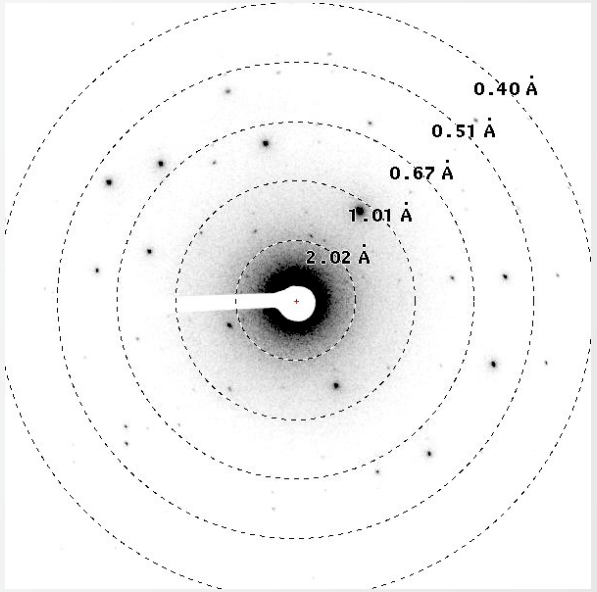
# i-DPC ultra low dose STEM imaging capabilities




Probe Current = <0.5pA
Frame time = 23.5 seconds
(Specimen courtesy of Professor Y. Han, King Abdullah University of Science and Technology)

- New, low dose STEM imaging capability on Spectra 300 with sensitive Panther STEM detection system
- High quality STEM imaging with lower probe currents and less specimen damage
- Complex structure of Metal Organic Framework (UIO-66) imaged with <0.5pA in STEM using iDPC

# MicroED (Continuous Micro Electron Diffraction Tomography)



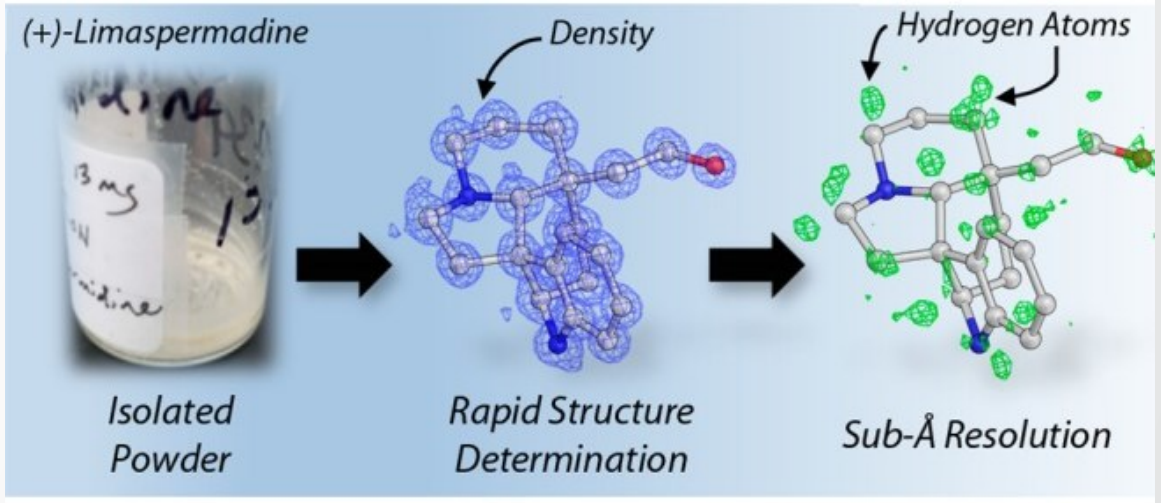

**MicroED can be used to determine the crystal structures of new materials**

## Gaining popularity

- Multiple high profile papers have raised interest recently
- **Big** potential for Materials Science
  - Organic Chemistry labs

## Why is this important?

- XRD needs larger samples
- MicroED gets excellent data from:
  - Small crystals < 1 µm (impossible with XRD)
  - Very small amounts of materials

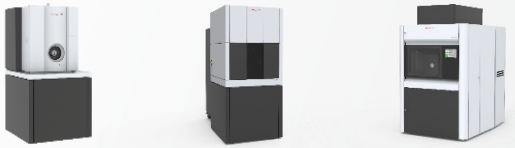


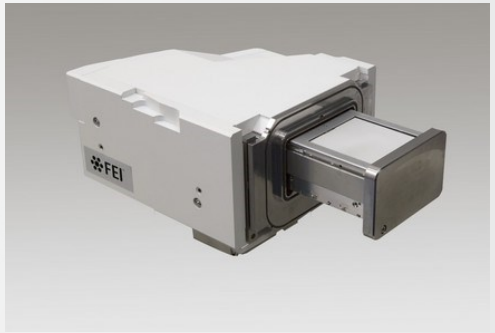

C. G. Jones et. al. ACS Cent Sci. 2018; 4(11)

# MicroED on Talos F200

## Ceta-D; high-sensitivity version of Ceta dedicated for low-dose diffraction

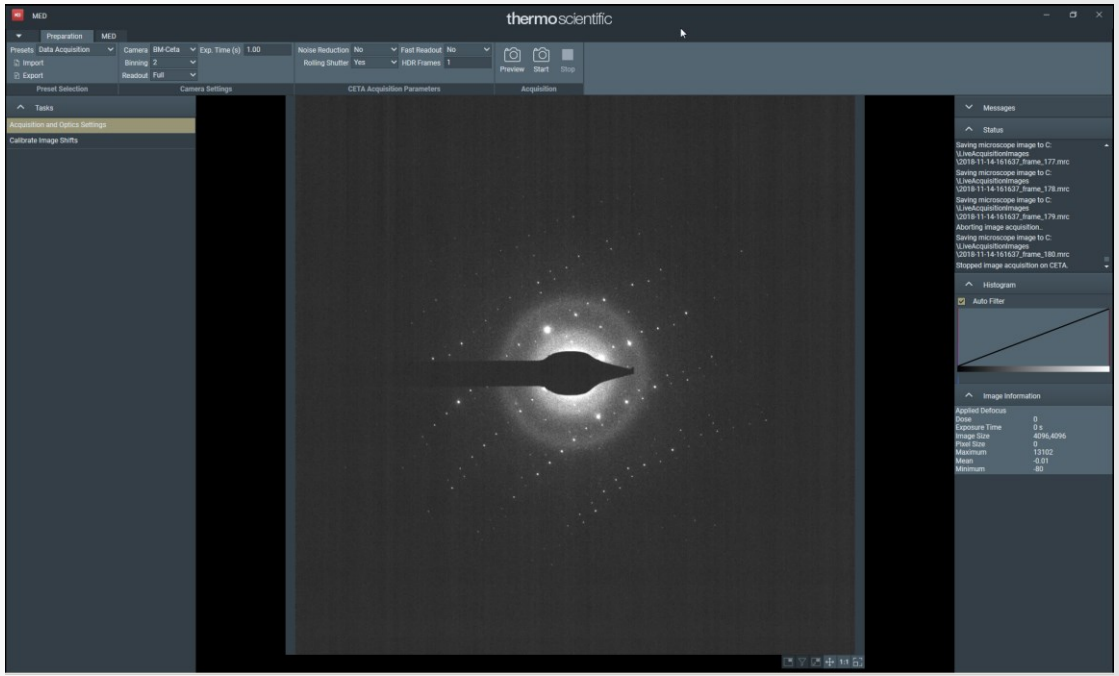
- Single crystal information using a minimum dose
  - ~0.01 e-/Å2 vs. 10 e-/Å2 for imaging techniques





## Solution enhancement package:

- MicroED SW for automated acquisition and storage
- Special diffraction finer lens series and 90º rotation
- Fischione small beam stop

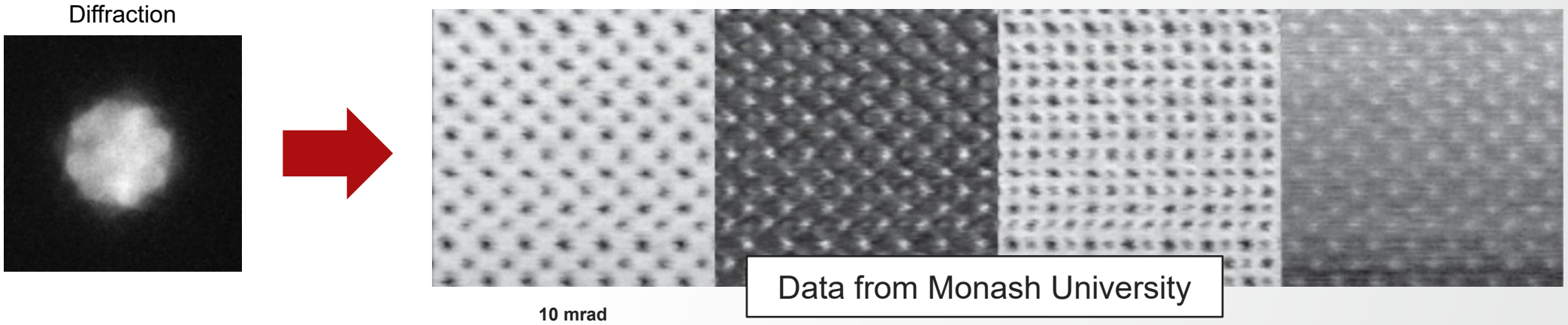


# 4D-STEM - Expanding STEM Imaging Capabilities

- To acquire diffraction patterns from every pixel in the sample
- The data is then post-processed to give: A/BF, A/DF, HAADF, DPC, iDPC, Strain, Orientation and Crystal phase mapping

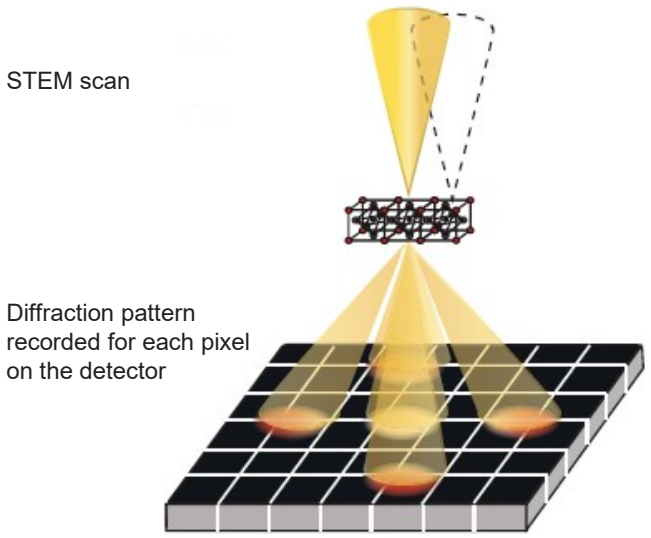
**Camera's that are excellent imaging cameras are typically bad cameras for diffraction because of dynamic range requirements**

- 4D stem can be acquired on ***Ceta with speed enhancement***
- 4D stem can be acquired on ***EMPAD (Electron Microscope Pixel Array Detector)***



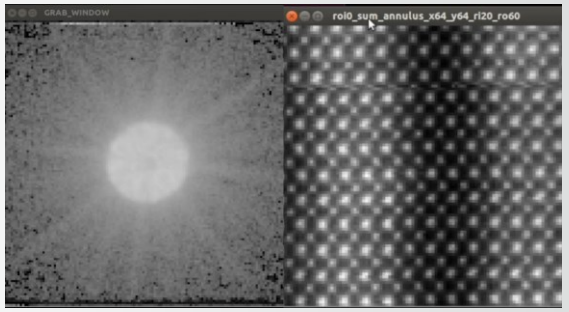
# Diffraction Camera – EMPAD Detector

**4D STEM on an EMPAD**



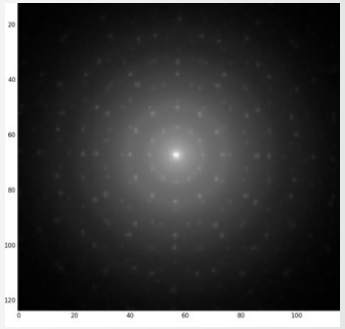

## Fast acquisition

- Maximum readout speed of 0.86 ms/frame (1100 frames/second)
- $128^2$ pixel STEM image in approx. 15 seconds
- Maximum information/minimum dose



## High dynamic range

- Maximum dynamic range > 1 to 1,000,000 e- per pixel
- Single electron sensitivity (noise is 1/140 $e^-$)
- Max. current 2 pA/pixel/frame
- Strong and weak signals visible simultaneously

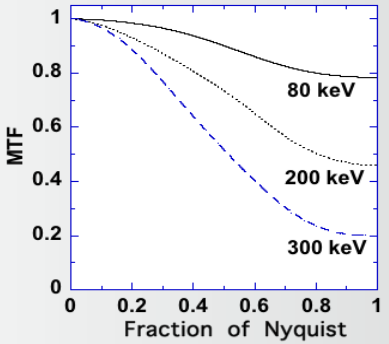


Diffraction pattern (log scale) of a double graphene layer @ 80kV.

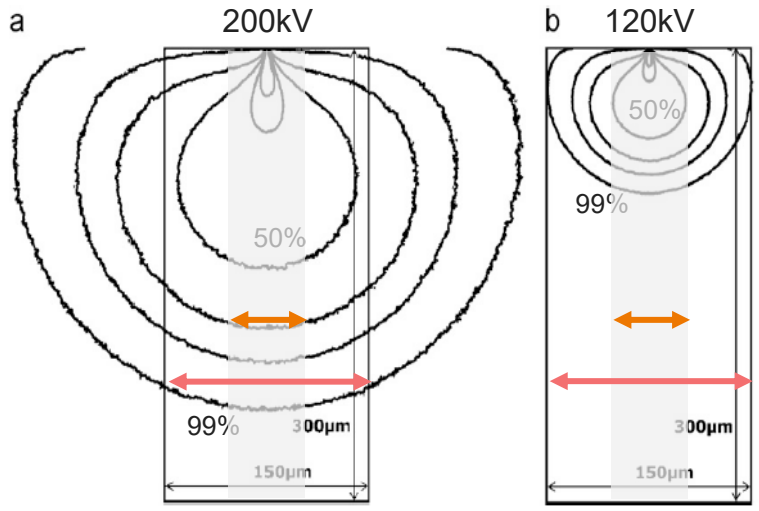
The central spot has $10^6$ the intensity of the outer spots

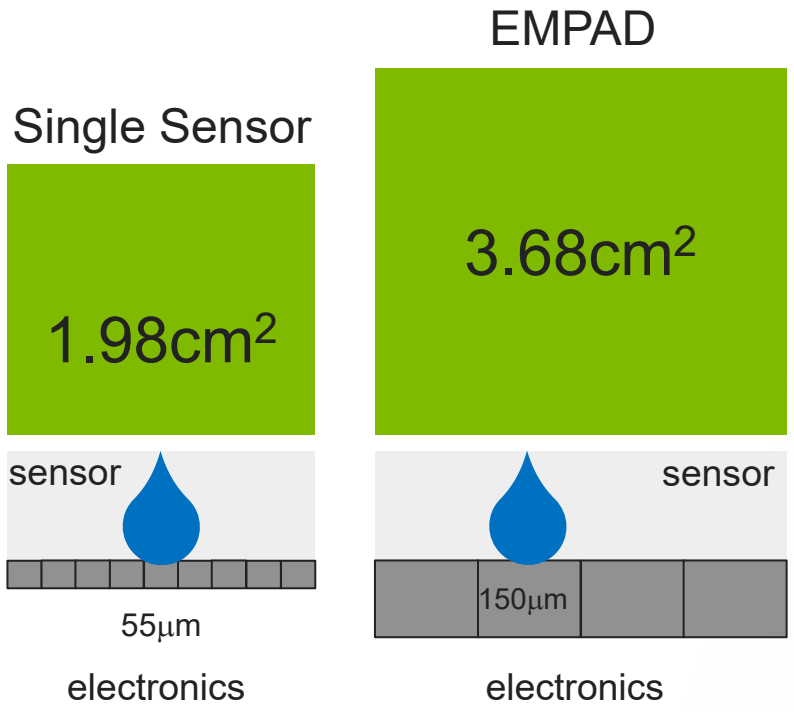
## For all accelerating voltages

- Very large pixel size (150 um) yields excellent MTF's at all accelerating voltages
- DQE(0) remains constant for all accelerating voltages
- Radiation hard (30 – 300 kV)



# Single Sensor – EMPAD comparison




## Pixel size

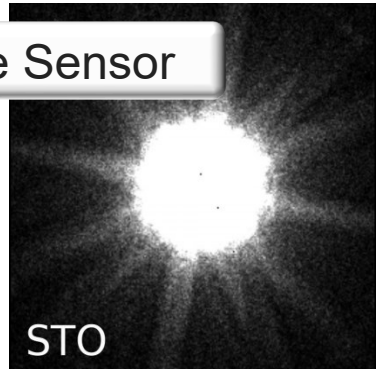
- Some single sensors have smaller pixels 55 x 55µm
- Signal is spread over more pixels (PSF worse)
- MTF drops significantly especially above 100kV

Single sensors are poor above 100-120kV

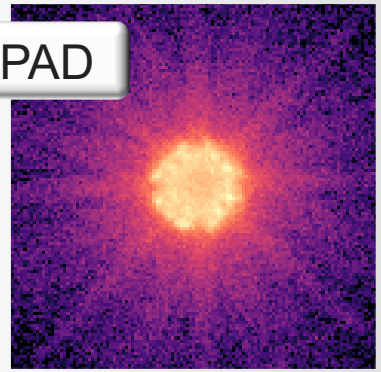
## Sensor size

- A bigger FOV while retaining the details

Single Sensor




EMPAD

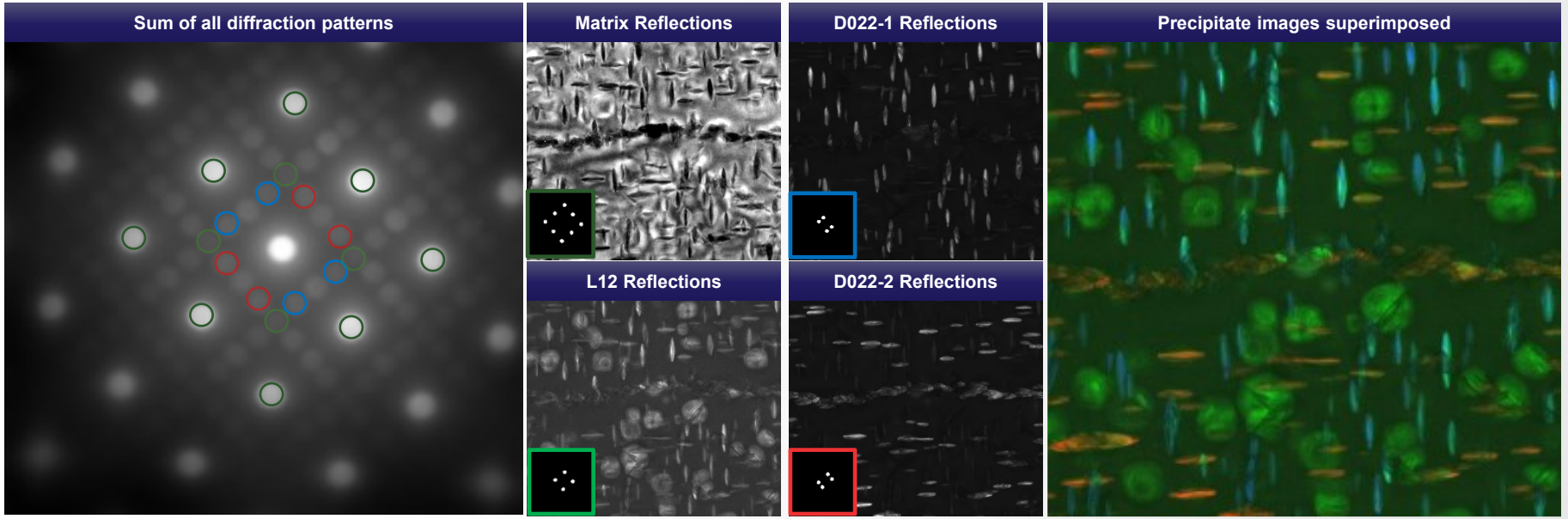


# Flexible Imaging in STEM – EMPAD Detector

## Crystallographic application

- Clear separation of different precipitates compared to ADF image
- Alloy 718 is a Fe- and Cr-rich Ni-superalloy which may be precipitation hardened
- New insight for superalloy design by orientation mapping of precipitates

**Precipitate Imaging in Fe and Cr Rich Ni-Superalloy 718 at 200kV**







*Sample Courtesy of Professor Grace Burke*
*The University of Manchester*

# S/TEM Maps Software

## Large area imaging and EDS at high resolution

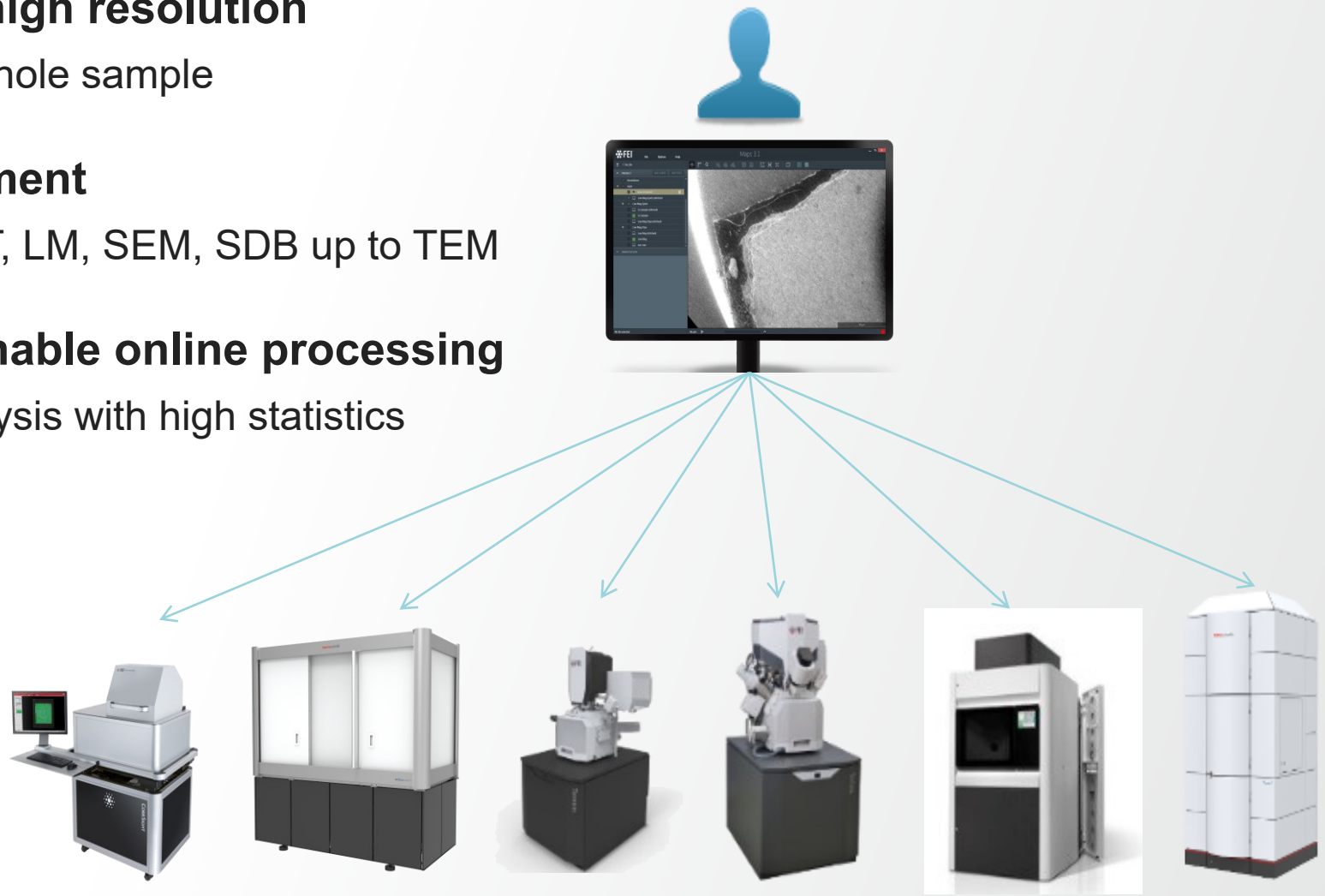
- Image-based navigation on the whole sample

## Image import, overlay and alignment

- Correlative experiments from µCT, LM, SEM, SDB up to TEM

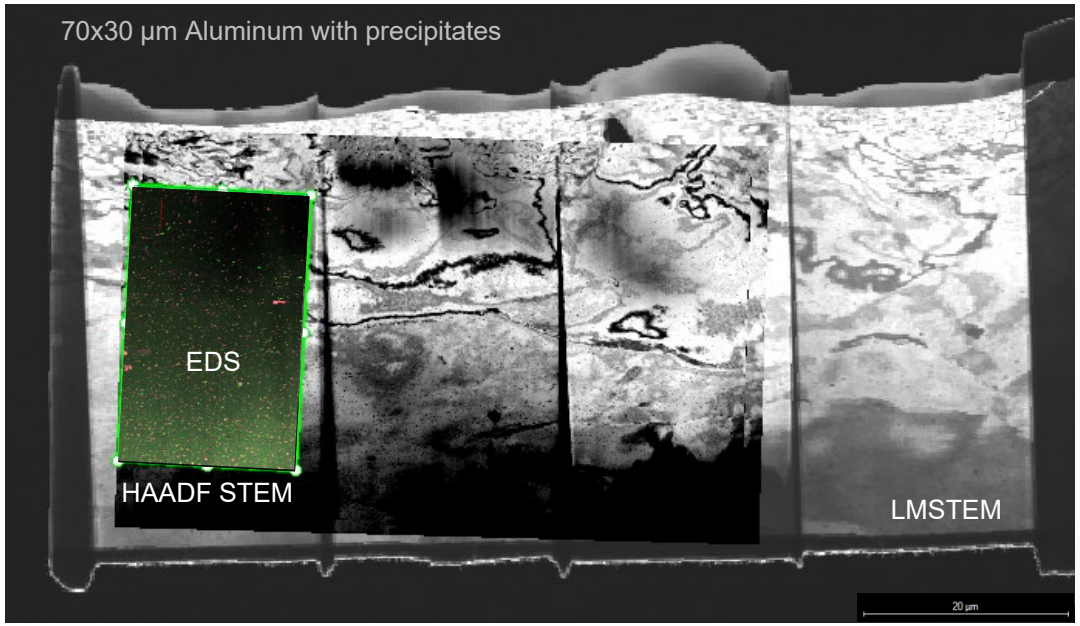
## *Powered by* Avizo Software to enable online processing

- Individual particle parameter analysis with high statistics

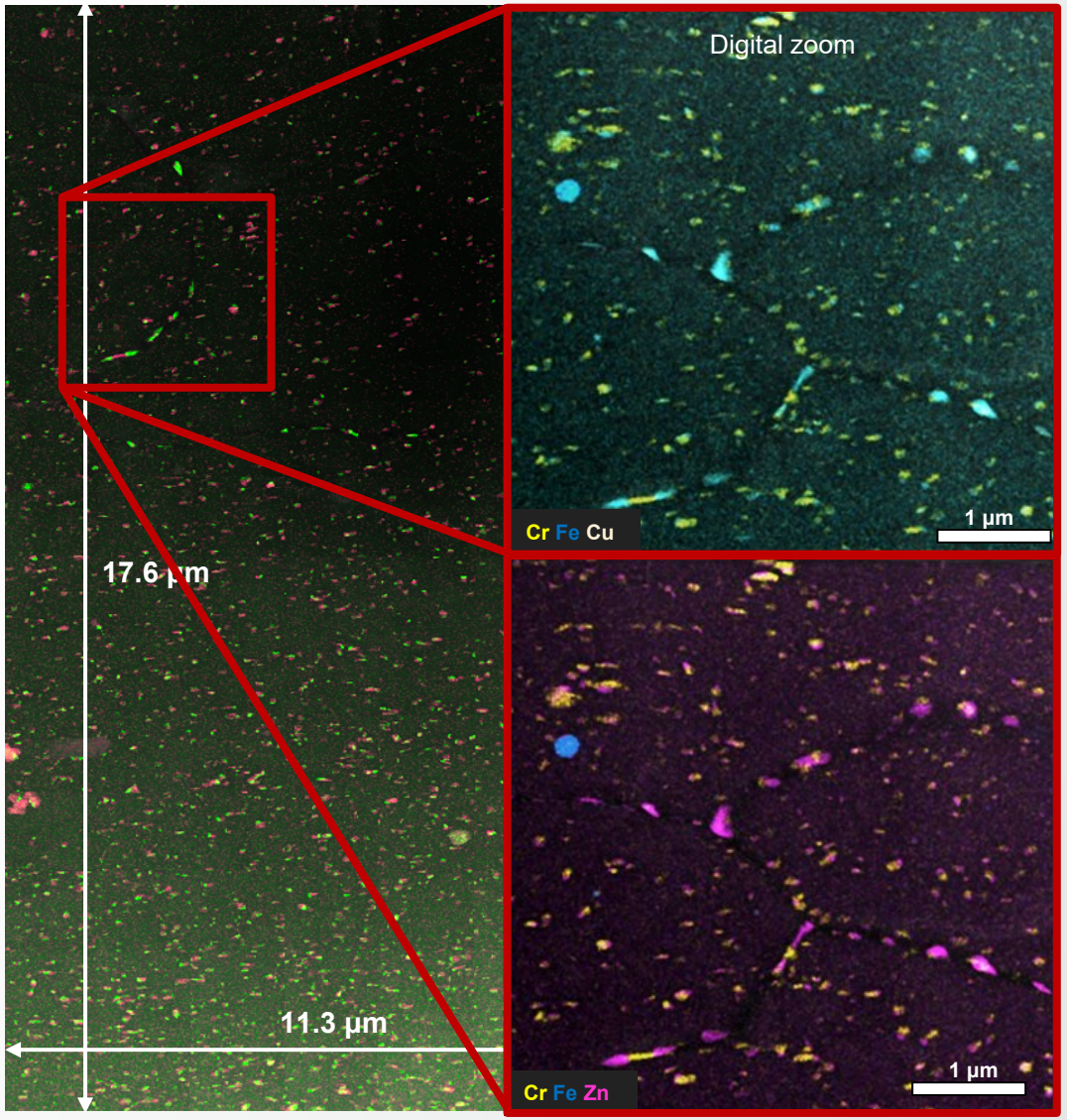


# Maps Software

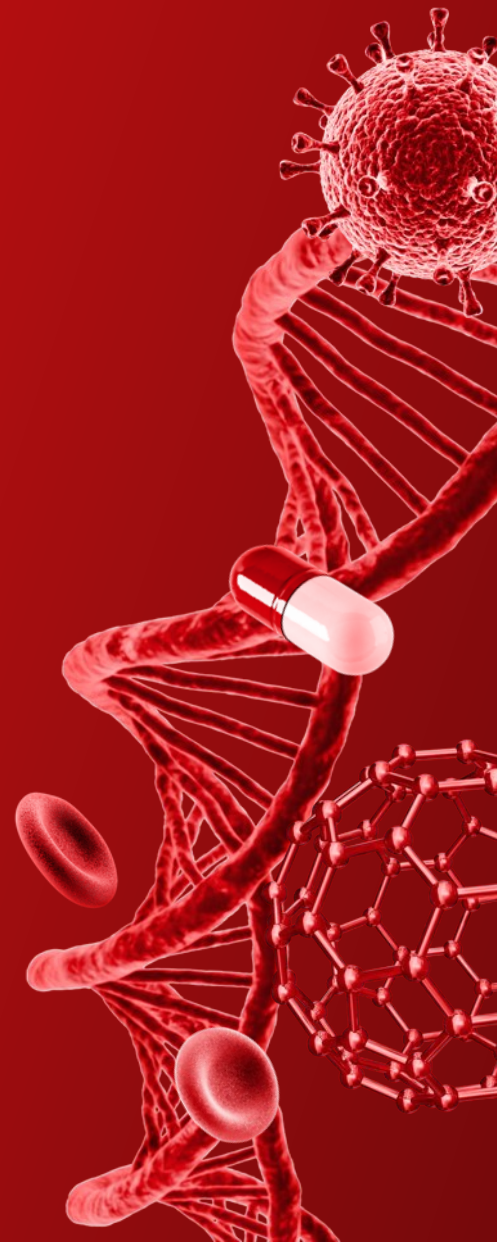
- **Analysis with Super-X & Dual-X EDS**
  - Automated large area EDS at high resolution
- **Aerospace grade aluminum alloy (PFIB prep.)**
  - Cr rich particles mainly in Al matrix
  - Fe/Mn inclusions
  - Zn-Cu-Mg rich particles on grain boundaries




*Sample courtesy: University of Manchester / University of Trento*



# Thank you



# Coming Up...



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## FAST CHARACTERIZATION OF NANOMETER THIN TO THICK COATINGS USING PULSED-RF GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY

SPEAKER:

**Philippe Hunault**

Technical Sales Elemental Analysis Specialist, HORIBA Scientific

December 2, 2021 | 11am PT

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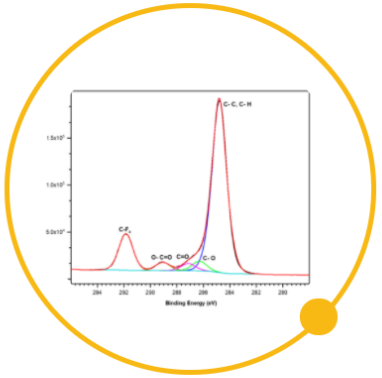

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# Q & A Session

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# Thank you