Past, Present and Future The Evolution of x-ray Analysis

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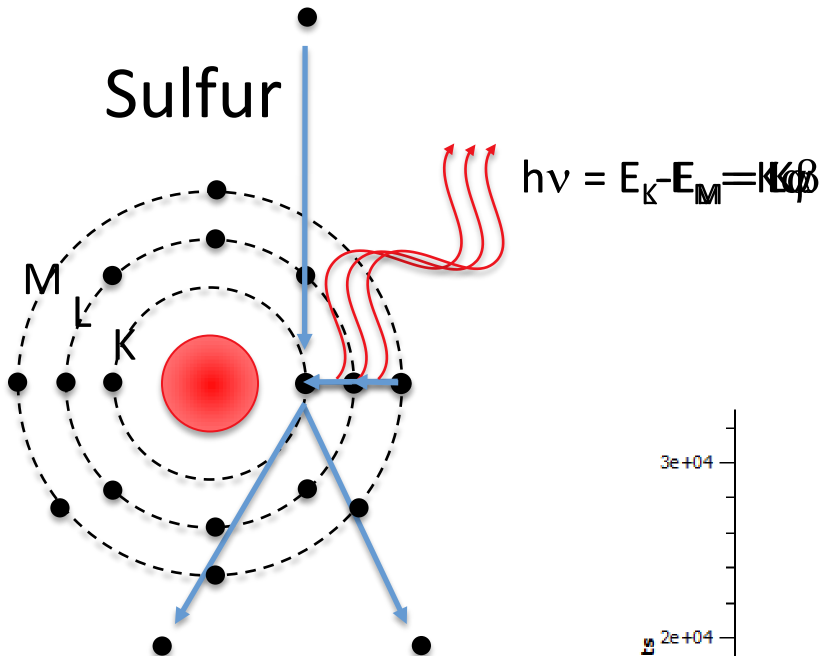
AMETEK MATERIALS ANALYSIS DIVISION

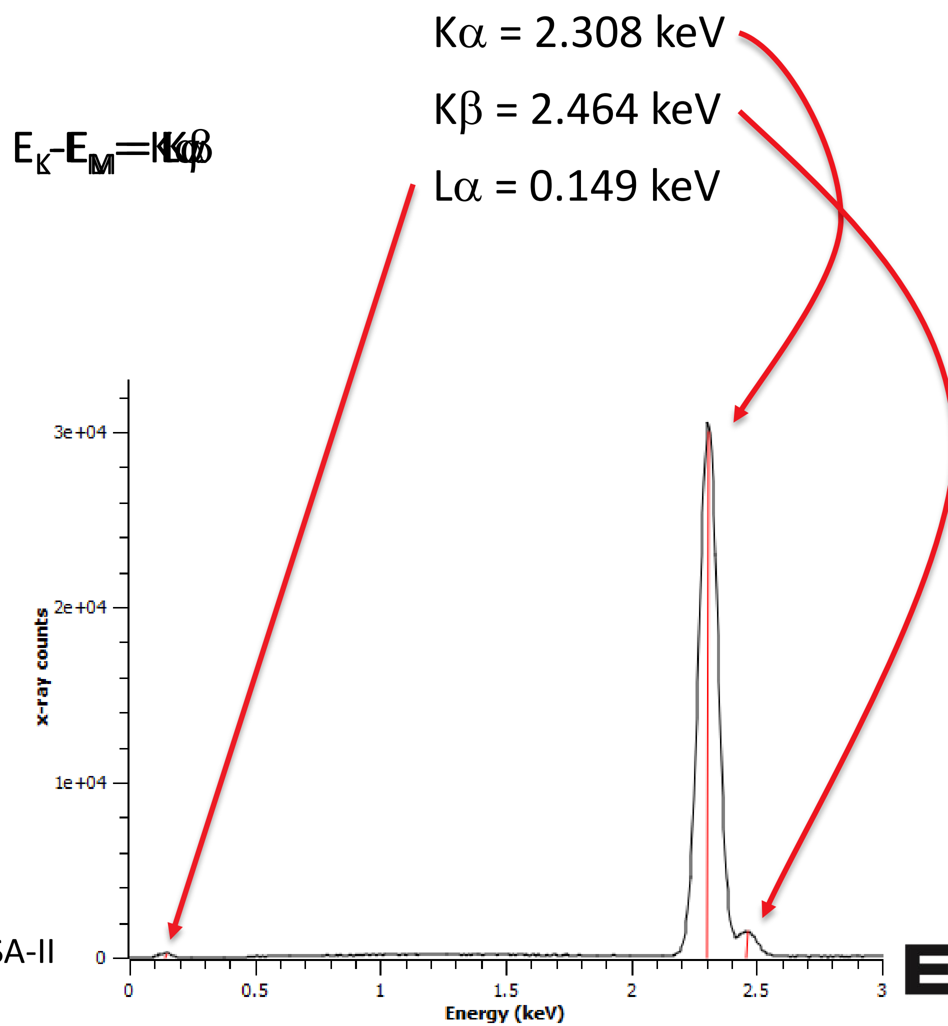
EDAX Smart Insight

Past, present, and future - the evolution of x-ray analysis

- Introduction to EDS fundamentals
- Evolution of EDS systems
- Examples

X-ray generation





NIST DTSA-II

Microscope parameters

To excite an x-ray line, we need electrons possessing energy greater than the corresponding absorption line. Rule of thumb: twice the energy of the x-ray line.

The electron energy is a function of the microscope acceleration voltage.

10 kV acceleration voltage → 10 keV electron energy

Number of x-rays ∝ Number of electrons

The number of electrons is measured by the beam current.

The beam current depends on spot size/probe size and aperture size.

Charge of 1 electron= $1.602\ 10^{-19} C$

$$1\ nA = 1 * 10^{-9} C/s$$

$$= \frac{1 * 10^{-9}}{1.602 * 10^{-19}} e^{-}/s \qquad = 6.24 * 10^{9} e^{-}/s$$

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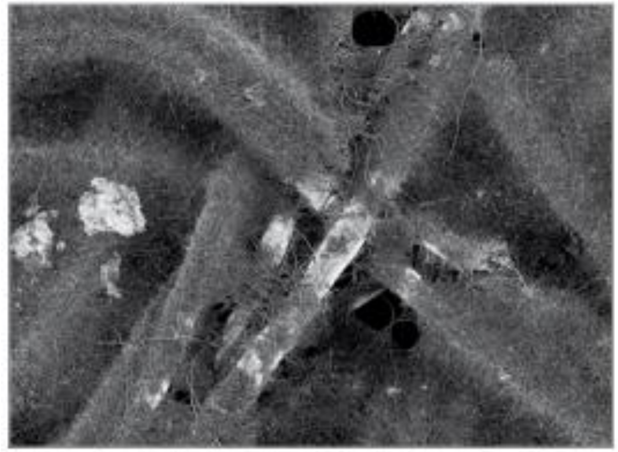
Microscope parameters

To get a good x-ray spectrum we need enough acceleration voltage to excite the elements of interest and enough current to get good count numbers.

On modern SEMs acceleration voltage, spot size and apertures are easy to adjust and typically on minor corrections are needed after changing any of the parameters.

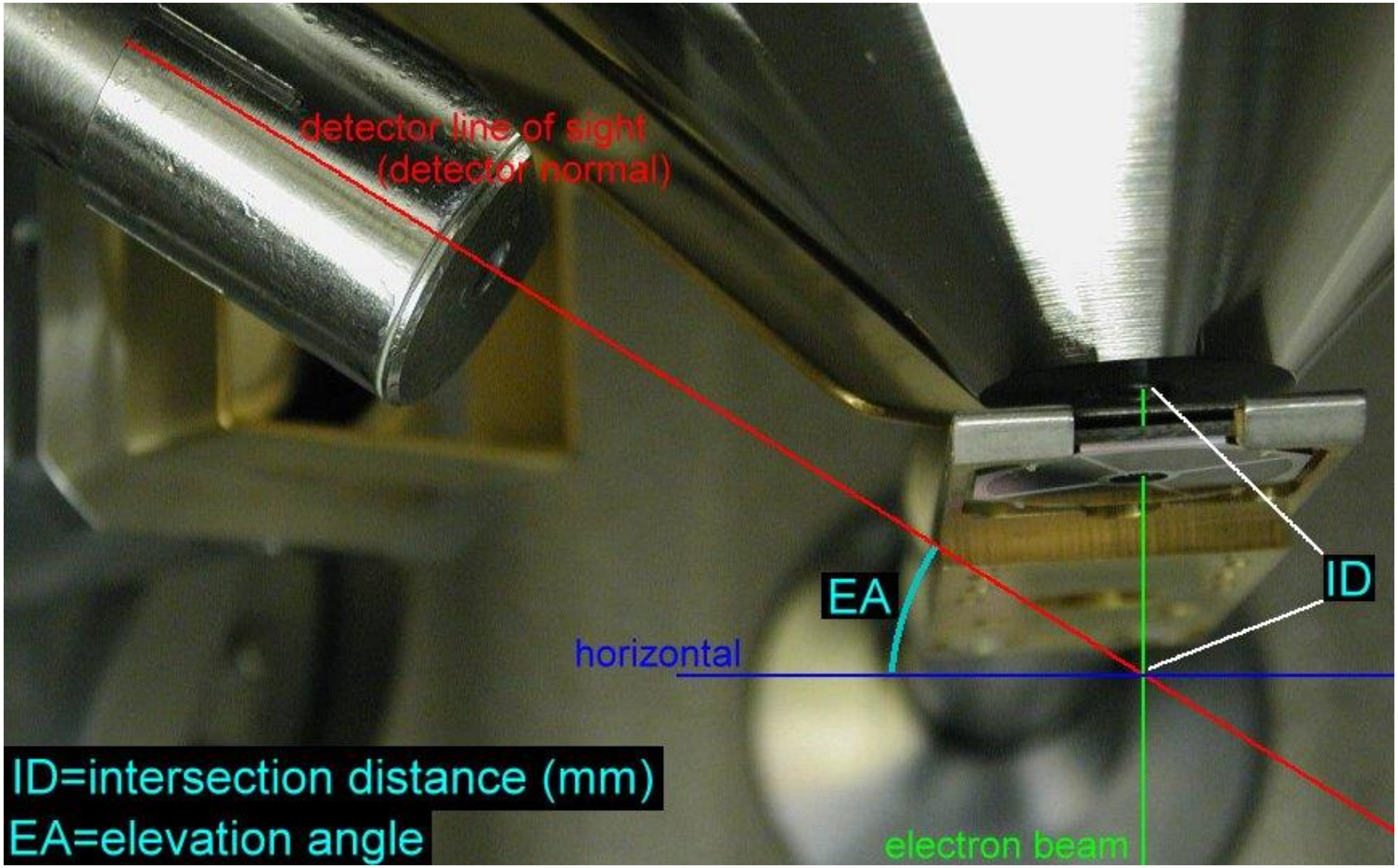
However, a good SEM image is not a guarantee for a good x-ray spectrum.



No x-ray generation!

Carbon nanotubes imaged at 30 V, 250 pA
(Zeiss Merlin product information pdf)

Geometry



detector line of sight
(detector normal)
EA
horizontal
ID
ID=intersection distance (mm)
EA=elevation angle
electron beam

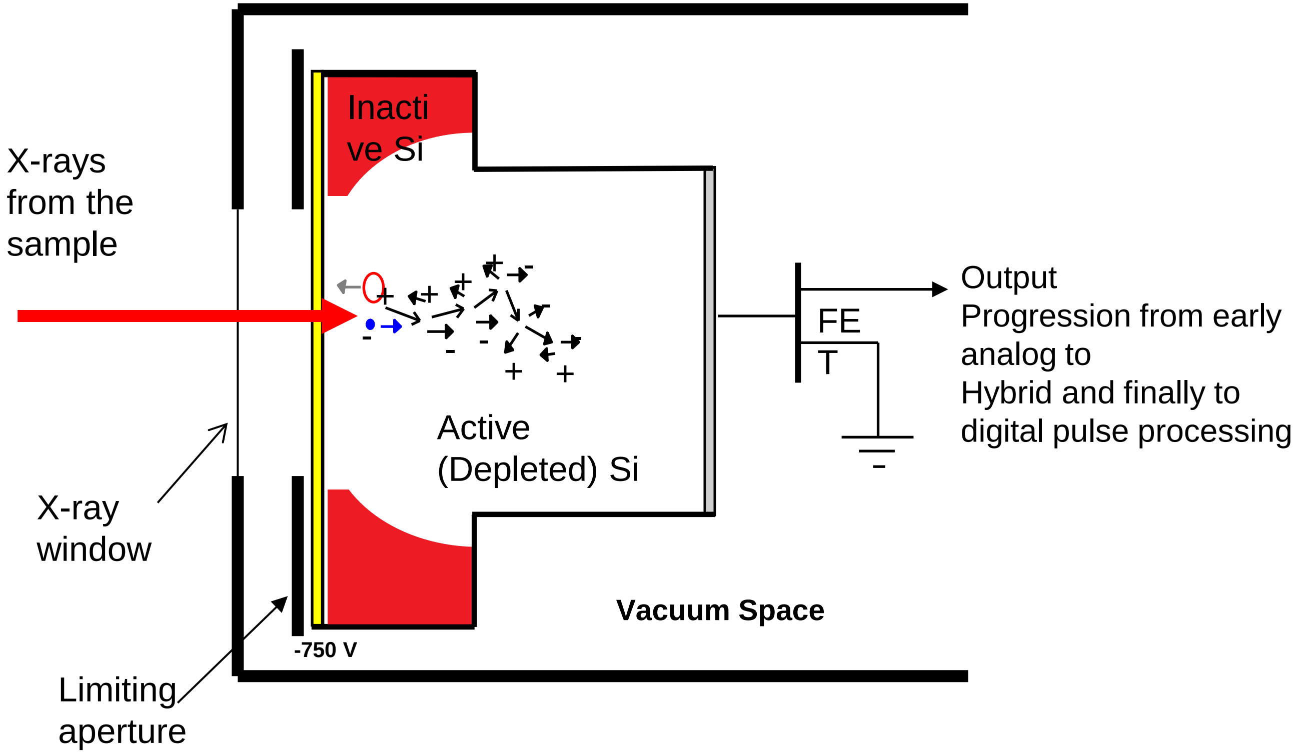
EDS Detector Technology

- Evolution of EDS Detectors
- Detector Components and Considerations

EDS Detector Technology

- SiLi, Silicon Lithium, detectors were the predominant technology in Energy Dispersive Spectroscopy for decades.

X-ray Si(Li) Detector & FET



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A Brief History of the SDD

- SDD technology has been around for 20 + years
- Late1990's began more exploration as a viable alternative to SiLi detectors in research environments.
- Early 2000's saw the first commercial SDD's for SEM/EDS with convenience of no LN.
- 2004 the SDD capability was feasible for use, but performance suffered compared to SiLi
- 2008 Size grew, Resolution improved, but electronics lagged
- 2012 First "Plug & Play" with fastest electronics to date and performance enhancements become priority

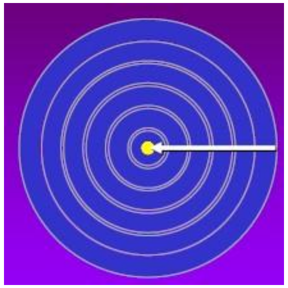
Detector Component Considerations

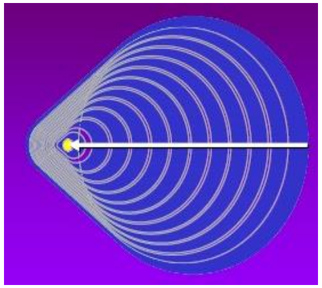
- The Silicon Drift Detector should be considered a system consisting of *traditionally* three main components:

- SDD Chip
- FET
- Electronics pulse processing

SDD Chip Types

- Various sizes, shapes and types available
- High purity silicon chip
- Voltage drift fields actively drive events to collecting anode
- Low capacitance



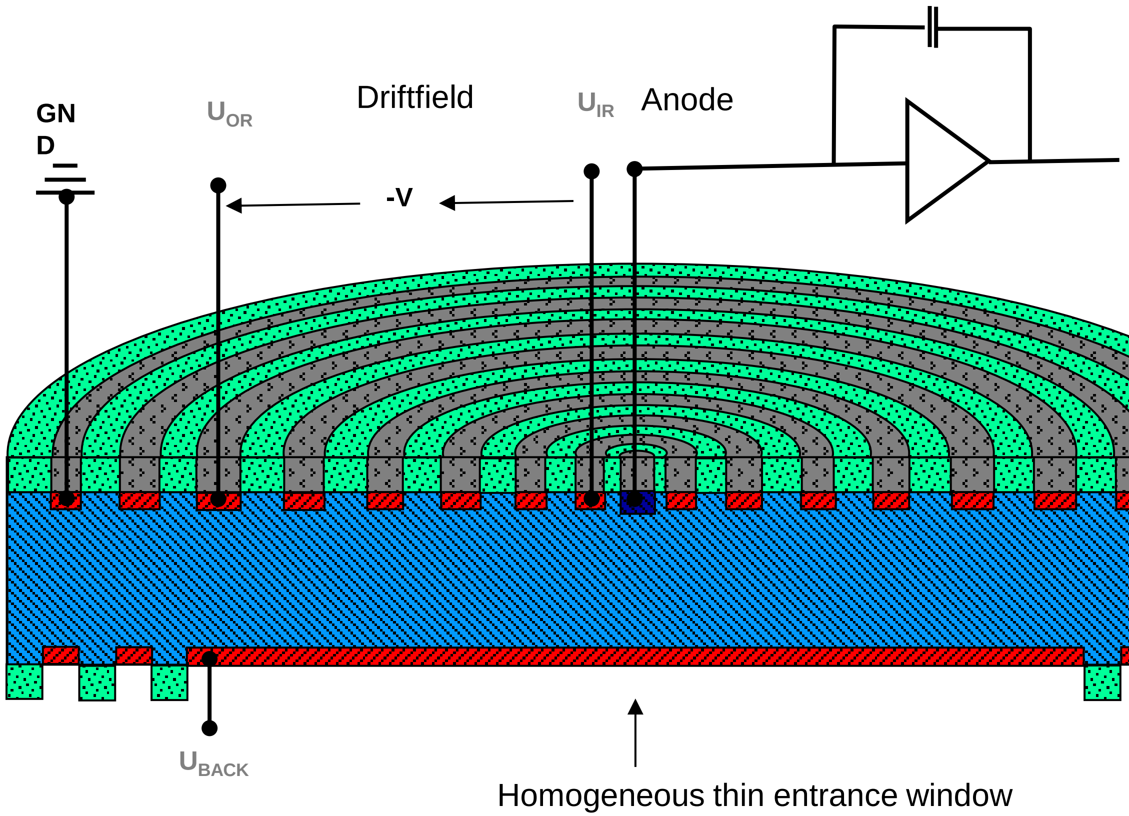


- 3 aspects together capture SDD premium performance:
  - Input (Solid angle, kV, beam current)
  - Output (process time, dead time)
  - Resolution (peak width, FWHM)

i.e. 127 eV at 100 k CPS and 30% DT or

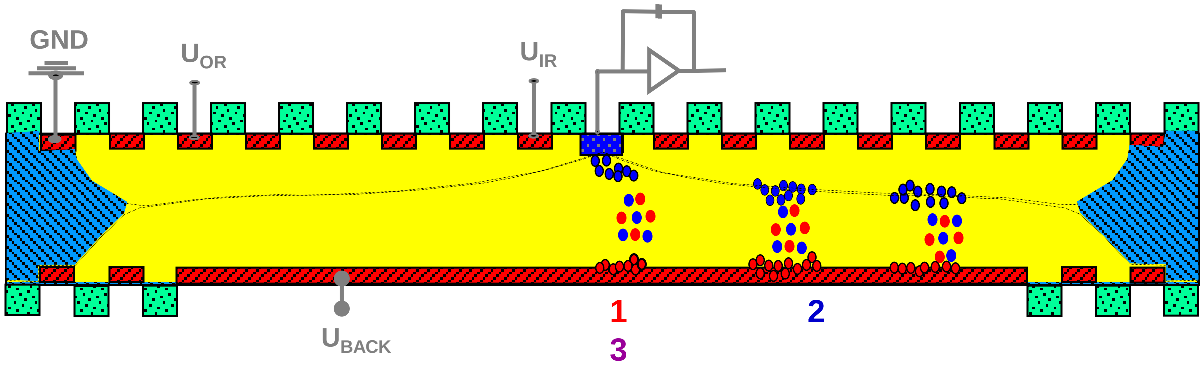
127 eV at 70 k CPS throughput

SDD Chip & FET

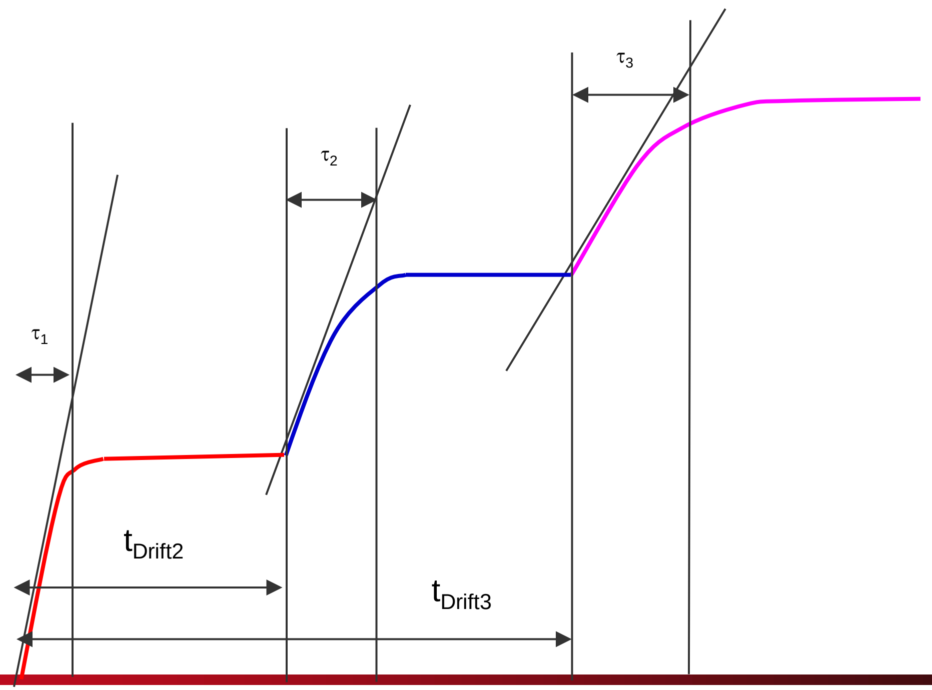


GN
D
U_OR
Driftfield
U_IR
Anode
-V
U_BACK
Homogeneous thin entrance window

SDDs vs SiLi – How the SDD works



Charge Collection:



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Electronics Processing – CUBE Technology

- CMOS charge preamplifier vs. JFET
- Allows superior noise performances at very short shaping times: "**the energy resolutions at short shaping time are, by far, better with CUBE than with any available state-of-the-art JFET connected to standard circular SDD**.*"
- Configured for compact SDD modules

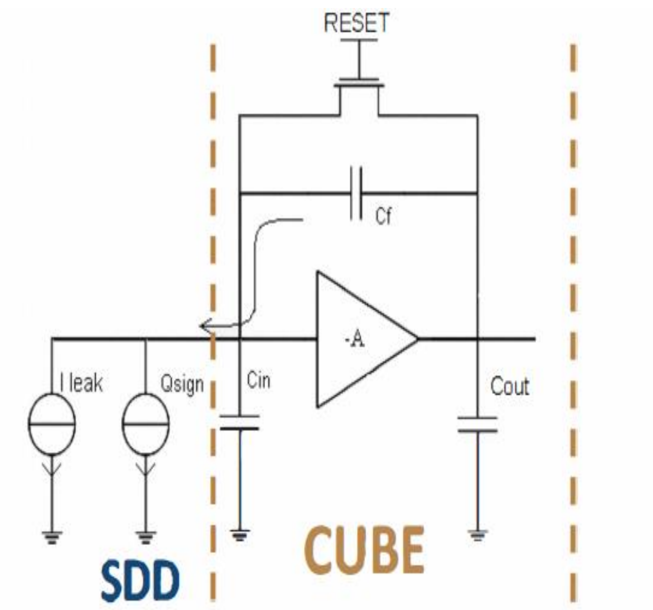


Fig.1. Simplified schematic of the CUBE preamplifier connected to a SDD detector.

* "CUBE", A Low-noise CMOS Preamplifier as Alternative to JFET Front-end for High-count Rate Spectroscopy. 2011 IEEE Nuclear Science Symposium Conference Record. Bombelli, L. et al.

Detector Component Considerations

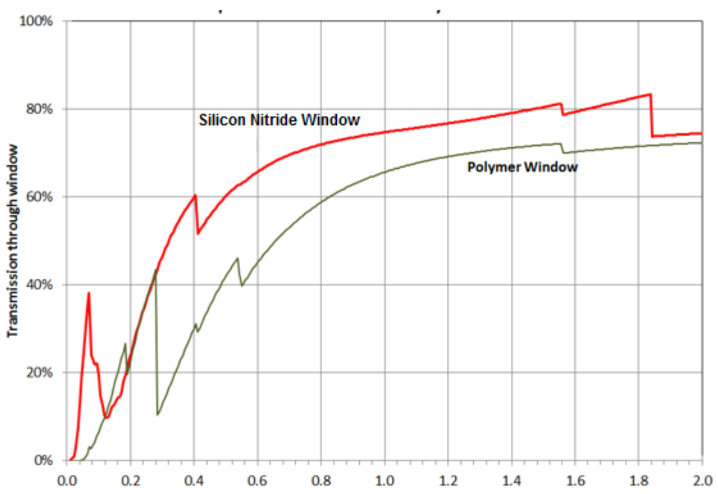
- The Silicon Drift Detector should be considered a system consisting of *traditionally* <u>three</u> main components:
  - SDD Chip
  - FET
  - Electronics pulse processing

Now <u>four:</u>

  - Window Type

Silicon Nitride Window

- Increased transmissivity
- Vacuum tight
  - Can achieve lower temperatures using less power
  - Compact size
  - Flexibility in environmental needs
- Can be plasma cleaned
  - Ideal for FIBs & low vac SEMs



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Silicon Nitride Window

- Si_3N_4 is known for
  - Thermal resistance
  - Corrosion & shock resistance
  - Chemically inert except to HF, H_2SO_4 and other strong acids in presence of humidity and high temps above 140°C
  - Use as a cutting tool due to fracture toughness, hardness and wear resistance (25 times stronger than WC, but not used due to cost)
  - Used as passivation barrier in microelectronics – chemical and diffusion barrier against water and Na ions.

Introducing EDAX Element Silicon Drift Detector (SDD)

First Commercially available major EDS detector with:

- CUBE technology
  - Fastest signal processing with highest quality resolution
- Silicon Nitride window
  - Increased transmission of x-rays for higher counts and low kV applications
- New applications
  - Low kV
  - Thin films, heavy metals
  - Semiconductor
  - Pharmaceutical

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Examples

- Spectrum matching
- Fast mapping
- Interconnect structure in semiconductor
- Low acceleration voltage measurements of acetaminophen
- Extreme low energy mapping

Spectrum Library Matching

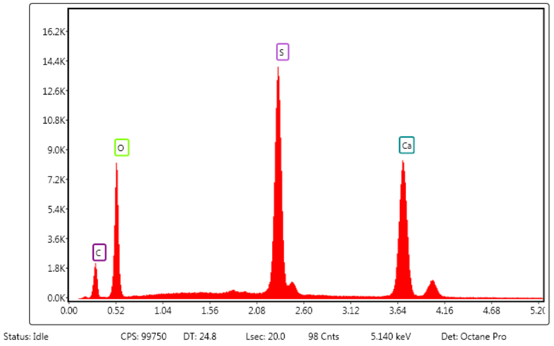
- A quick and convenient method for identifying compounds present in a material.
- The software matches an “unknown” spectrum to a library of reference spectra.
- An analyst can conclusively identify a material without relying on data interpretation.

What is it?

- Quantitative analysis reporting concentrations
- An experienced analyst can use At% to infer compound:

O:S:Ca ≈ 4:1:1

Element	Weight %	**Atomic %**
C K	0	**0**
O K	45.79	**65.64**
S K	23.29	**16.66**
Ca K	30.92	**17.69**

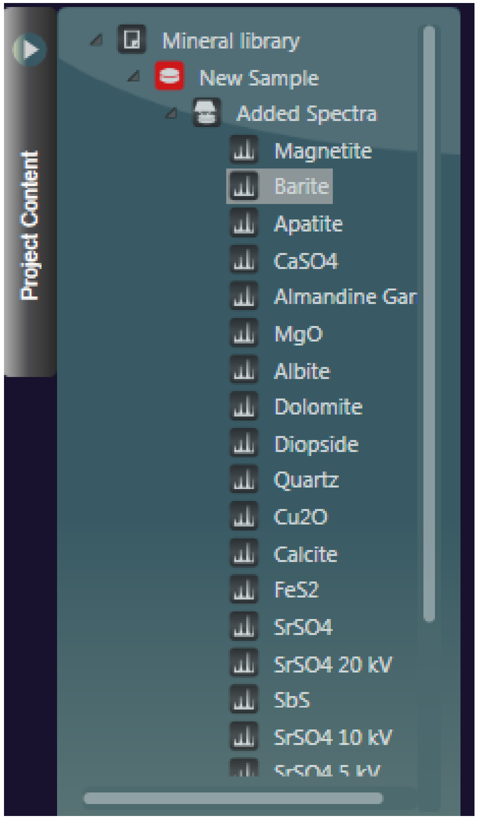


Note: Carbon coating correction used

It is $CaSO_4$
It is Calcium Sulfate

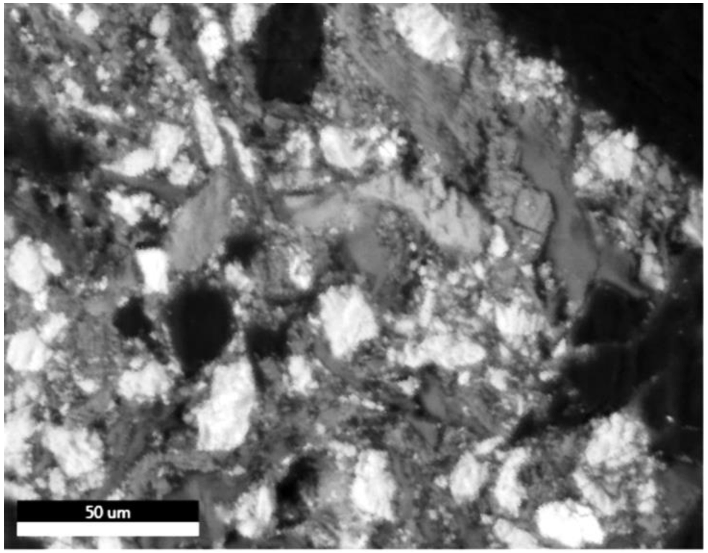
Building a Library – Example Mineral Library

- The SPI #2753, 53 mineral standard was used for the library generation.
- 15 kV
- 20 second acquisition time per spectra
- 123 eV resolution



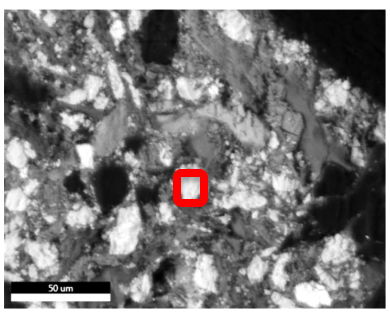
Spectrum Matching – Data Example

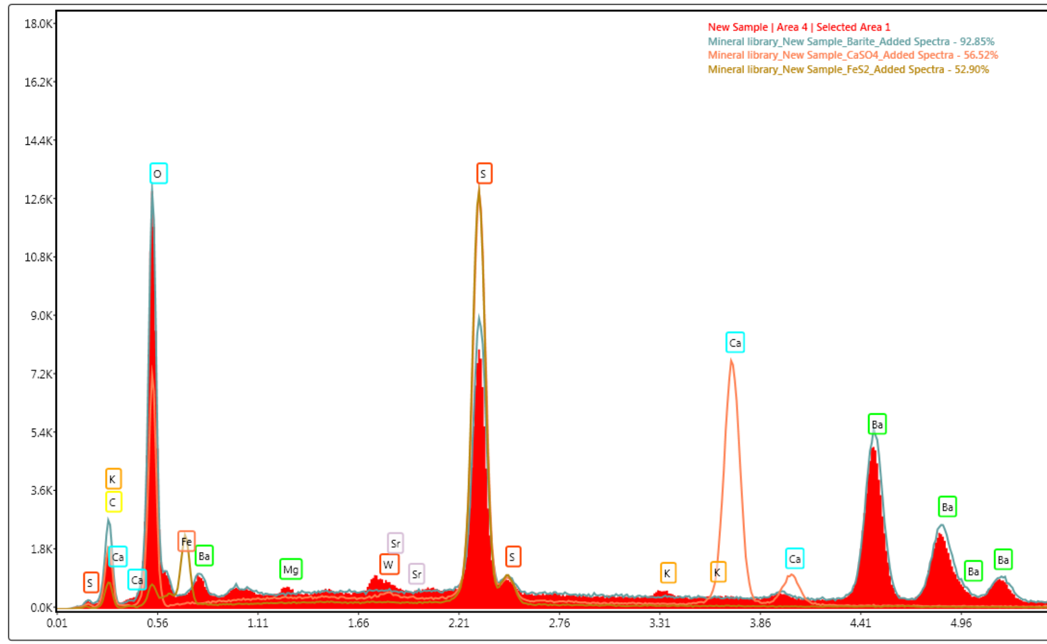
- Brake pad composite material at:
- 15 kV
- 700 x mag



Spectrum Matching – Data Example

- Multi area spectrum collection
- Three closest matches
- The bright features are barite, with a 92% fit match





Status: Idle CPS: 17047 DT: 8.7 Lsec: 20.0 233 Cnts 5.330 keV Det: Octane Pro

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Spectrum Matching – Data Example

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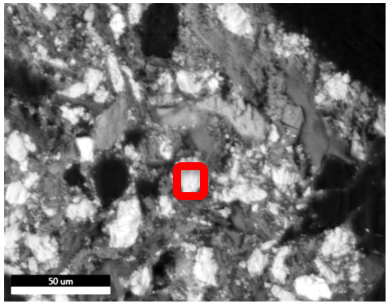

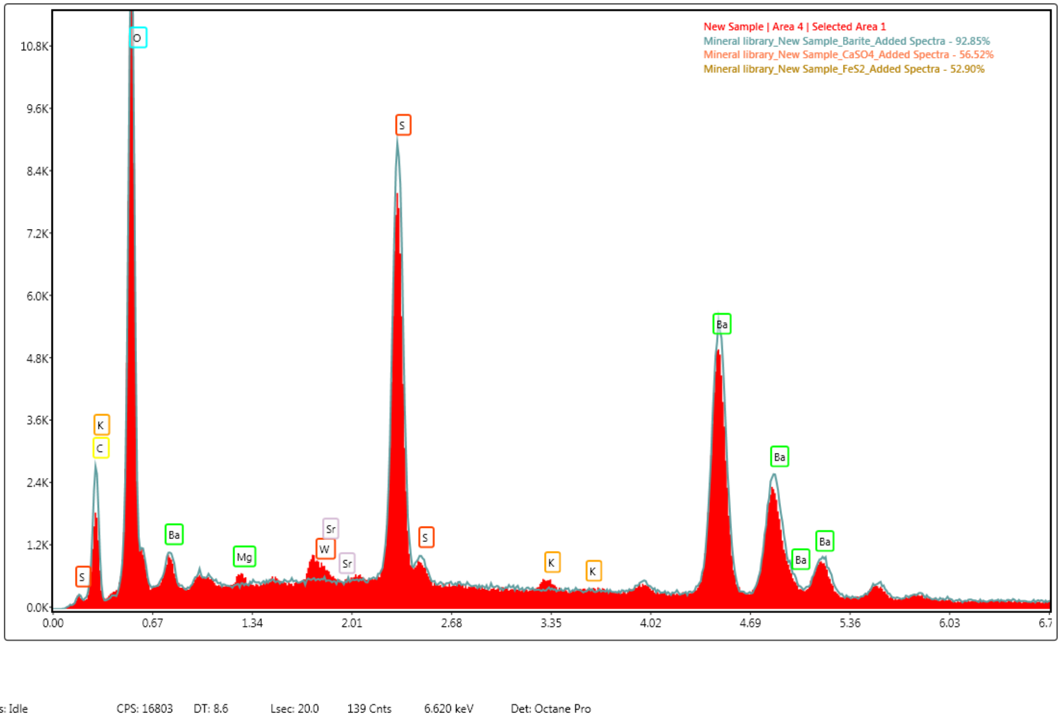

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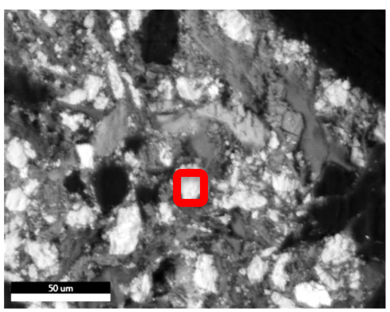

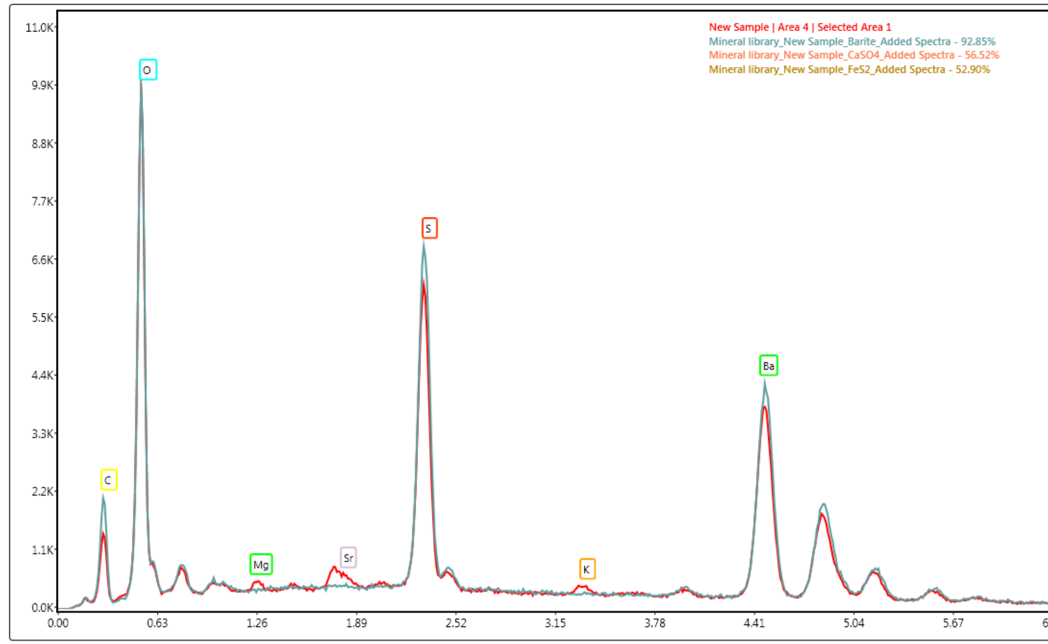

Status: Idle CPS: 16316 DT: 8.0 Lsec: 20.0 131 Cnts 6.620 keV Det: Octane Pro

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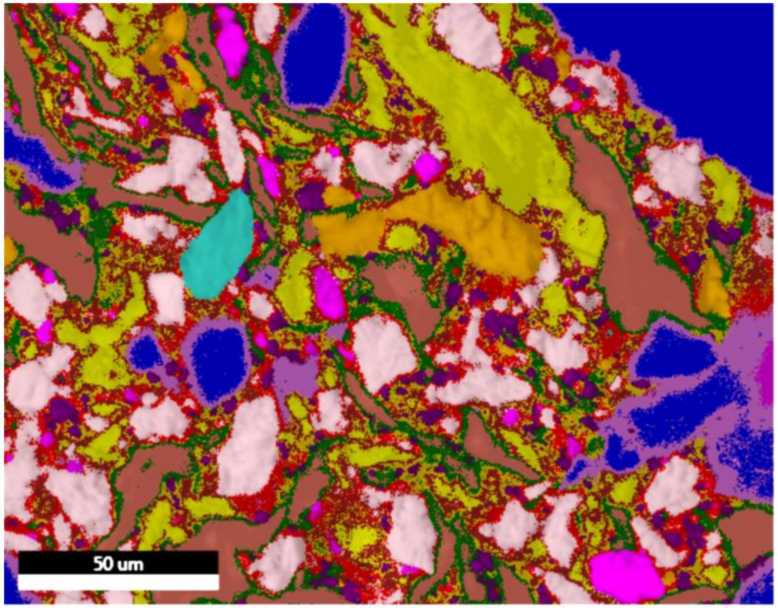
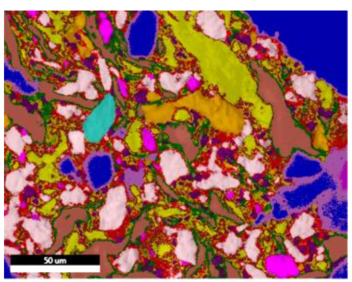
Spectrum Matching – Data Example

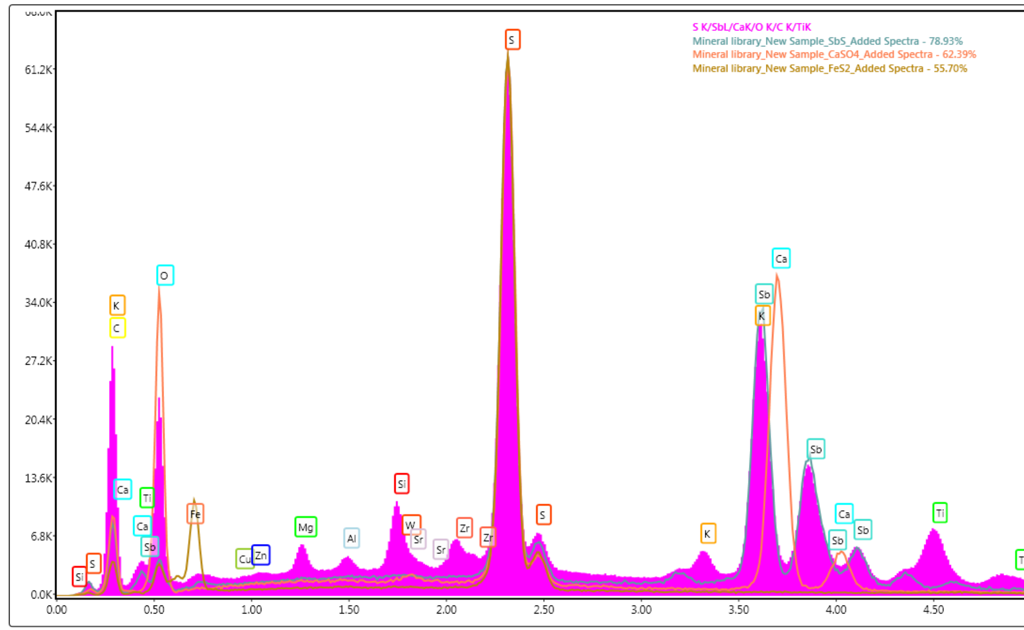
- Brake pad composite material at:
- 15 kV
- 700 x mag
- Auto phase mapping



Spectrum Matching – Data Example

- Phase spectra used for match
- The pink phase matches stibnite at 79%.





Status: Idle CPS: 2 DT: 0.0 Lsec: 76.7 3.299K Cnts 4.390 keV Det: Octane Pro

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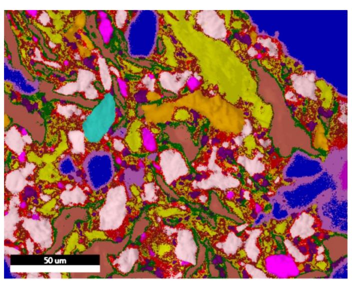
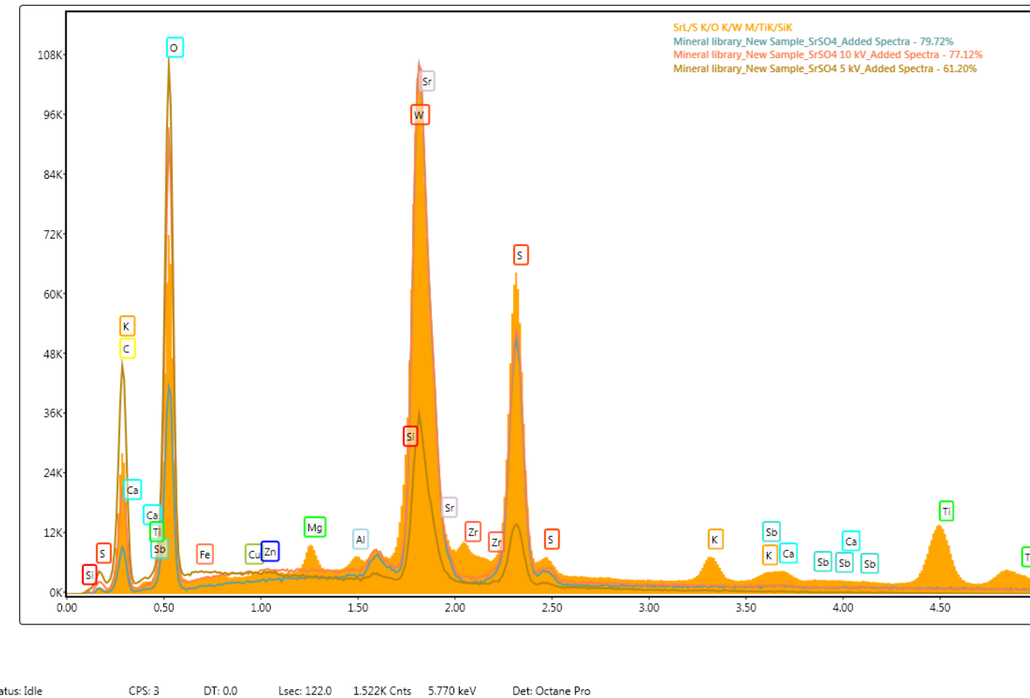
Spectrum Matching – Data Example

- Phase spectra used for match
- The orange phase matches celestite, $SrSO_4$ at 80%.





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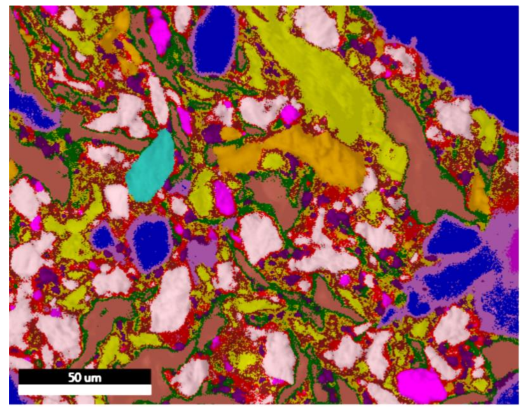
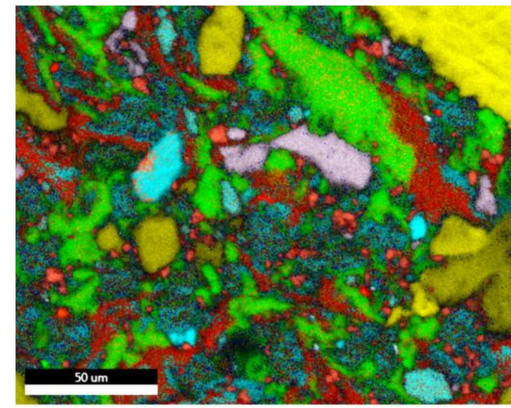
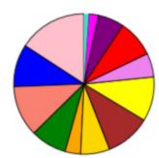
Spectrum Matching – The Conclusive Solution!

- Auto Phase mapping
- Complete compound matching

1% O K/FeK (2232 Pixels)
2% S K/SbL/CaK/O K/C K/TiK (4621 Pixels)
6% ZrL/SiK/O K/W M/TiK/C K/S K/SrL (12233 Pixels)
9% O K/S K/TiK/C K/ZrL/SiK (17575 Pixels)
5% C K/O K/S K/TiK/ZrL/SiK (11216 Pixels)
10% TiK/K K/O K/C K (20967 Pixels)
10% TiK/O K/K K/S K/C K/ZrL/SiK (21321 Pixels)
0% Unallocated (1 Pixels)
7% TiK/O K/C K/SiK/ZrL/K K/S K/W M (13785 Pixels)
4% SrL/S K/O K/W M/TiK/SiK (7351 Pixels)
8% O K/SiK/MgK/TiK/W M/K K/C K/S K/AlK/ZrL/SrL (16995 Pixe
12% SiK/O K/MgK/W M/AlK/K K/SrL (24042 Pixels)
10% C K/O K (20032 Pixels)







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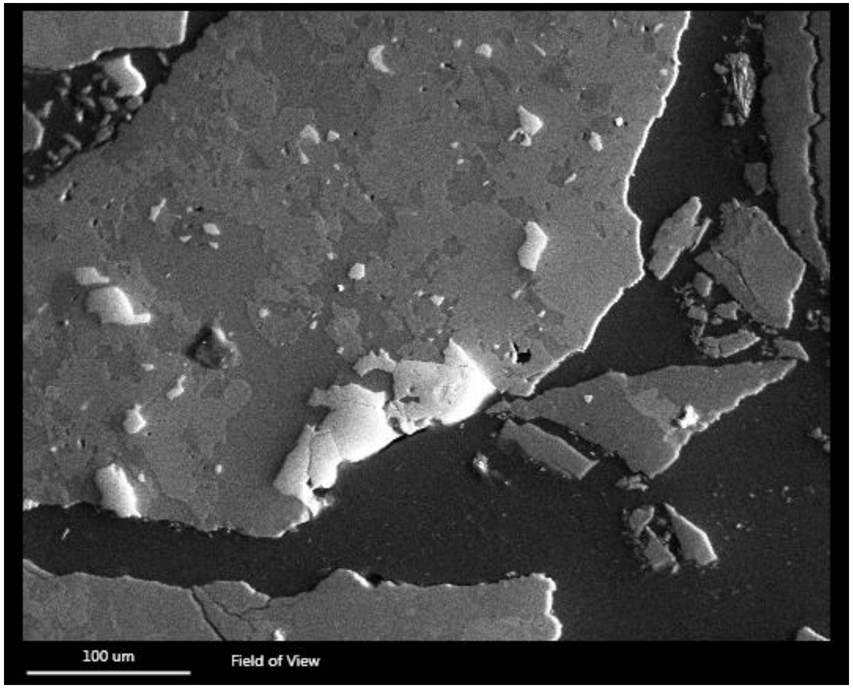
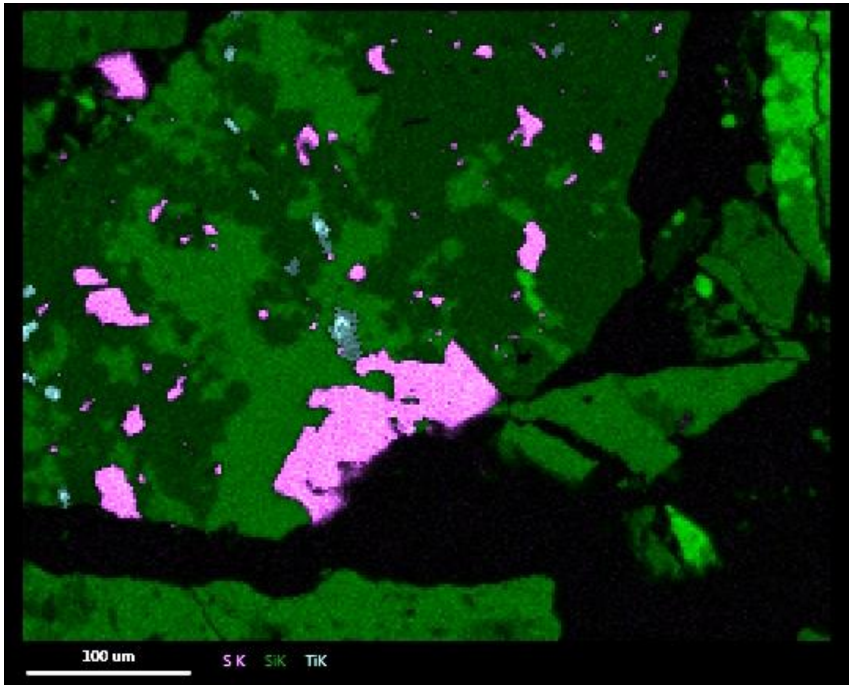
Fast mapping

Using SDDs we can now acquire maps in the time we previously would set aside to acquire spectra.





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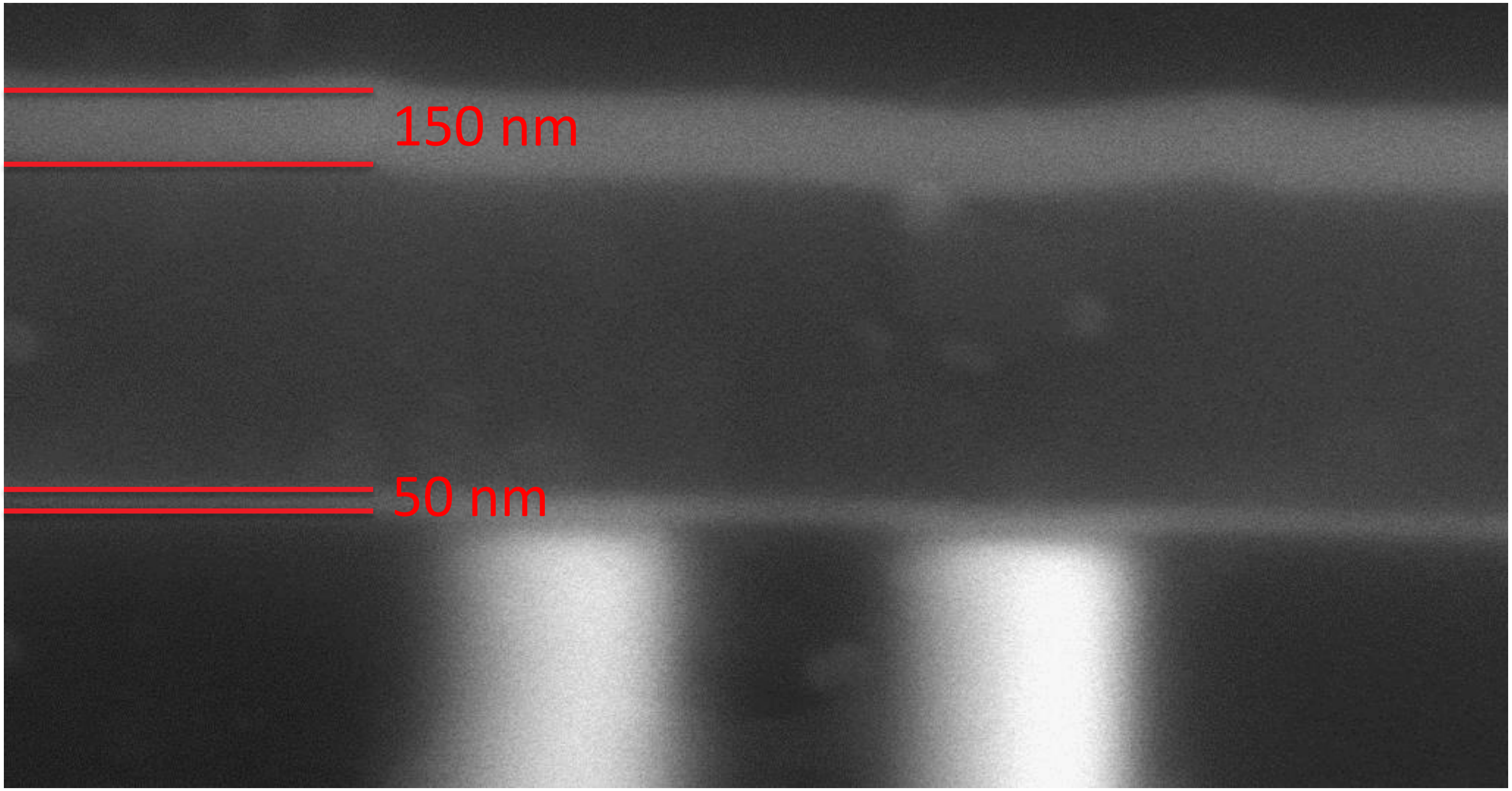
Interconnect structure in semiconductor



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Interconnect structure in semiconductor

C Kα = 0.277 keV

N Kα = 0.392 keV

O Kα = 0.523 keV

Al Kα = 1.486 keV

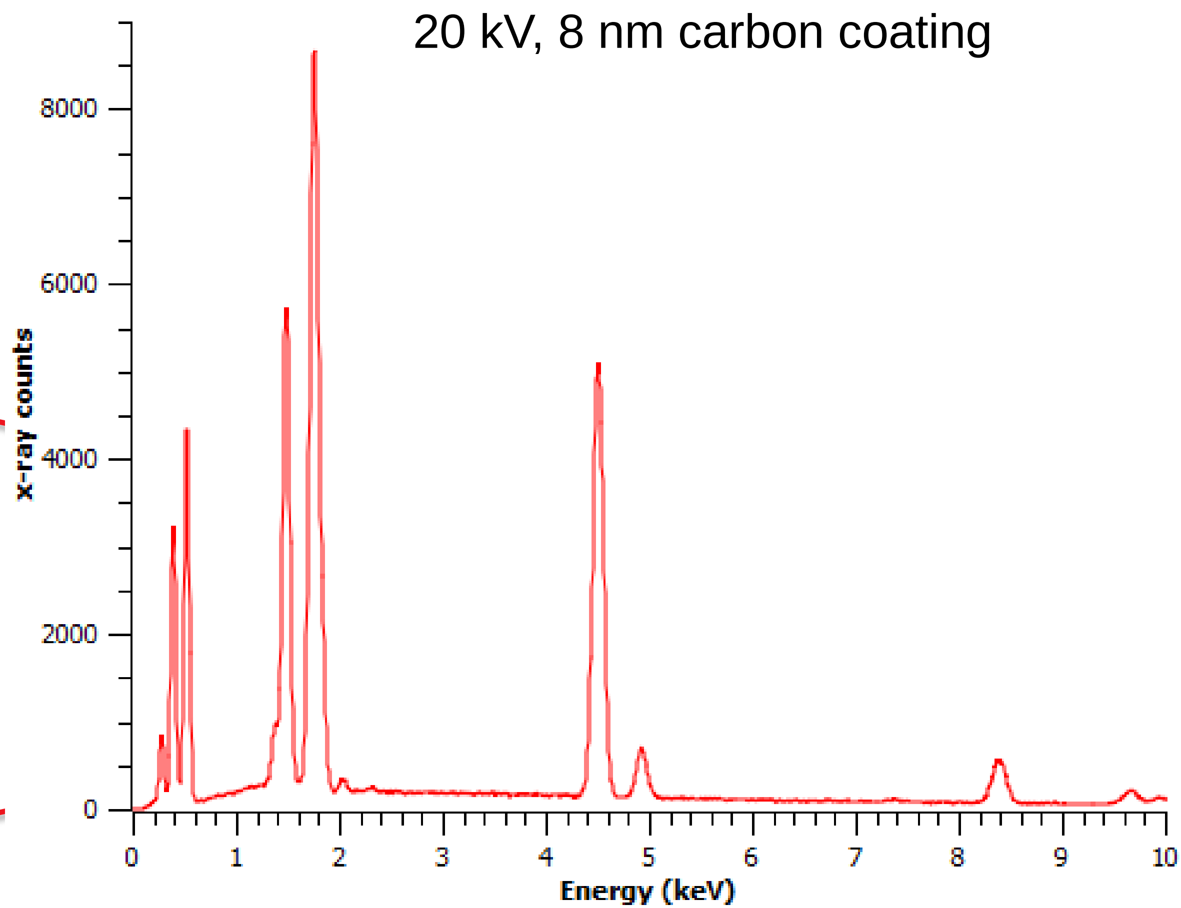
Si Kα = 1.740 keV

Ti Kα = 4.510 keV

W Kα = 59.305 keV

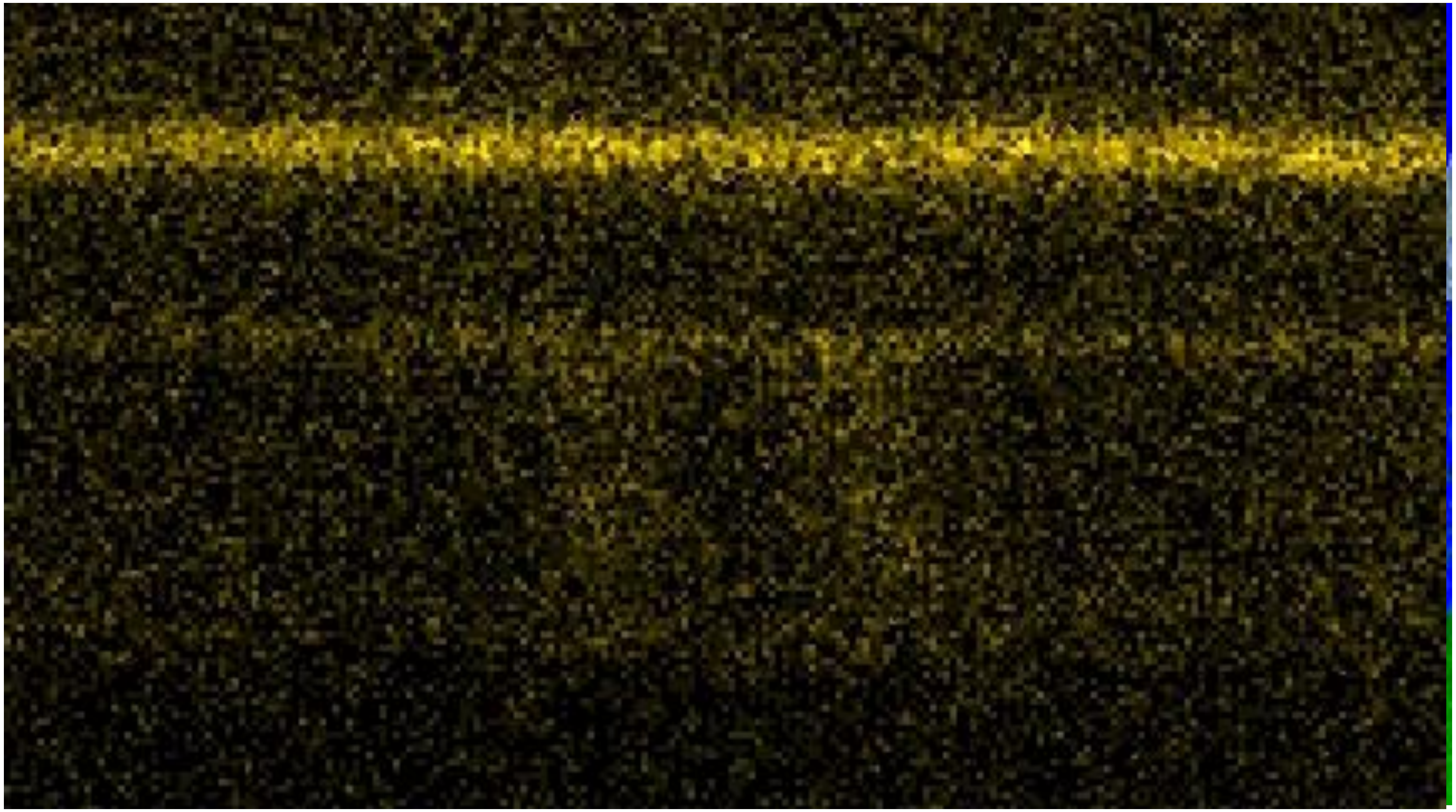
W Lα = 8.396 keV

W Mα = 1.774 keV



Interconnect structure in semiconductor

3 minute map at 20 keV



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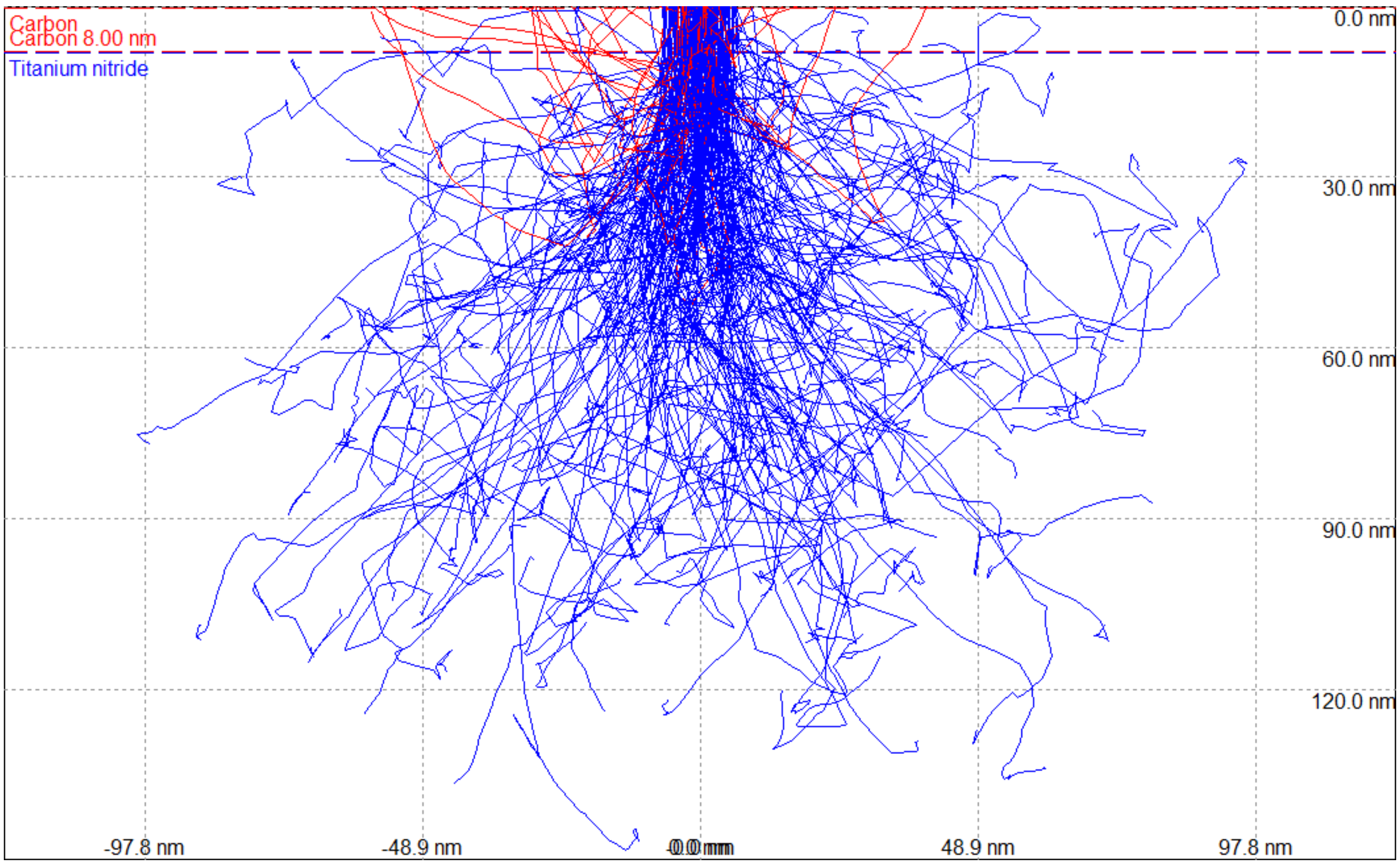
Interconnect structure in semiconductor

CASINO simulation, electron energy = 30 keV



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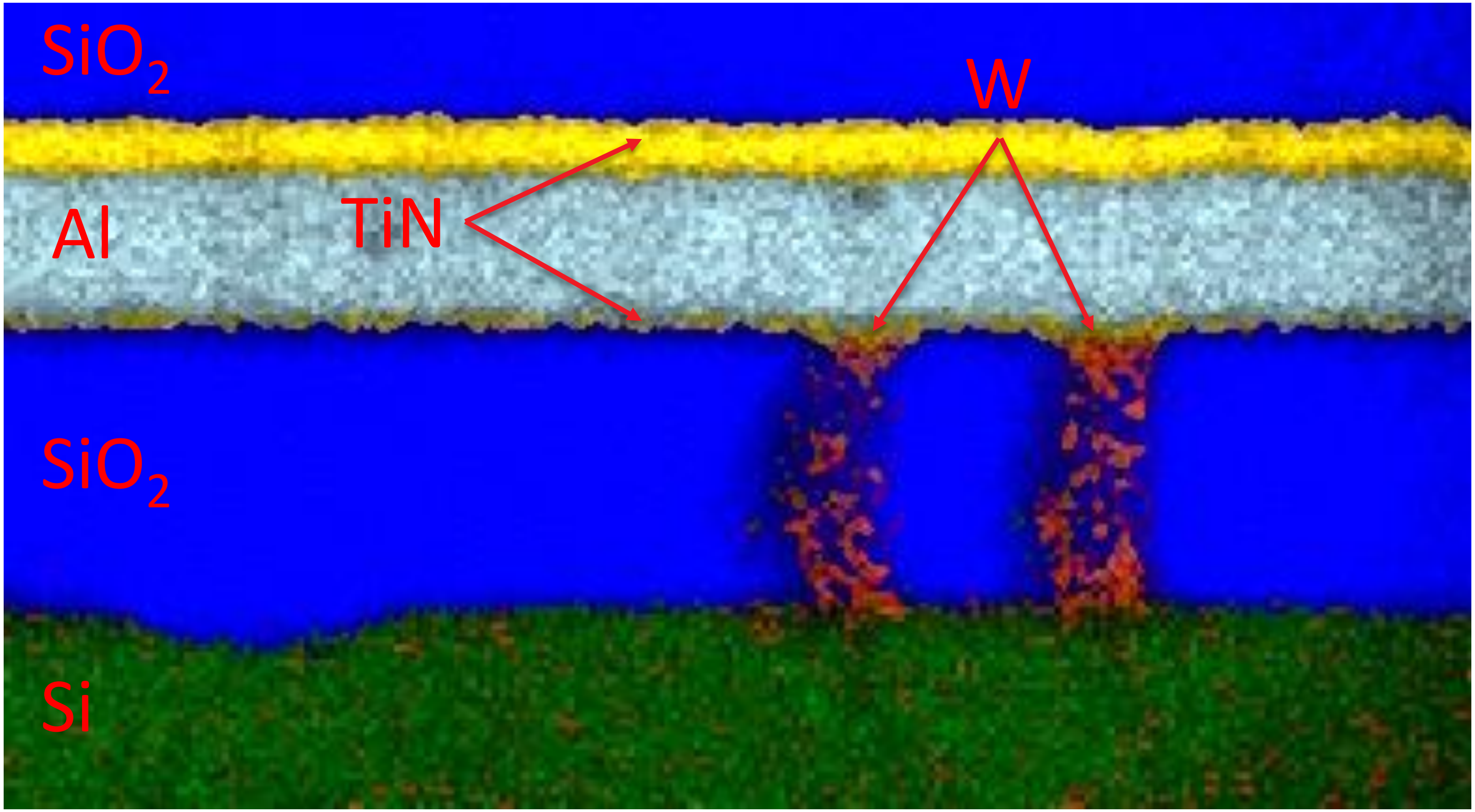
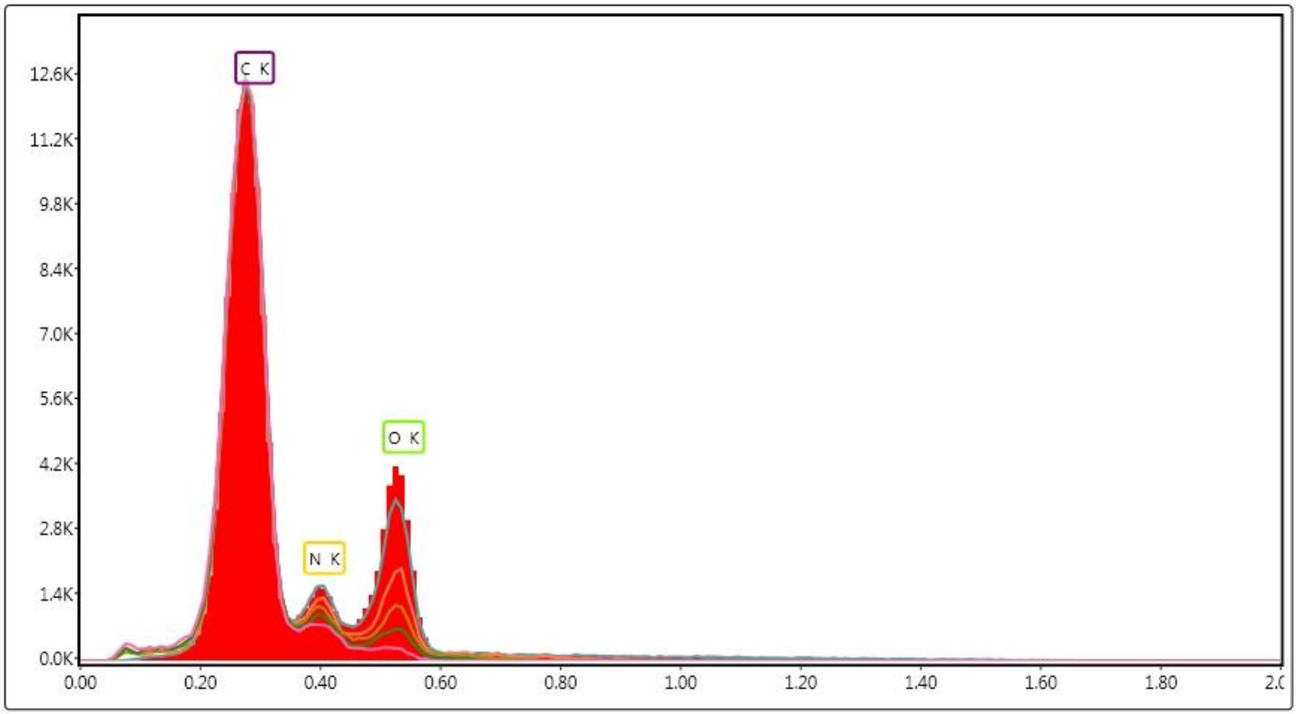
Interconnect structure in semiconductor



x-ray FWHM spatial resolution extracted from Al layer ≈ 70 nm

Low acceleration voltage measurements of acetaminophen

Acetaminophen = $C_8H_9NO_2$

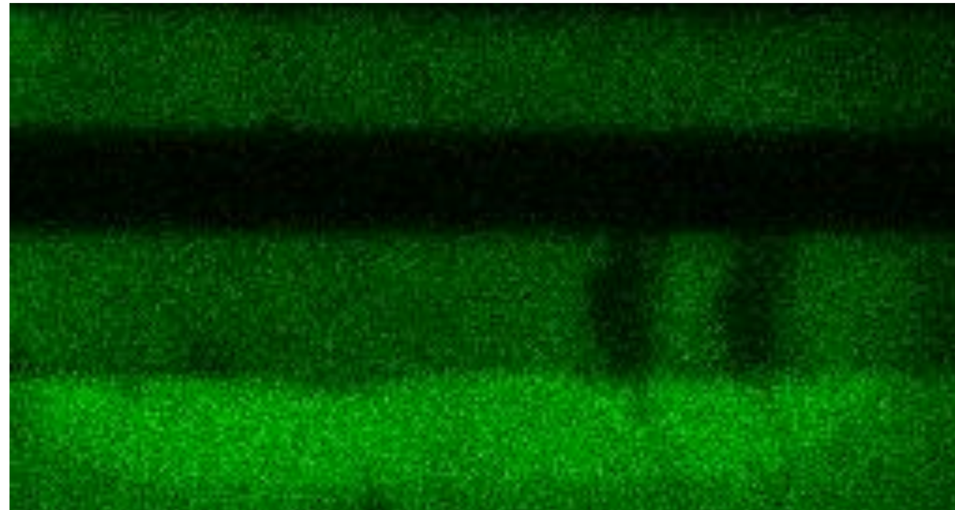


Status: Idle CPS: 99750 DT: 24.8 Lsec: 92.8 6 Cnts 1.990 keV Det: Element-C2

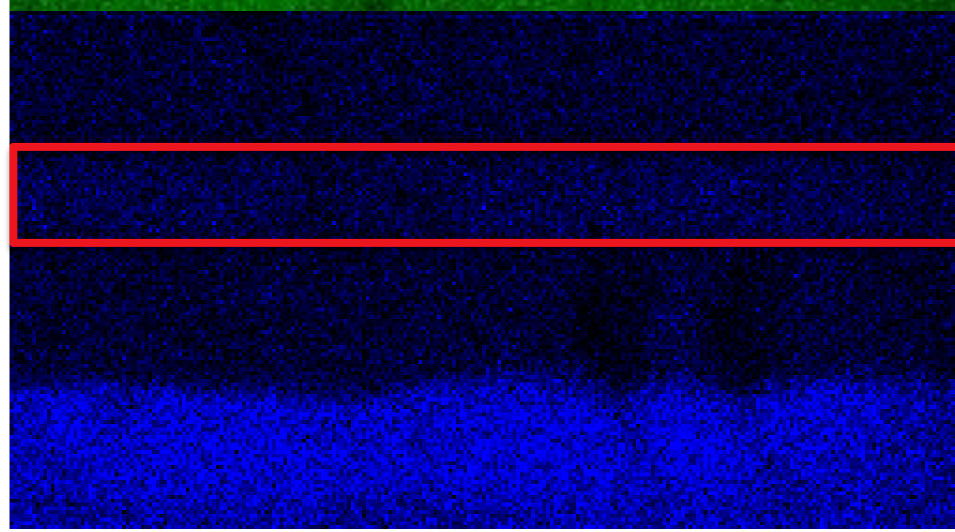
3 keV + 2 keV + 1 keV + 800 eV + 700 eV + 600 eV

Extreme low energy mapping

ROI map 1.680-1.790 keV
(Si K)



ROI map 70 eV-110 eV
(Si L)



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Thank you!

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