

Quantitative Electron Energy-Loss Spectroscopy

Lecture 3 : Machine Learning in STEM

GERD DUSCHER

GDUSCHER@UTK.EDU

Professor: Materials Science
Director: Microscopy Facility

Why Quantification

- ▶ Comparison with Theory
- ▶ Comparison of Different Methods
- ▶ Comparison of Different Materials
- ▶ Comparison of Different Instruments
- ▶ Comparison of Different Days
- ▶ Comparison of Different Parts of Datasets
- ▶ Assessment of Quality of Data

Additional Information

GOOD TRAINING DATASETS and WIDE APPLICABILITY

Choice of Parameters and Variable for

- **Policy:** what do we do depending on observation
- **Reward:** what do we hope to achieve
- **Value:** anticipated reward

Gleaned from Sergei's lecture 1

Quantification

$$I = N \sigma I_0$$

I: signal (edge,...) [pA*s, C/s, #e⁻, counts]

I_0 : intensity of incident beam [pA*s, C, #e⁻]
]

N: areal density [atoms/nm²]

σ : cross section [nm²]

$$1 \text{ barn} = 10^{-28} \text{ m}^2 = 10^{-10} \text{ nm}^2$$

Quantification

$$I = N \sigma I_0$$

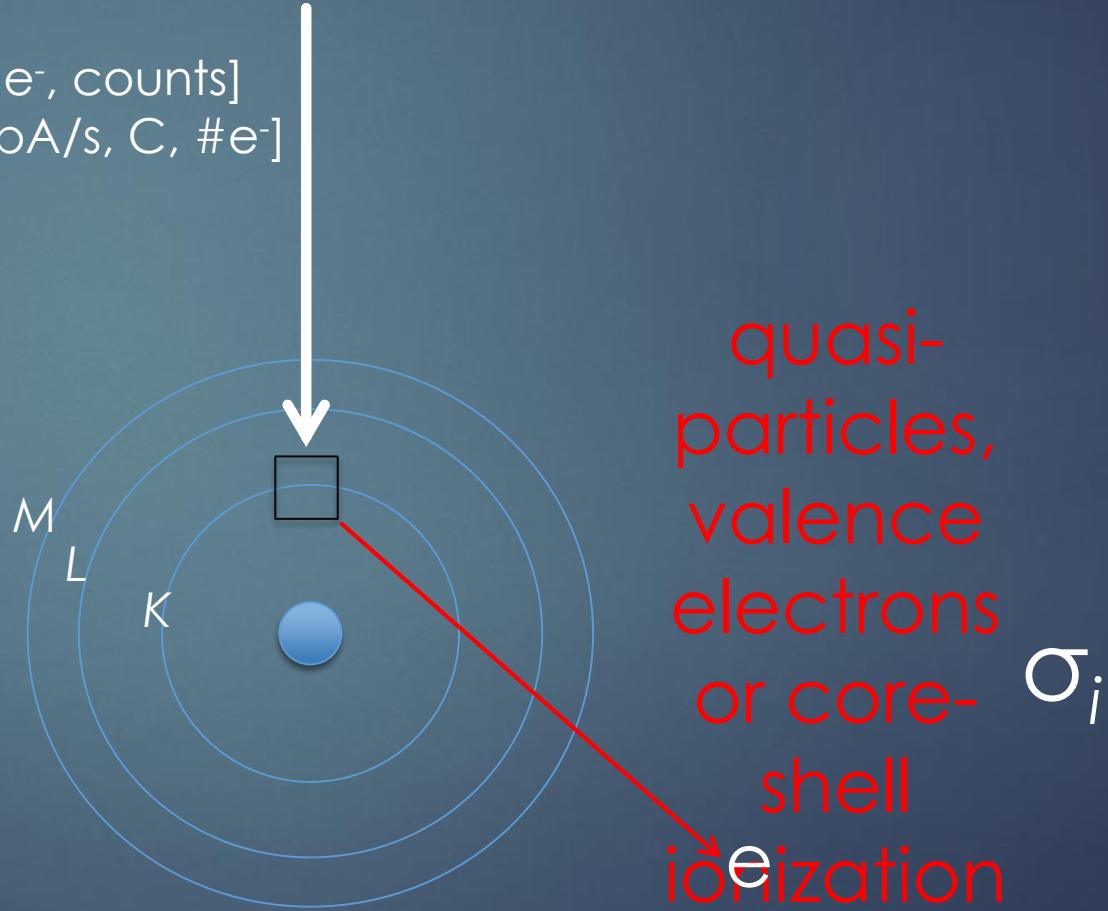
I : signal (edge,...) [pA/s, C, #e⁻, counts]

I_0 : intensity of incident beam [pA/s, C, #e⁻]

N : areal density [atoms/nm²]

σ : cross section [nm²]

atom
element
 Z



quasi-
particles,
valence
electrons
or core-
shell
ionization

σ_i

1 barn = 10^{-28} m² = 10^{-10} nm²

Electron Energy-Loss Spectroscopy in the Transmission Electron Microscope (EELS)

1.3.2

In Electron Energy-Loss Spectroscopy (EELS) a nearly monochromatic beam of electrons is directed through an ultrathin specimen, usually in a Transmission (TEM) or Scanning Transmission (STEM) Electron Microscope. As the electron beam propagates through the specimen, it experiences both elastic and inelastic scattering with the constituent atoms, which modifies its energy distribution. Each atomic species in the analyzed volume causes a characteristic change in the energy of the incident beam; the changes are analyzed by means of a electron spectrometer and counted by a suitable detector system. The intensity of the measured signal can be used to determine quantitatively the local specimen concentration, the electronic and chemical structure, and the nearest neighbor atomic spacings.

Range of elements	Lithium to uranium; hydrogen and helium are sometimes possible
Destructive	No
Chemical bonding information	Yes, in the near-edge structure of edge profiles
Depth profiling	None, the specimen is already thin
Quantification	Without standards $\pm 10\text{--}20\%$ at.; with standards $\pm 1\text{--}2\%$ at.
Detection limits	$\sim 10^{-21}$ g
Depth probed	Thickness of specimen (≤ 2000 Å)
Lateral resolution	1 nm–10 µm, depending on the diameter of the incident electron probe and the thickness of the specimen
Imaging capabilities	Yes
Sample requirements	Solids; specimens must be transparent to electrons and $\sim 100\text{--}2000$ Å thick
Main use	Light element spectroscopy for concentration, electronic, and chemical structure analysis at ultra-high lateral resolution in a TEM or STEM
Cost	As an accessory to a TEM or STEM: \$50,000–\$150,000 (does not include electron microscope cost)

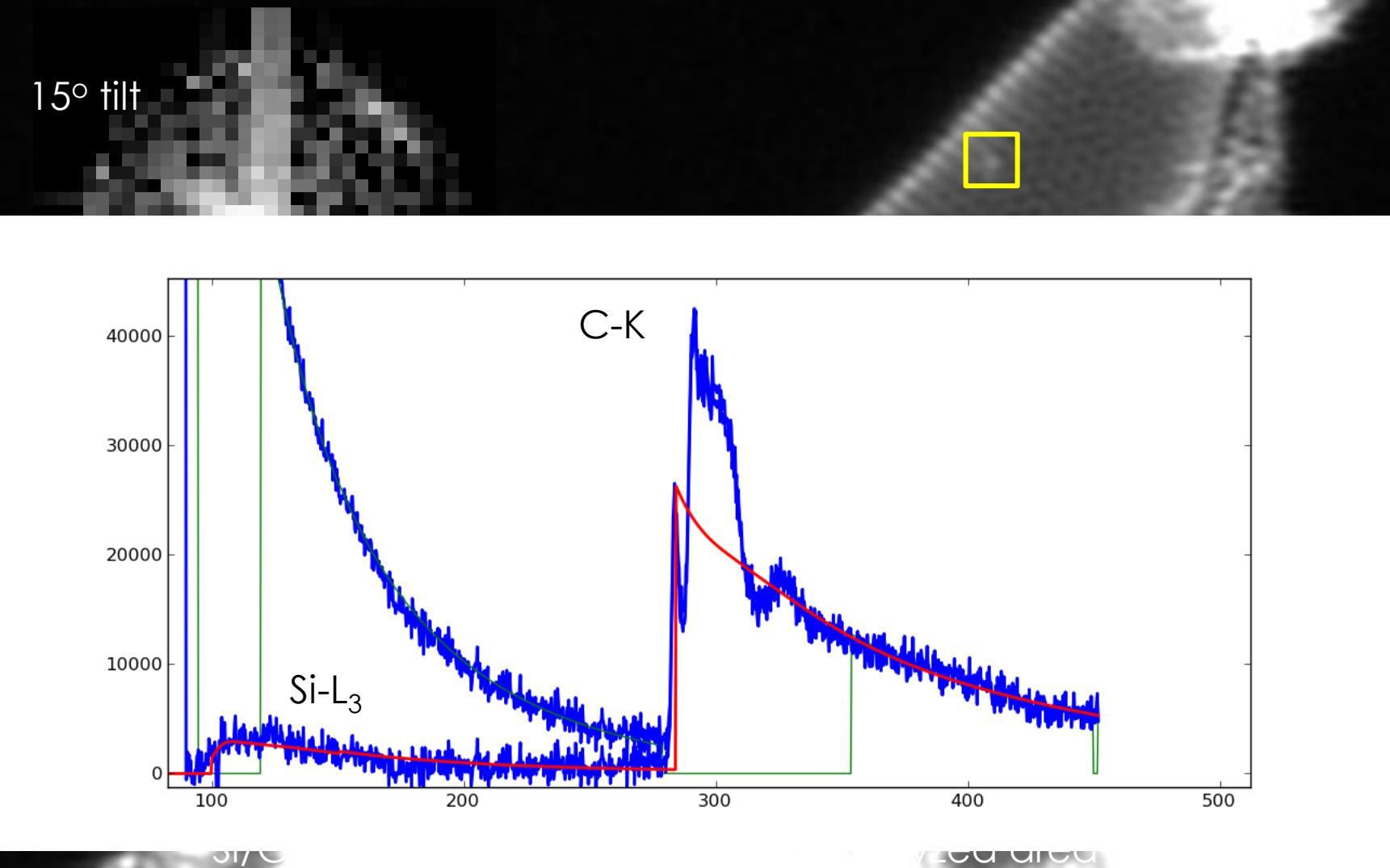
Energy-Dispersive X-Ray Spectroscopy (EDS)

1.3.1

When the atoms in a material are ionized by a high-energy radiation they emit characteristic X rays. EDS is an acronym describing a technique of X-ray spectroscopy that is based on the collection and energy dispersion of characteristic X rays. An EDS system consists of a source of high-energy radiation, usually electrons; a sample; a solid state detector, usually made from lithium-drifted silicon, Si (Li); and signal processing electronics. EDS spectrometers are most frequently attached to electron column instruments. X rays that enter the Si (Li) detector are converted into signals which can be processed by the electronics into an X-ray energy histogram. This X-ray spectrum consists of a series of peaks representative of the type and relative amount of each element in the sample. The number of counts in each peak may be further converted into elemental weight concentration either by comparison with standards or by standardless calculations.

Range of elements	Boron to uranium
Destructive	No
Chemical bonding information	Not readily available
Quantification	Best with standards, although standardless methods are widely used
Accuracy	Nominally 4–5%, relative, for concentrations $> 5\%$ wt.
Detection limits	100–200 ppm for isolated peaks in elements with $Z > 11$, 1–2% wt. for low-Z and overlapped peaks
Lateral resolution	.5–1 µm for bulk samples; as small as 1 nm for thin samples in STEM
Depth sampled	0.02 to µm, depending on Z and keV
Imaging/mapping	In SEM, EPMA, and STEM
Sample requirements	Solids, powders, and composites; size limited only by the stage in SEM, EPMA and XRF; liquids in XRF; 3 mm diameter thin foils in TEM
Main use	To add analytical capability to SEM, EPMA and TEM
Cost	\$25,000–\$100,000, depending on accessories (not including the electron microscope)

What is that bright atom in the carbon nanohorn?



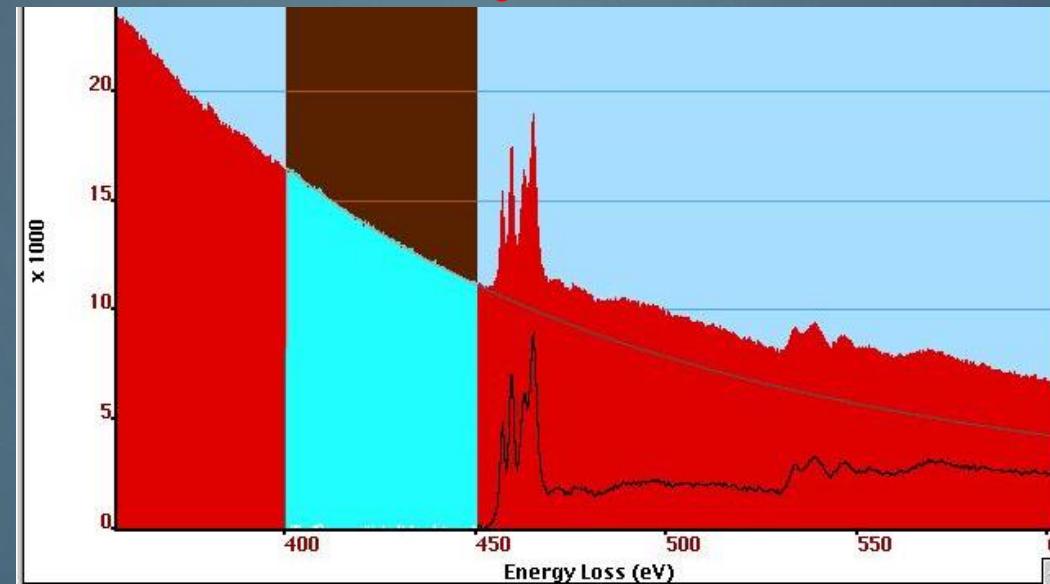
Detection Limit in EELS

- ▶ $M_u = 1 \text{ g/mol}$
- ▶ $M_u/N_A = 1.992\ 646\ 54(10) \times 10^{-23} \text{ g}$
- ▶ Si: $Z = 14$; $M_A = 28$
- ▶ Weight of one silicon atom:
 $28 * M_u/N_A = 5.6 * 10^{-22} \text{ g}$
- ▶ B: $Z = 5$; $M_A = 10$
- ▶ Weight of one boron atom: $2.0 * 10^{-22} \text{ g}$

Edge Intensity: Conventional Analysis

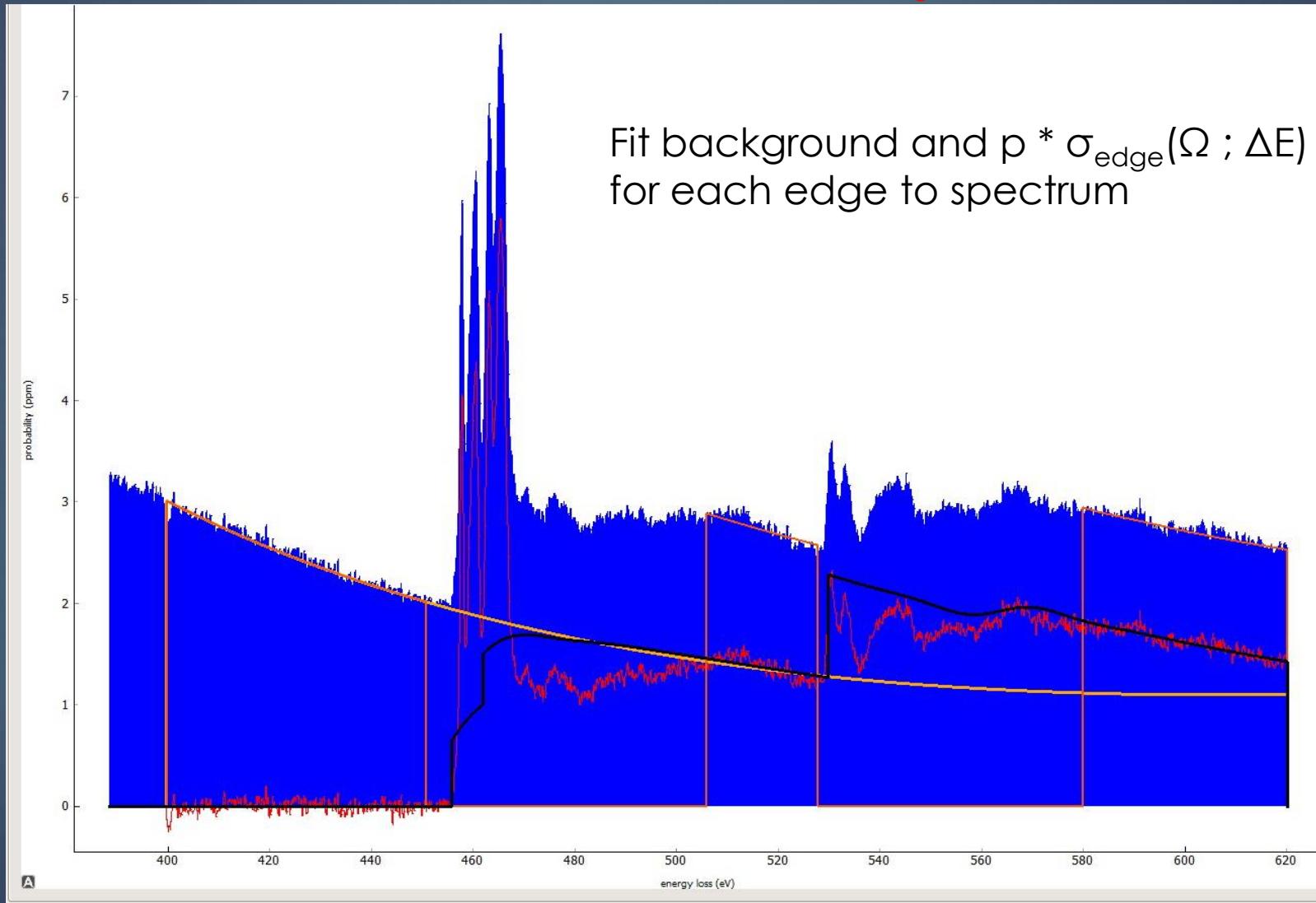
- Remove background

$I_{\text{edge}}, I_0, \text{X-section}$



Edge Intensity: Model Based Analysis

I_{edge} , I_0 , X-section



Fitting a spectrum

Exclude spectrum regions you don't know exactly:

- ▶ exclude edge onset
- ▶ exclude ELNES

Fit what you know:

- ▶ background before all edges
- ▶ high energy part of edges, which behaves like free electron gas - continuum

Edge Intensity: Model Based Analysis

$$I_{\text{edge}}(\Omega; \Delta E) = N I_0(\Omega) \sigma_{\text{edge}}(\Omega ; \Delta E)$$

- ▶ Now we express I_{edge} with our fit:

$$I_{\text{edge}}(\Omega; \Delta E) = p_{\text{edge}} * \sigma_{\text{edge}}(\Omega ; \Delta E)$$

- ▶ and get: $p_{\text{edge}} = N I_0(\Omega)$ and:

- ▶ $N = p_{\text{edge}} / I_0(\Omega)$ = number of atoms per nm²
-

$$\frac{N_A}{N_B} = \frac{I_0(\Omega)}{I_0(\Omega)} \frac{I_{\text{edgeA}}(\Omega; \Delta E)}{\sigma_{\text{edgeA}}(\Omega ; \Delta E)} \frac{\sigma_{\text{edgeB}}(\Omega ; \Delta E)}{I_{\text{edgeB}}(\Omega; \Delta E)} = \frac{p_{\text{edgeA}}}{p_{\text{edgeB}}}$$

Background

Always inspect background for non-negative values
– not easy in EELSmodel program

- ▶ Power Law: $A \cdot E^{-r}$
 - ▶ We know that r is not constant over even moderate energy ranges
- ▶ Polynomial $A + E + E^2 + E^3$
 - ▶ May give unphysical result, beyond fitting region
- ▶ Mixture (linear combination) of above
 - ▶ Mathematically more stable, less flexible

X-sections

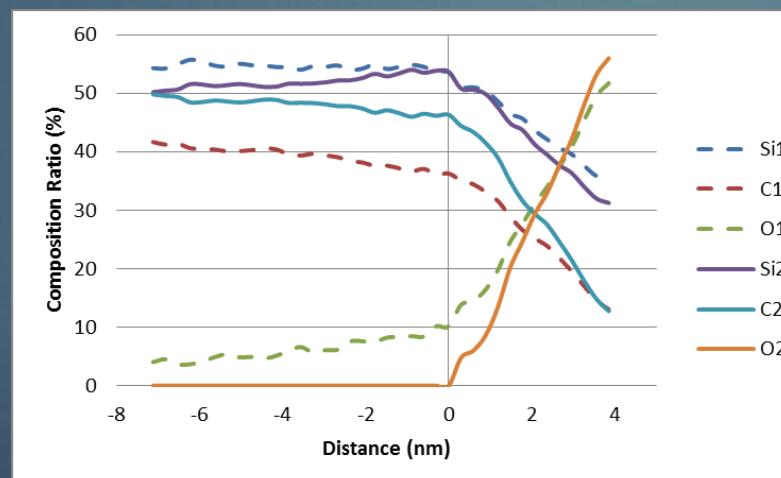
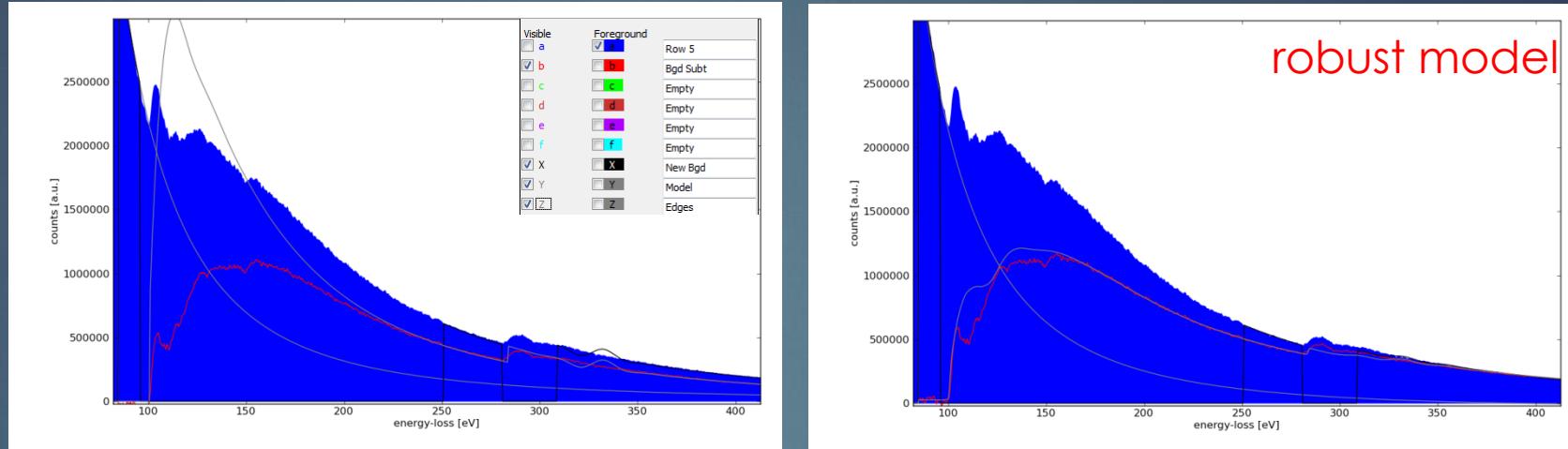
- ▶ Hydrogenic
 - ▶ Not bad at all
 - ▶ Only K and L edges
- ▶ Hatree-Slater (HS)
 - ▶ Tabulated GOS by Gatan for limited energy range
 - ▶ Do not use higher than L edges
- ▶ X-ray photoabsorption (XRPA)
 - ▶ X-section: NIST:
<http://physics.nist.gov/PhysRefData/FFast/html/form.html>
 - ▶ Dispersion: Egerton, Ultramicroscopy 50 (1993) 13-28 equation (4)
 - ▶ Low energies have some uncertainty
(high energy: M and N edges ok)

X-sections

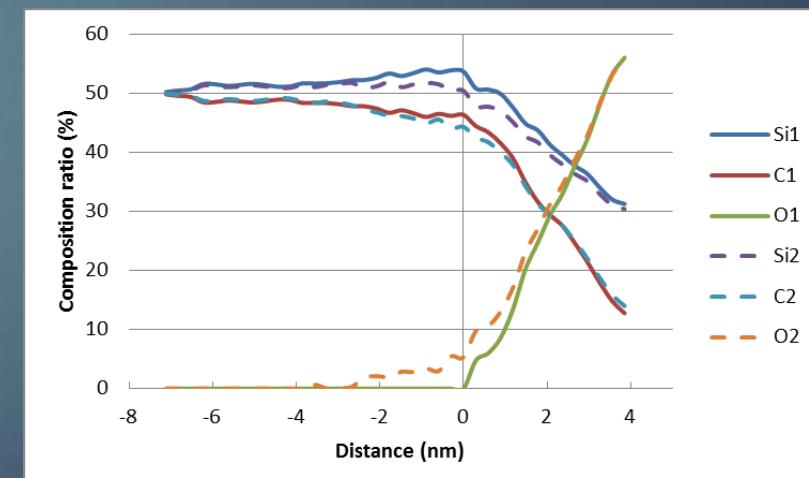
Comparison of Different Sources

- ▶ K edges are all the same
- ▶ L edges are generally worse than K edges but still give good results (+- 3 atom % absolute).
- ▶ M edges are about 100% to 200% off except for XRPA
- ▶ All but Hatree-Slater have sufficient high energy range for multiple elements

Thickness Correction – Why?

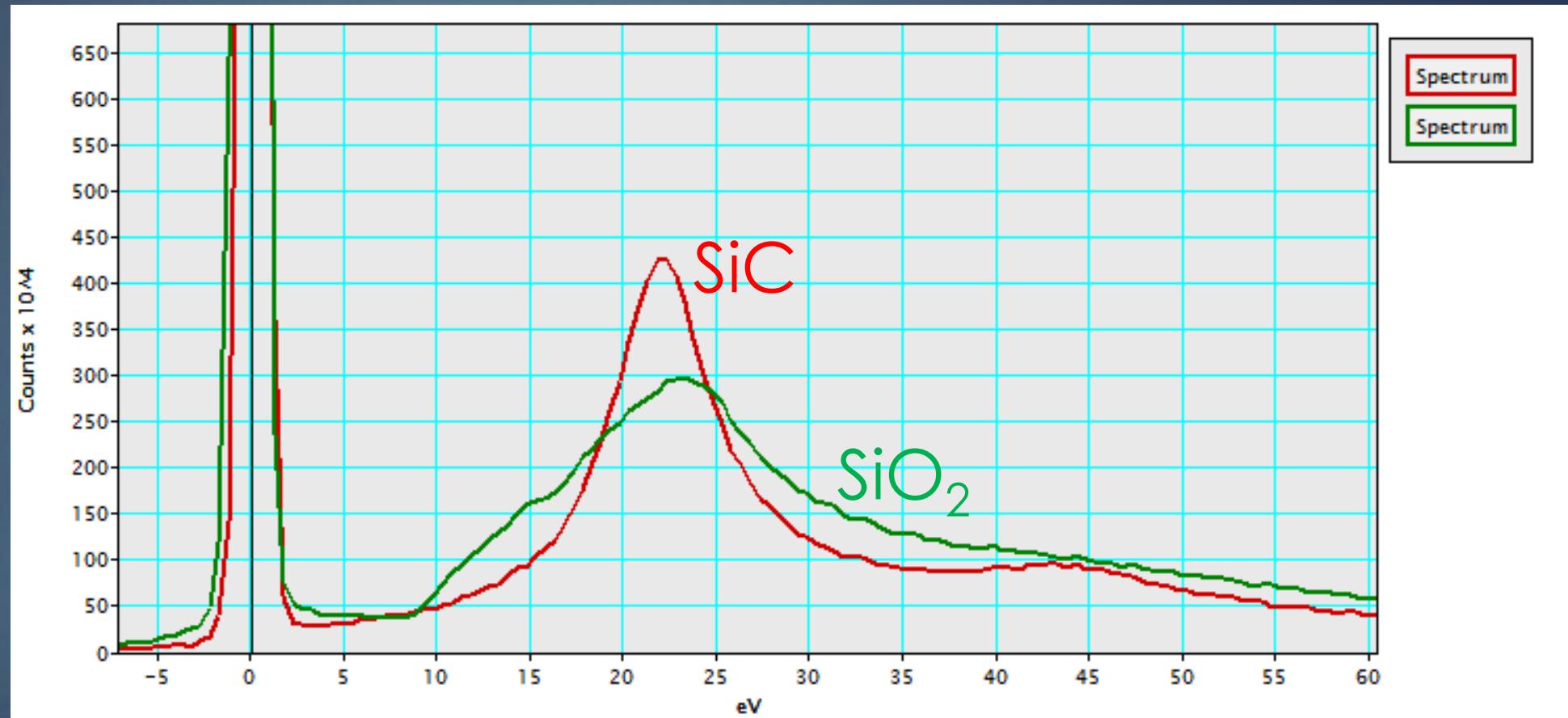


Composition ratio across interface without LL correction (1) and with LL correction (2)



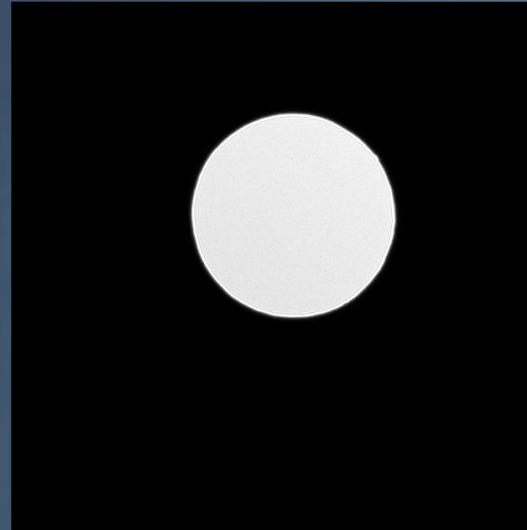
Corrected with different LL spectrum: (1) thickness = 0.5509 IMFP, (2) thickness = 1.001 IMFP

Two very different plasmons



Incident Beam Intensity

- Here “ronchigram” on same camera as EELS



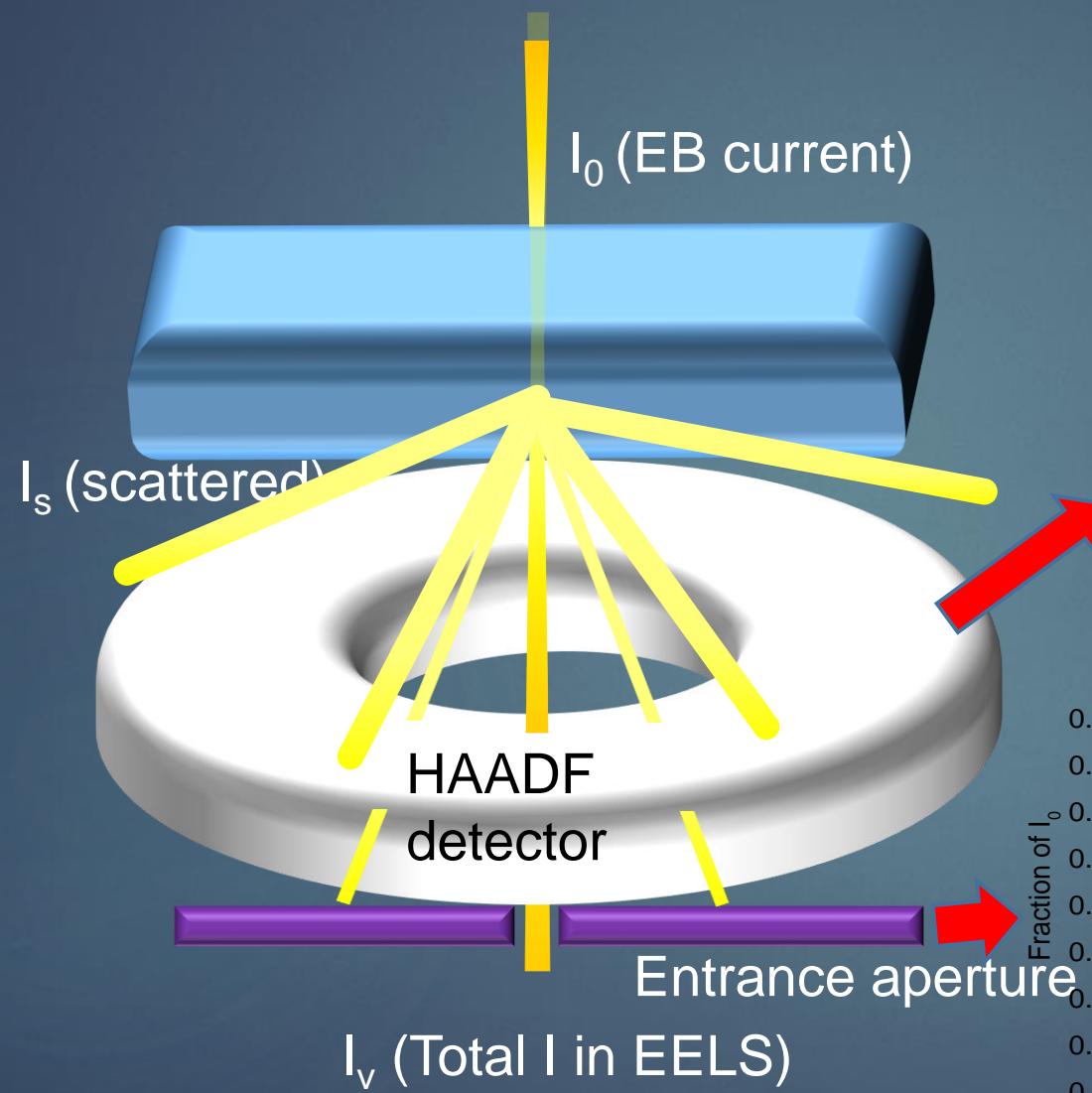
Sum=8.79327e+009 counts

- Can be low-loss spectrum (time constant?)
- Or defocused zero-loss peak

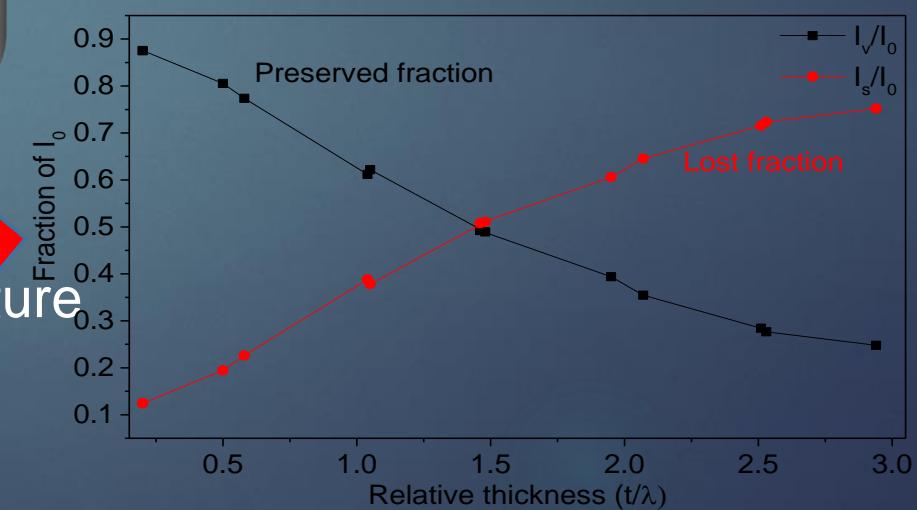
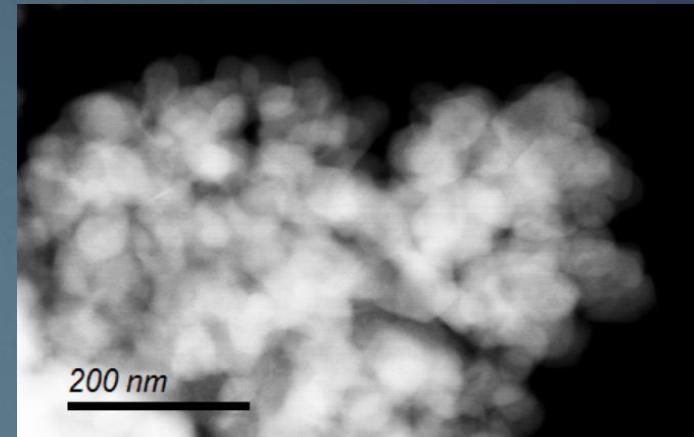
Detector

- ▶ Conversion rate (counts / # electrons)
- ▶ Efficiency (dynamic range)
- ▶ Detectum Quantum Efficiency (DQE)
 - ▶ noise in / noise out
 - ▶ dependent on dose
- ▶ Point Spread Function

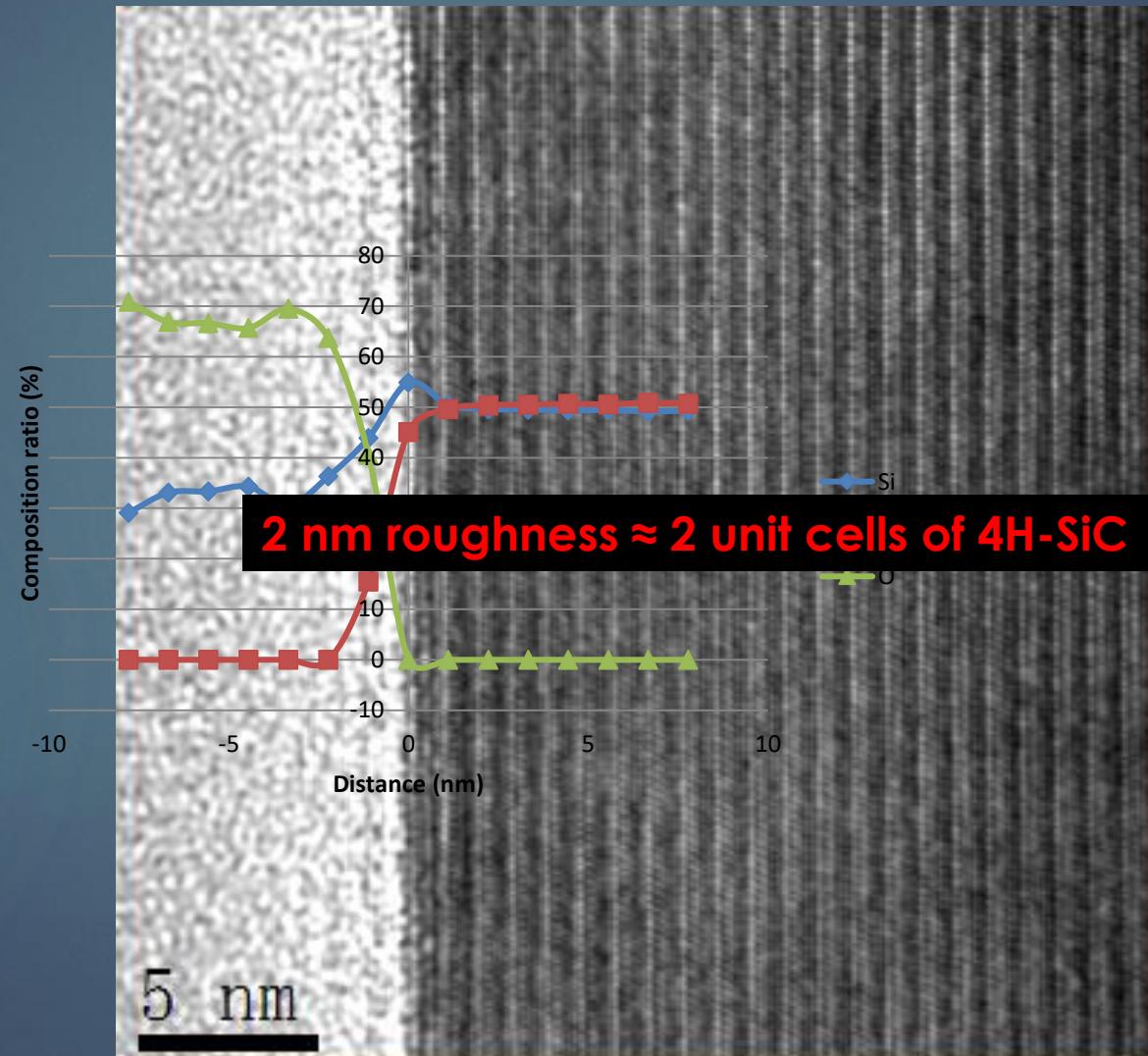
Determination of I_0



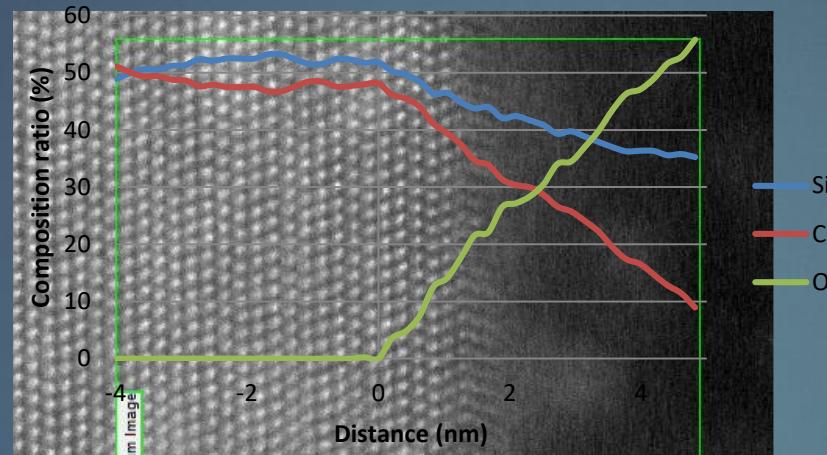
Z-contrast image



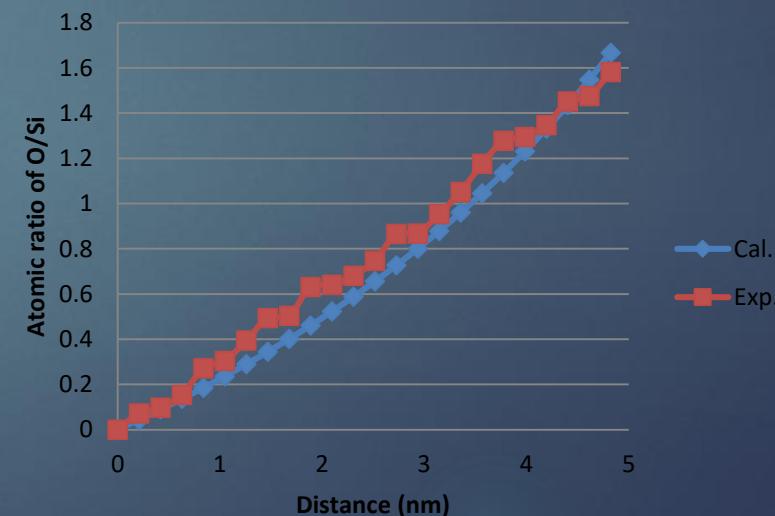
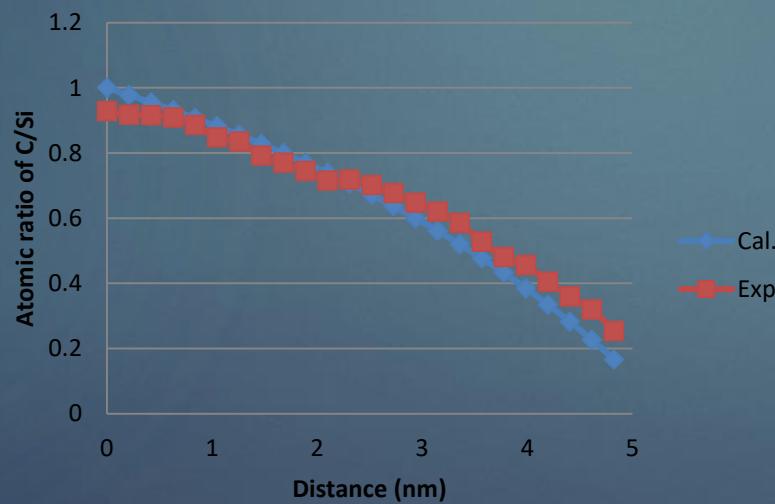
Composition ratio at IF: on-axis cut



Composition ratio at IF: 8° off-axis cut along the e-beam



	Si	C
COMPOS	50	50
AVERAGE	51.73622	48.26378
STD DEV	1.142015	1.142015
Rel %	2.207379	2.366194
ABS %	3.472445	3.472445



Thickness with Low-Loss

- Log Ratio method: $\frac{t}{\lambda} = \ln \left(\frac{I_t}{I_0} \right)$

Problems:

- How accurate is I_0, I_t
- What is λ
 - λ depends on collection angle
 - λ depends on acceleration voltage
 - λ depends on refractive index n
 - λ depends on atomic number

JOURNAL OF ELECTRON MICROSCOPY TECHNIQUE 8:193-200 (1988)

EELS Log-Ratio Technique for Specimen-Thickness Measurement in the TEM

T. MALIS, S.C. CHENG, AND R.F. EGERTON

$$\lambda = \frac{2a_0 T}{(1-n^{-2})} \frac{\int \frac{S(E) dE}{E \ln(\beta/\theta_E)}}{\int S(E) dE}$$

$$\lambda \approx \frac{106 F E_0}{E_m \ln(2\beta E_0/E_m)}$$

$$F = \frac{1 + (E_0/1022)}{(1 + (E_0/511))^2}$$

$$E_m = E_1 Z^m$$

Inelastic mean free path is only tabulated for a small assortments of acceleration voltages and collection angles

Best Practices Low-Loss Thickness Measurements

- ▶ Determine effective collection angle:
 - ▶ Pierre Trebbia
- ▶ Check tables
 - ▶ Don't trust the approximations?
- ▶ Check zero-loss extrapolations

Very Best Practice: Don't use it quantitatively

Drude Theory

- Egerton 3rd edition: equations 3.57 and 3.58

$$\sigma_p(\beta) = \frac{E_p \ln(1 + \beta^2/\theta_{E_p}^2)}{2n_a a_0 m_0 v^2} \approx \frac{E_p \ln(\beta/\theta_{E_p})}{n_a a_0 m_0 v^2}$$

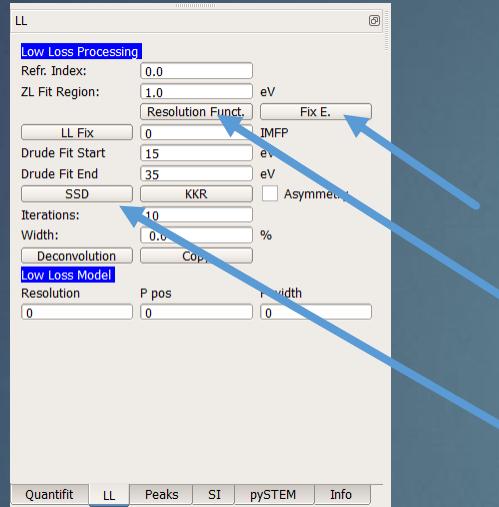
$$\lambda_p(\beta) = \frac{2a_0 m_0 v^2}{E_p \ln(1 + \beta^2/\theta_{E_p}^2)} \approx \frac{a_0}{\gamma \theta_{E_p} \ln(\beta/\theta_{E_p})}$$

$$\theta_E = E / (\gamma m_0 v^2)$$

$$\beta \gg \theta_E$$

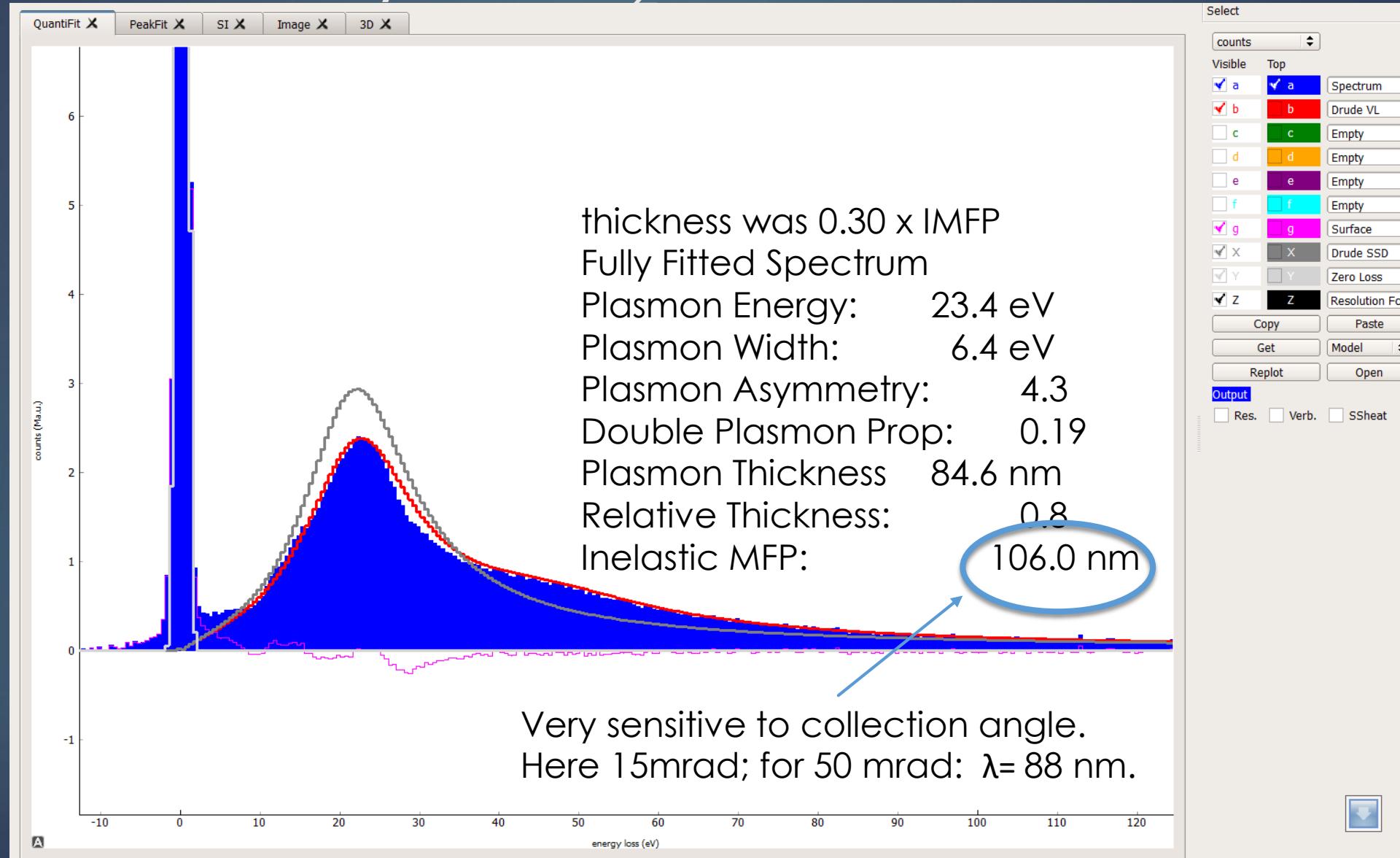
- n_a = volume density;
- Use plasmon energy to determine inelastic mean free path

Drude Analysis

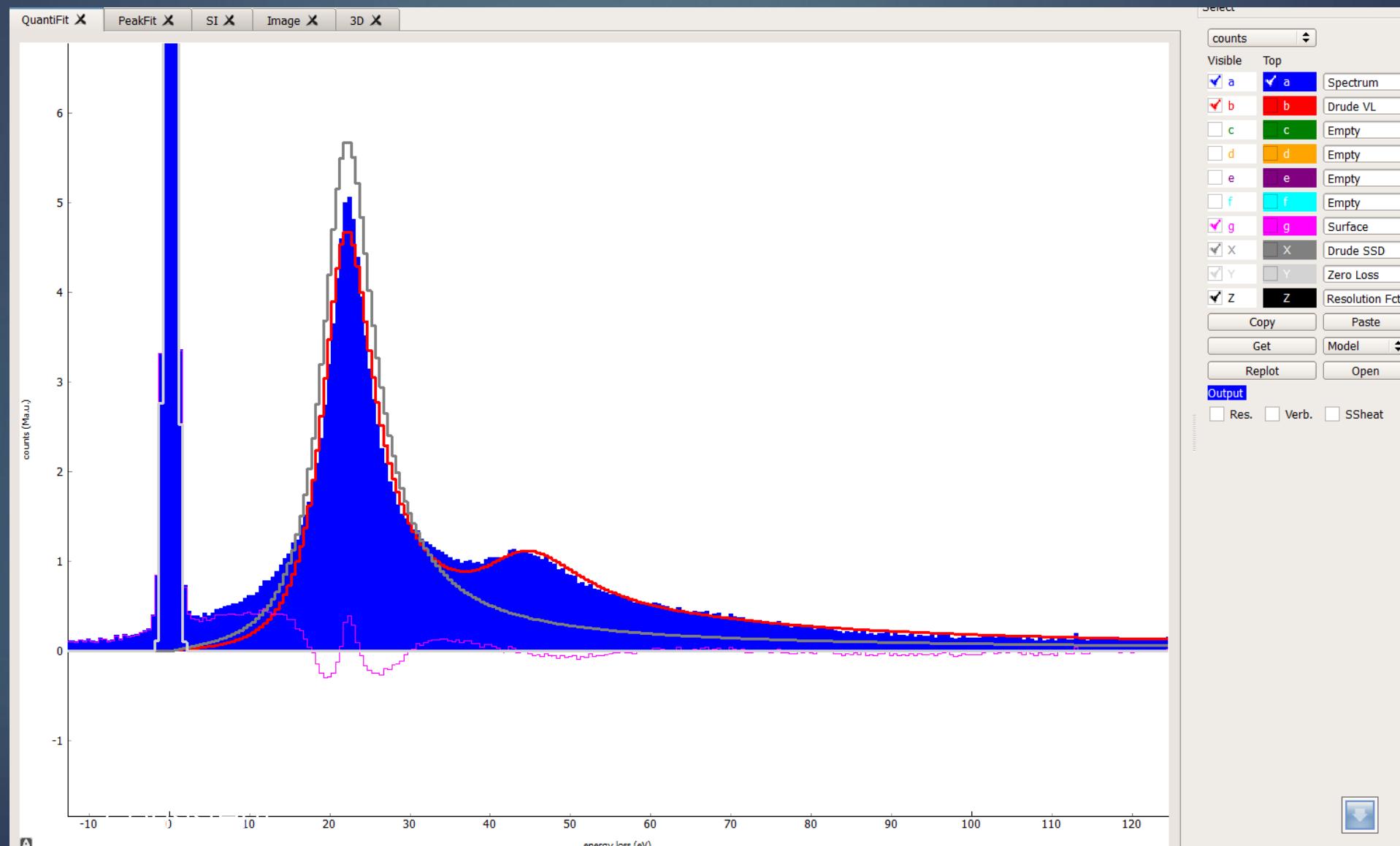


- ▶ Load Spectrum
- ▶ Zero-Loss to zero eV
- ▶ Fit Zero-Loss
- ▶ Single Scattering Analysis and Drude Analysis

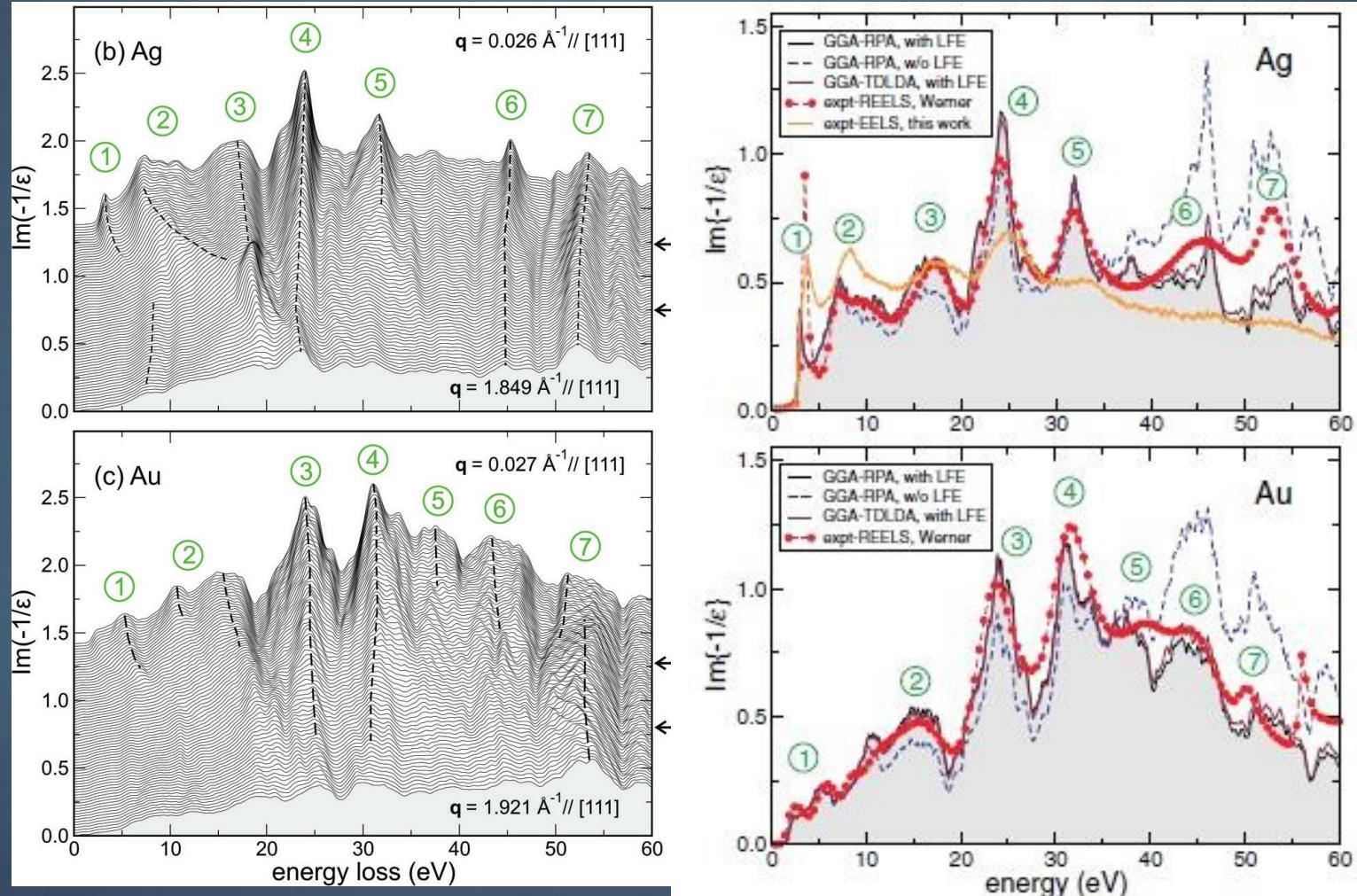
Drude Theory – SiO_2



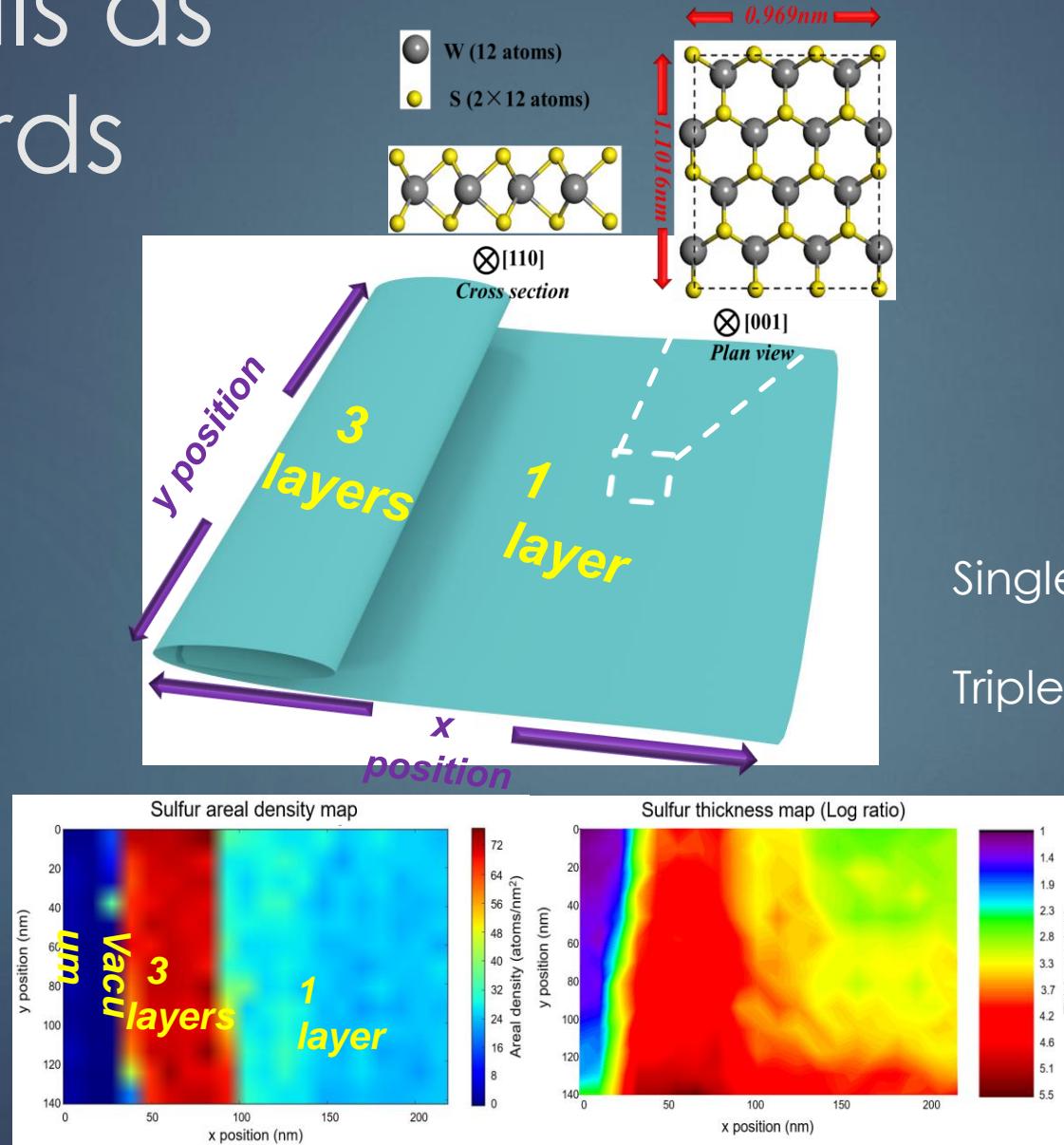
Drude Theory – SiC



Which peak is the plasmon?



Using Single Layer Materials as Standards

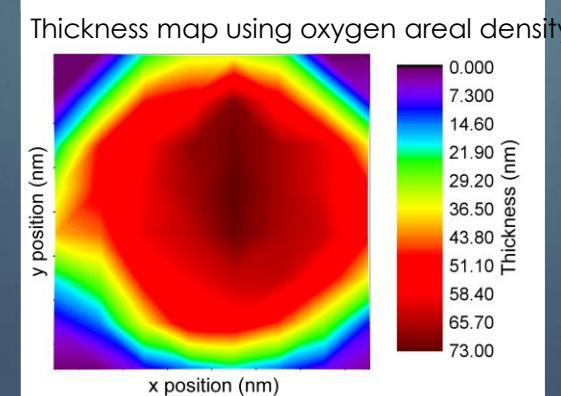
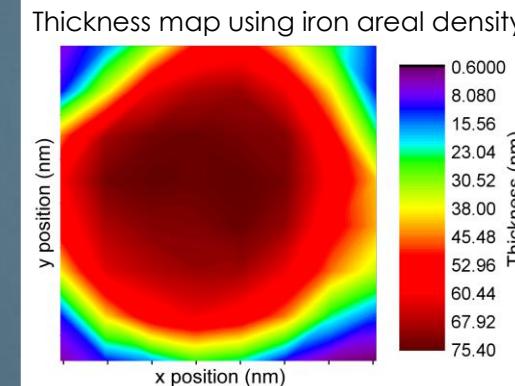
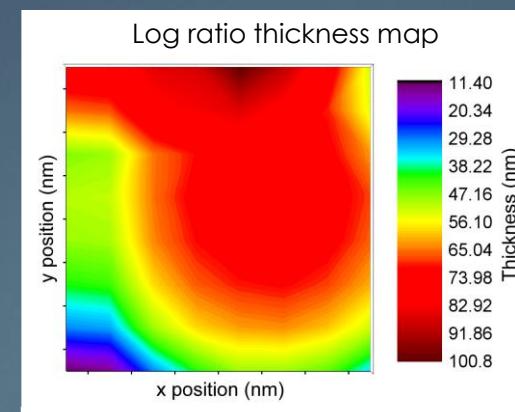
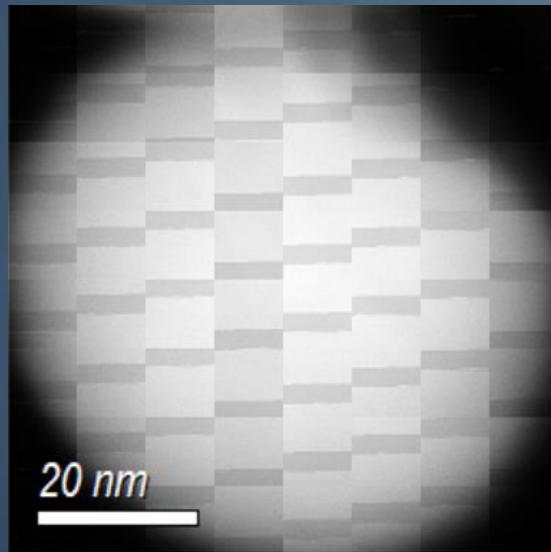
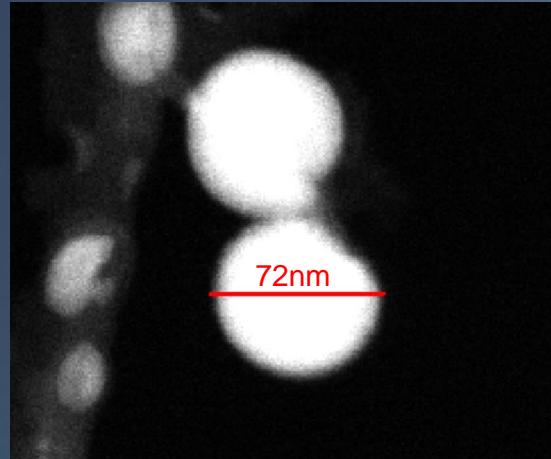


Single layer: 23.3 atoms/nm²
deviation: 2.2%
Triple layer: 65.7 atoms/nm²
deviation: 4.0%

Log Ratio at thin specimen

- ▶ At very thin specimen, from the pure bulk loss probability, one has to subtract a term which is due to the so-called '**Begrenzungseffekt**', first pointed out for the thin film case by Boersch, Geiger and Stickel (1968) Z. Phys. **212**, p130
 - ▶ bulk and surface modes are orthogonal and couple with each other (coupled oscillators are the basis for low-loss)
 - ▶ The intensity of volume plasmon is decreased due to depolarization of surface charge by surface modes
 - ▶ **surface plasmon steals intensity from bulk plasmon**
- ▶ See also: Schmeits (1981) J. Phys. C: Solid State Phys. **14**, 1203

Contamination obscures thickness measurement of nano-particle



Pressure of Ar Gas Bubbles

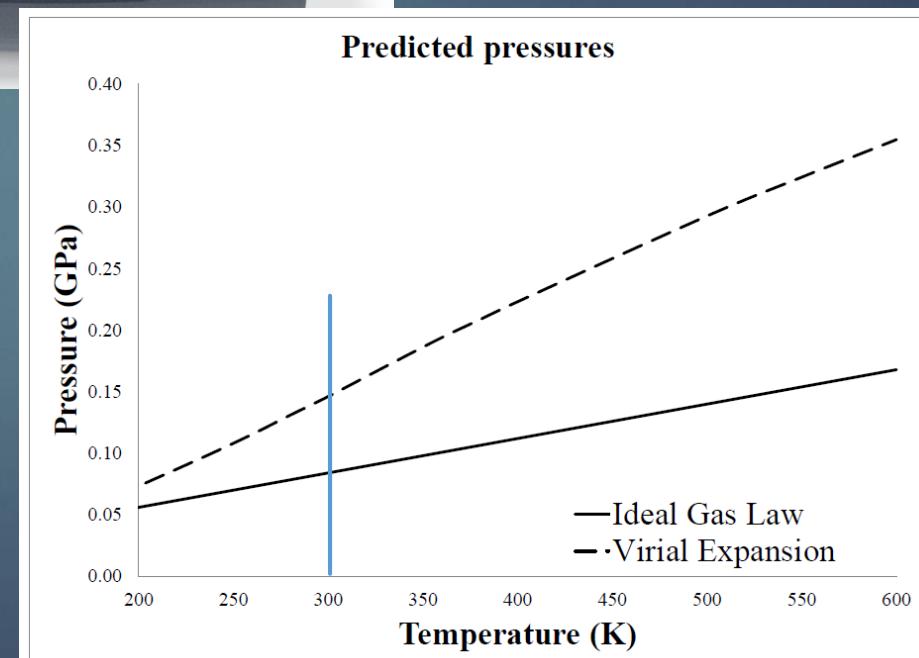


Ideal Gas law:

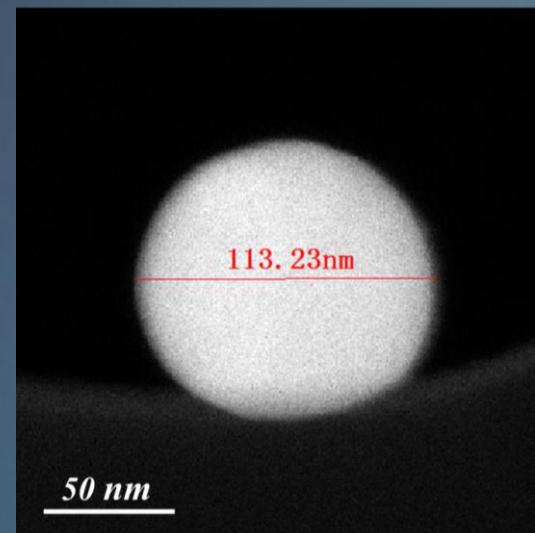
$$\Rightarrow P = \frac{Nk_B}{V}$$

Virial Expansion:

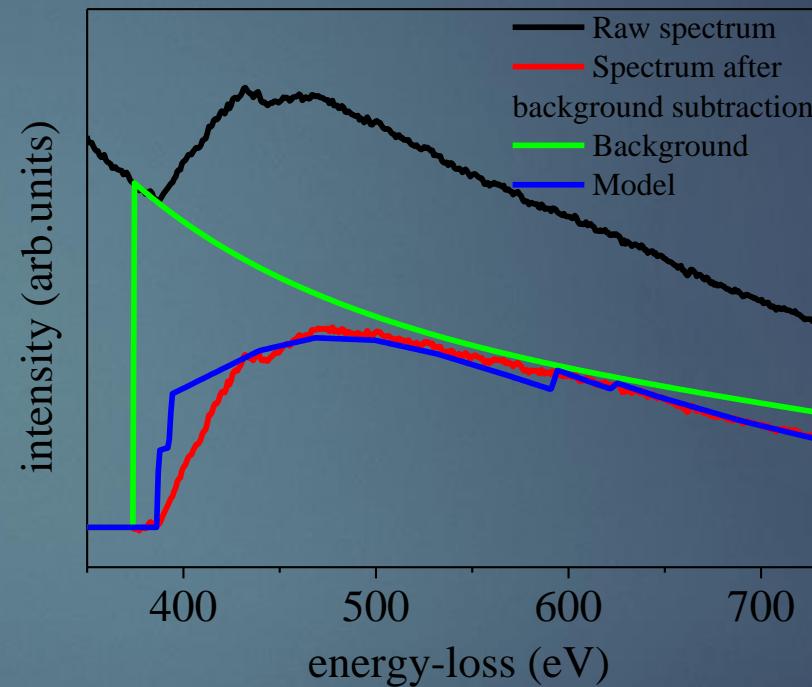
$$P = k_B T \rho (1 + B\rho + C\rho^2)$$



Fit result $t_{\text{initial}}=25\text{nm}$, this is wrong because of lost current.
After consideration of lost current, we obtain $t_{\text{real}}=114\text{nm}$



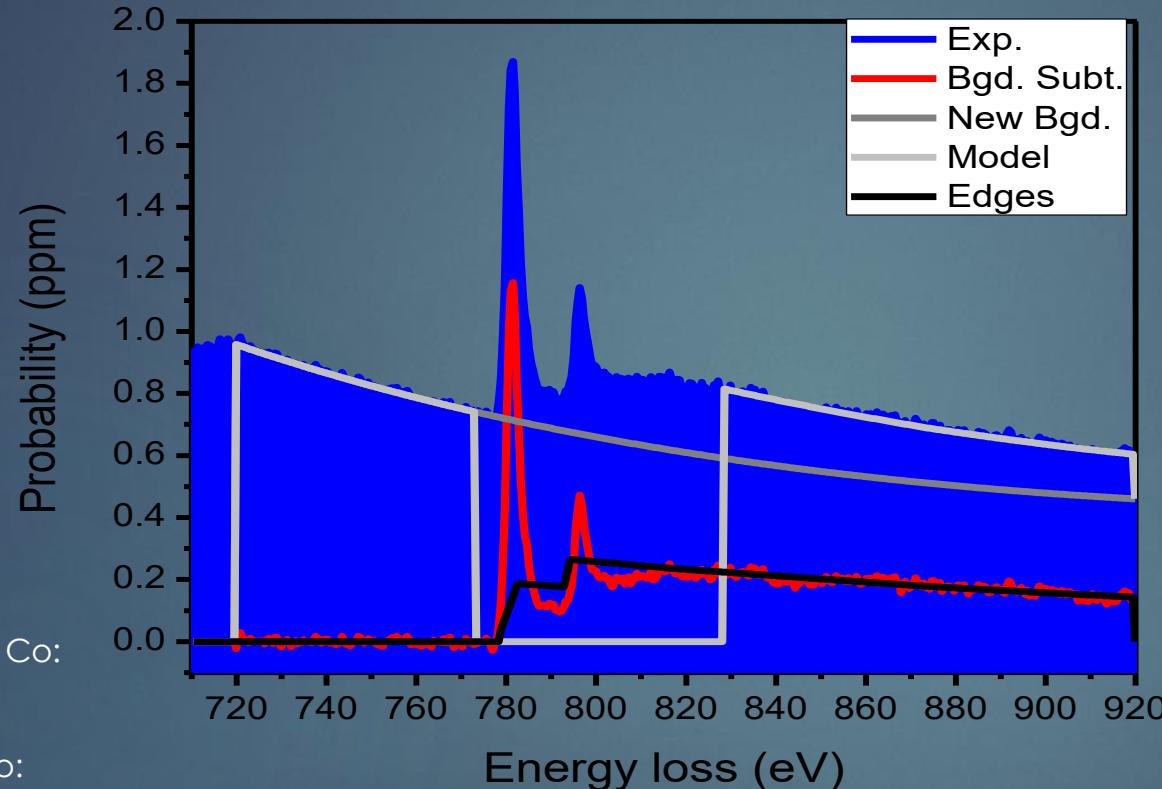
Ag-M edge



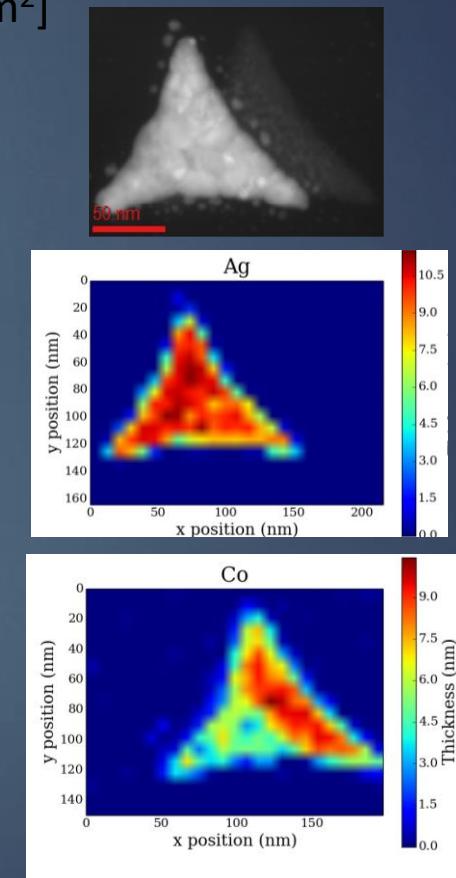
Fit error $\pm 7\%$. (by changing different fit energy window and background subtraction energy window)

➤ EELS Spectra Quantification For Core Loss :

Thickness Determinations

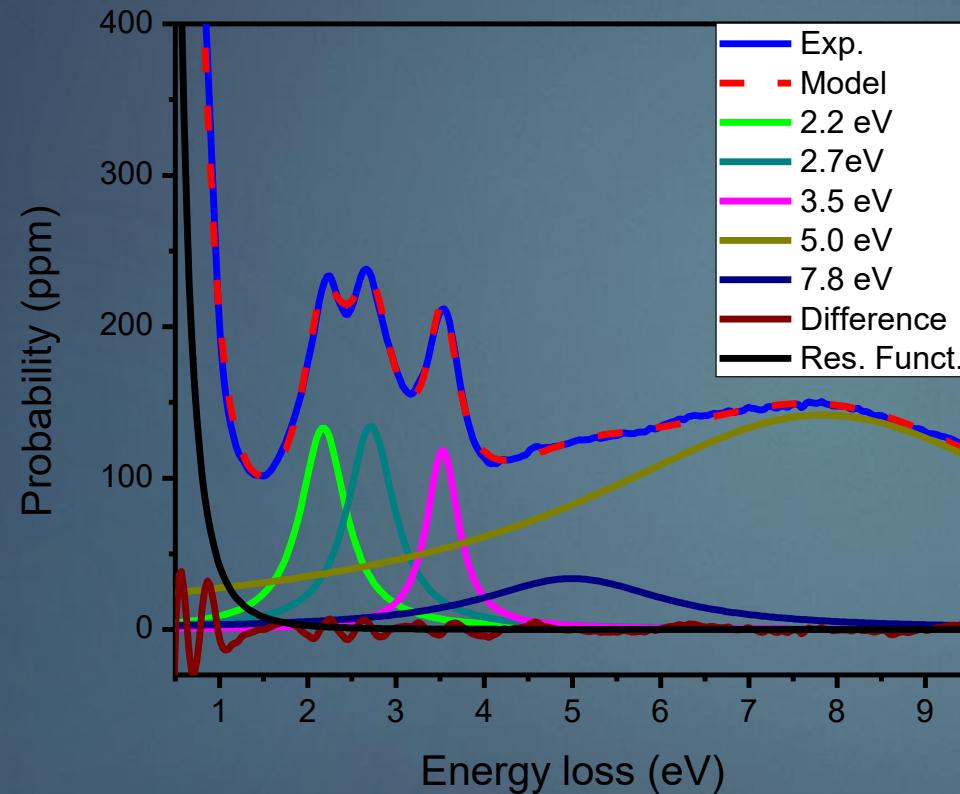


- ❖ Areal Density of elements:
[atoms/nm²]



Modelling of core loss spectrum has been developed within this and other works

➤ EELS Spectra Quantification For Low Loss



Determine:

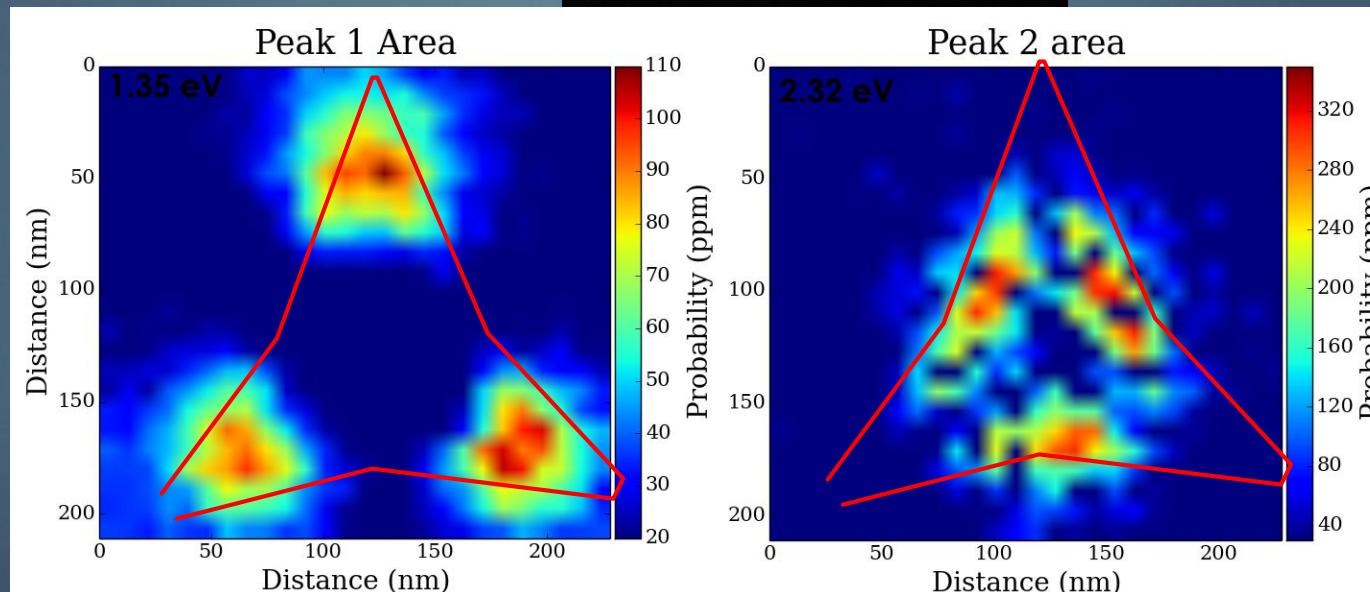
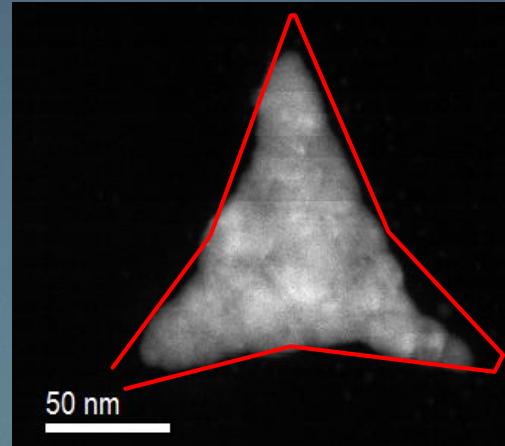
- ❖ Position--Energy
- ❖ Width--Lifetime
- ❖ Area in scattering probability (ppm)
- ❖ Shape
- ❖ Fitting error

Position (eV)	Width(eV)	Area (ppm)	Shape
2.2	0.63	131.65	Loren
2.7	0.66	138.57	Loren
3.5	0.45	82.80	Loren
5.0	2.58	136.31	Loren
7.8	6.71	1491.30	Loren

Modelling of complete LL spectrum has been developed within this work.

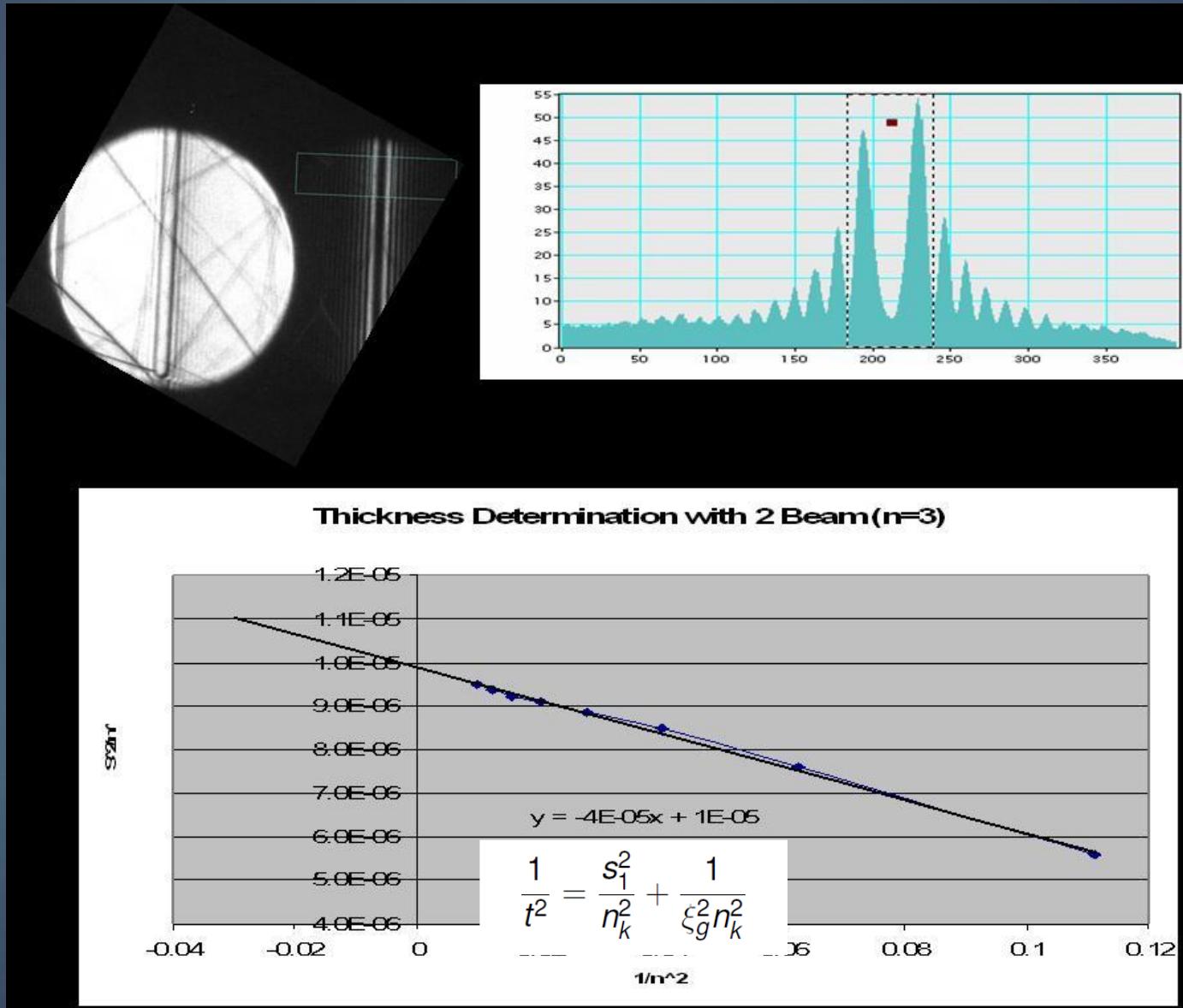
❖ STEM Images & EELS mapping

➤ Isolated Ag Triangle



Triangular Ag is plasmonic – No interaction with Co in these geometries

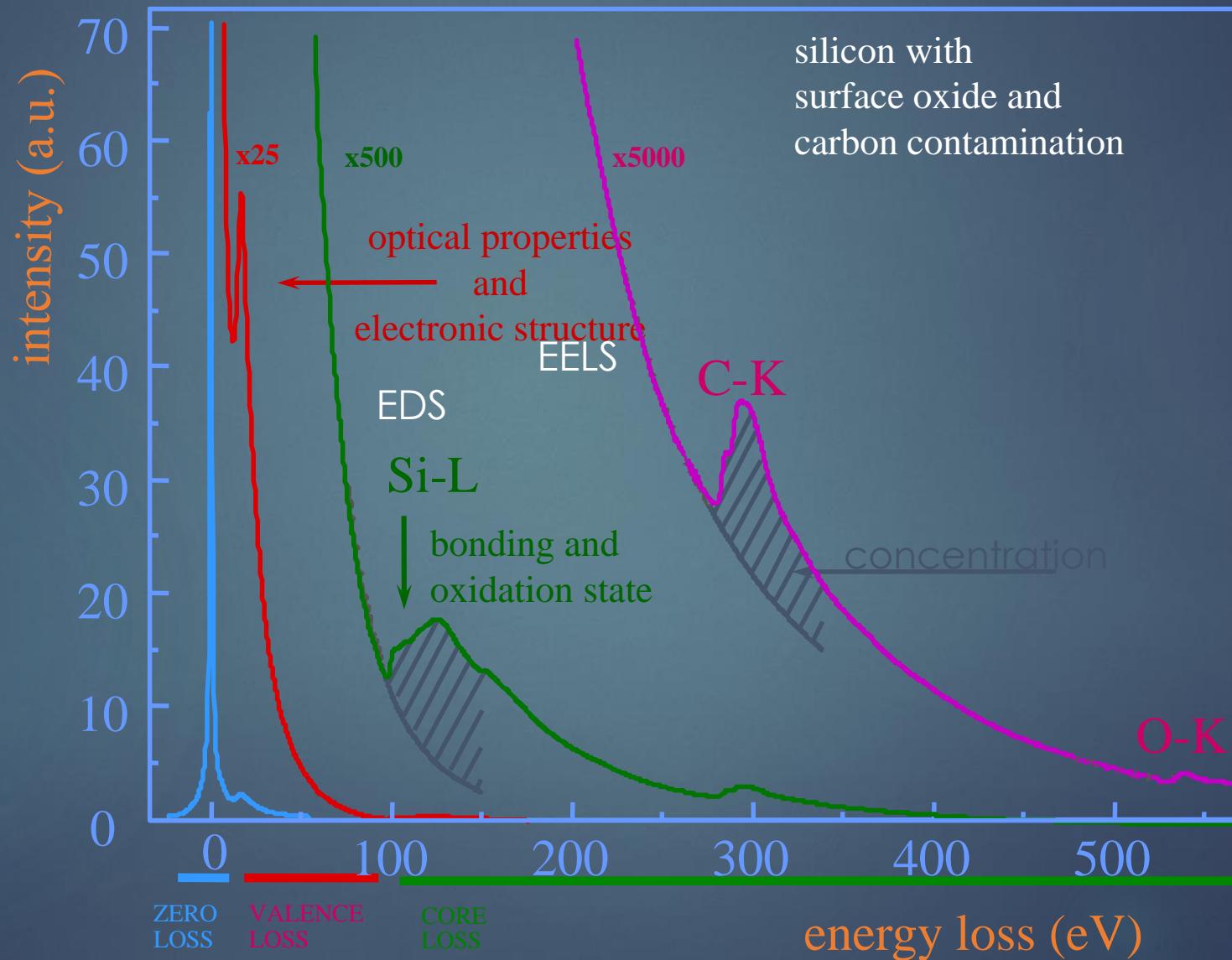
Thickness with CBED



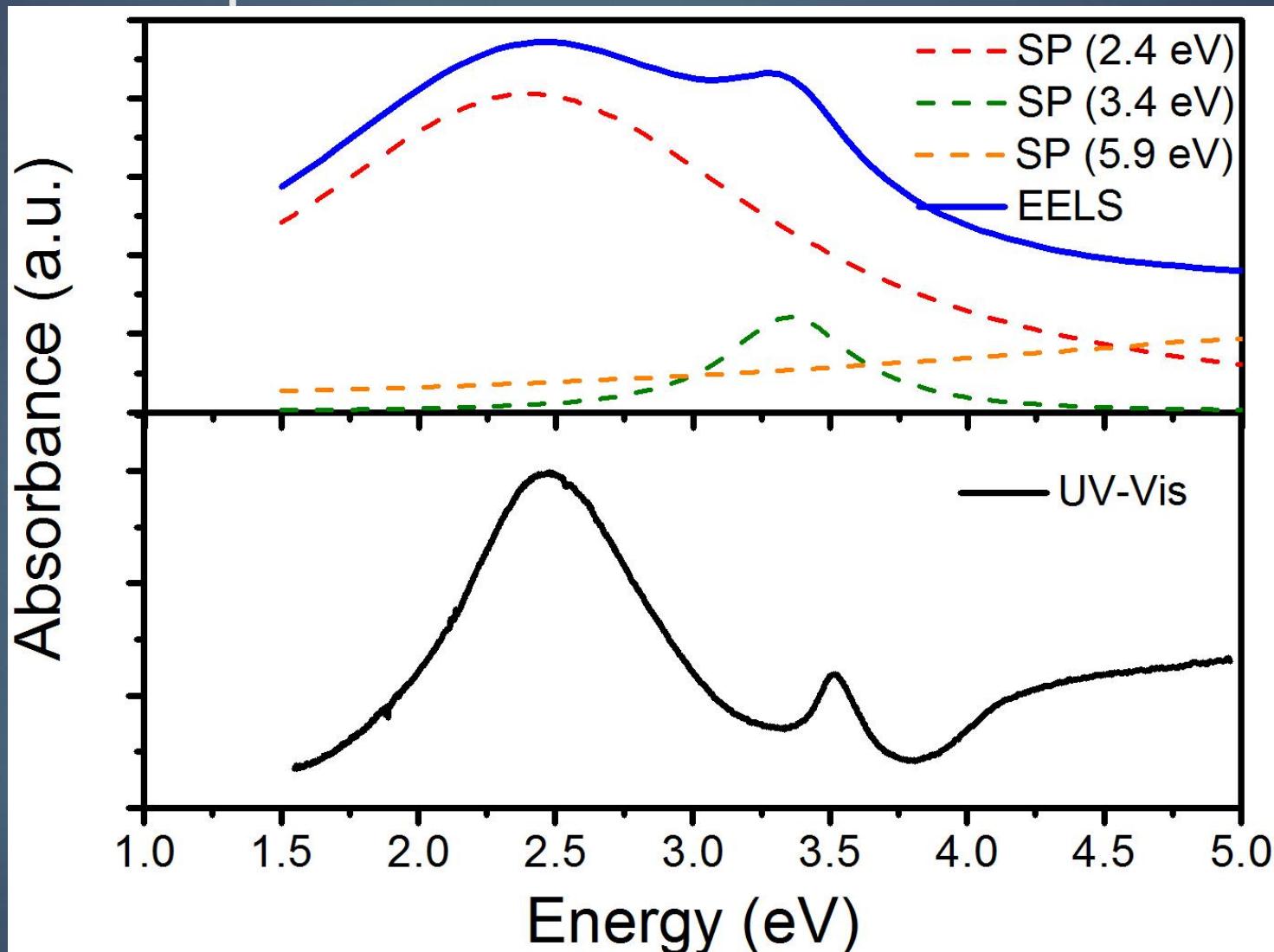
Summary

- ▶ Quantification is possible
- ▶ Quantification is not much trouble
- ▶ We learn how many atoms are involved in experiment
- ▶ We could start analyzing noise for information content
- ▶ Provide data for quantitative comparison to theory

But there is more in EELS

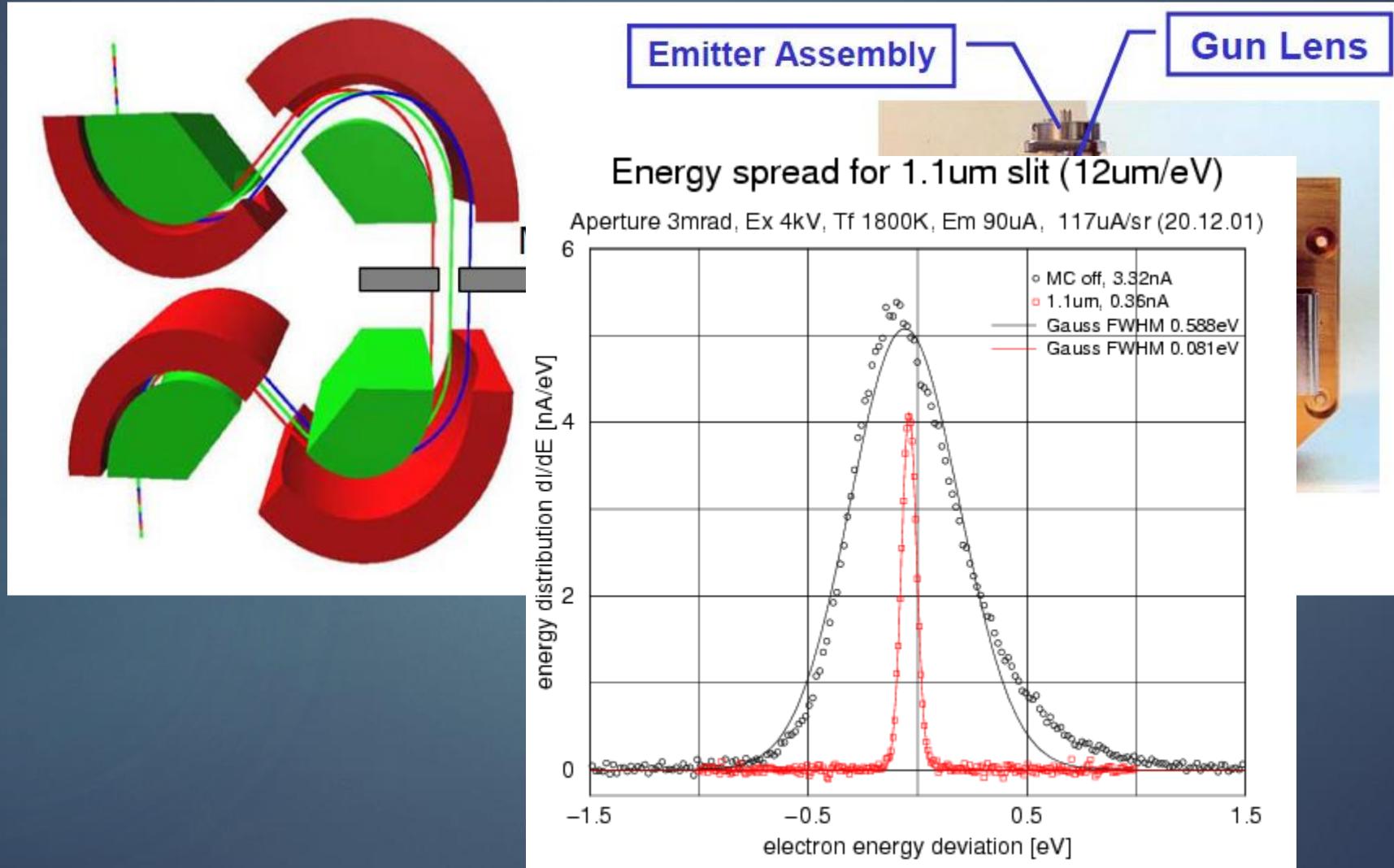


Optical Response

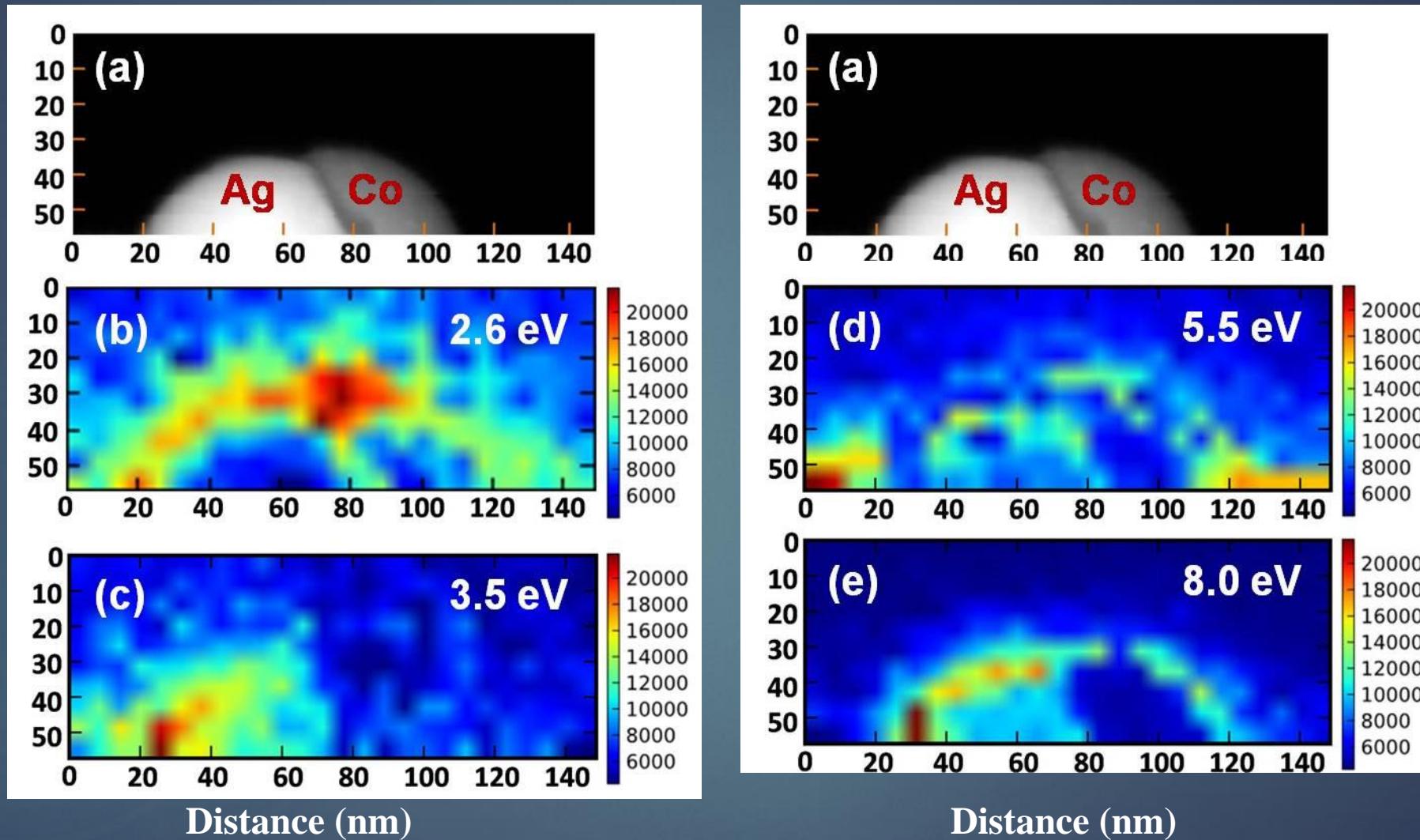


With monochromator in TEM we are getting close to
the energy resolution of optical spectroscopy (here absorption)

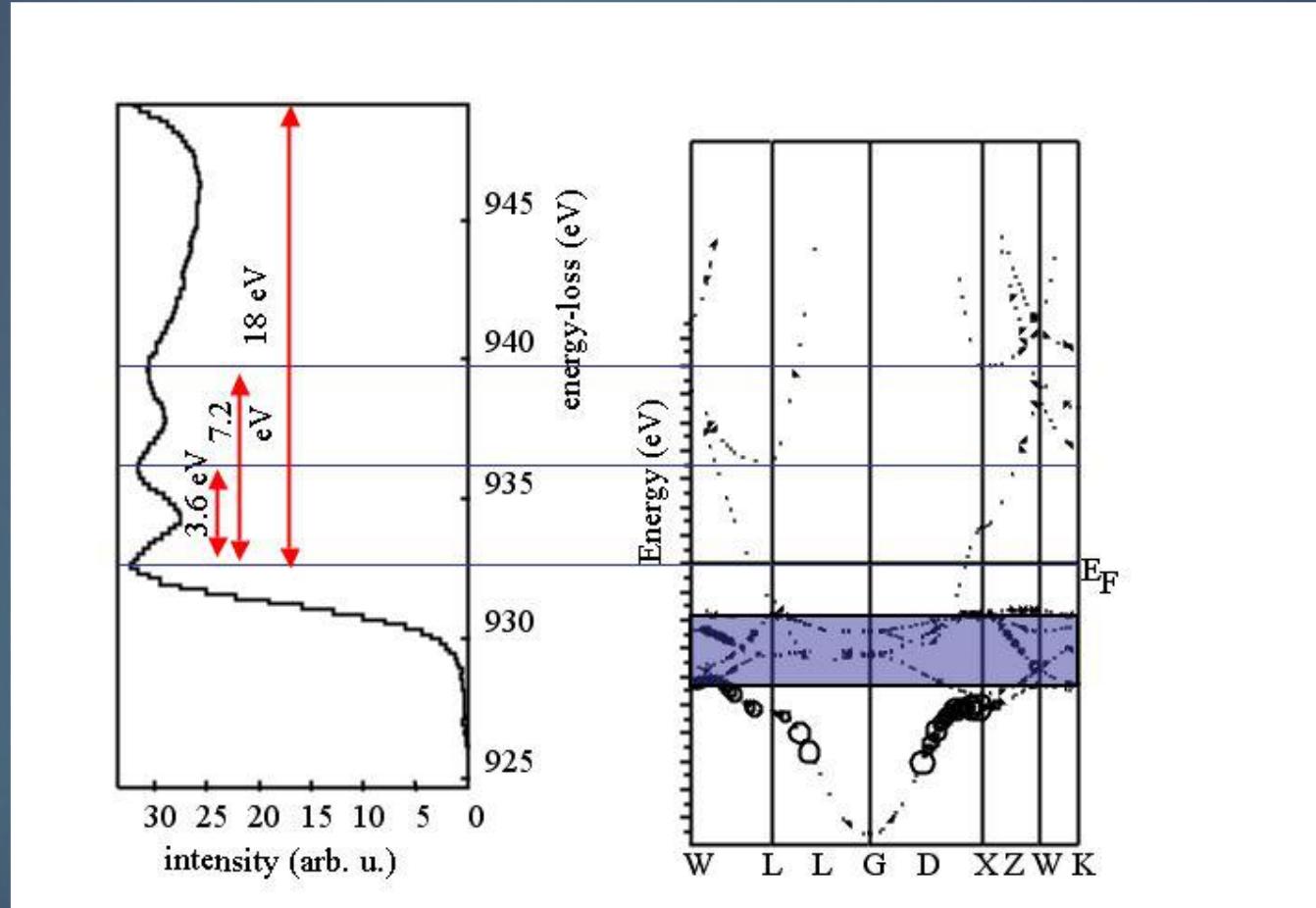
Monochromated EELS



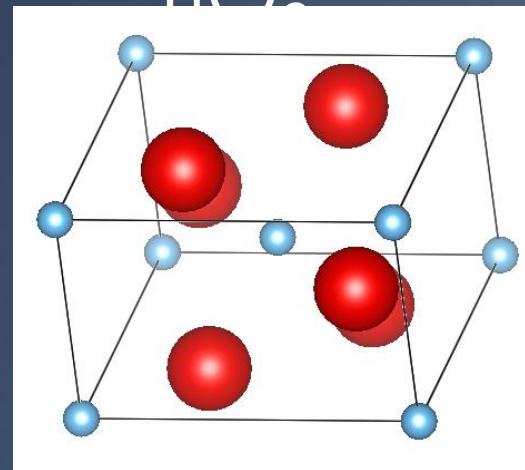
Spatial Resolution of Optical Response



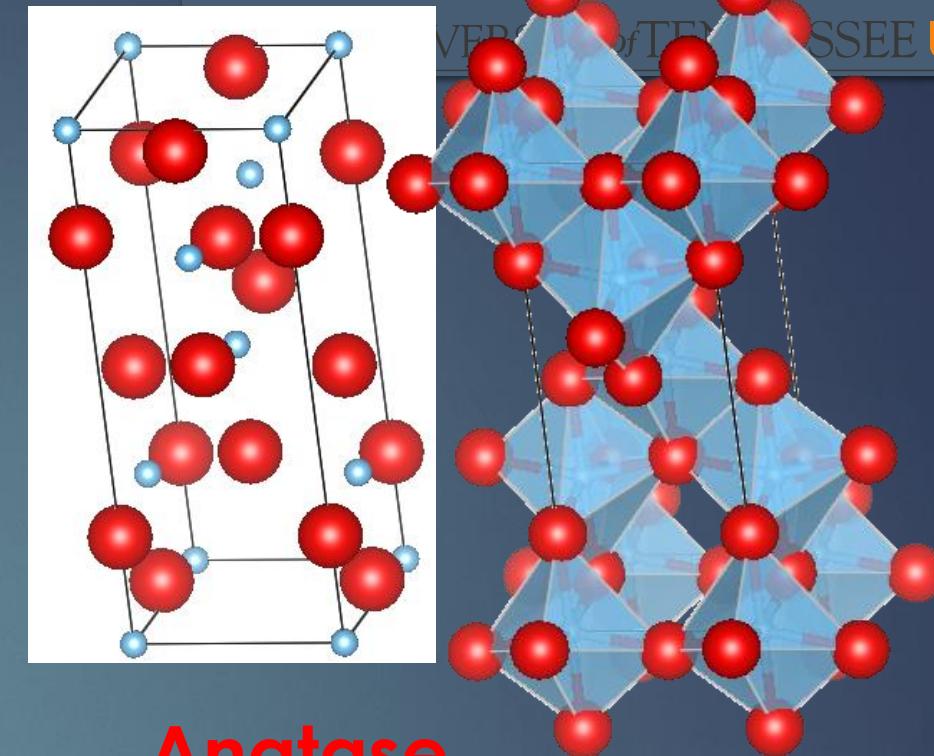
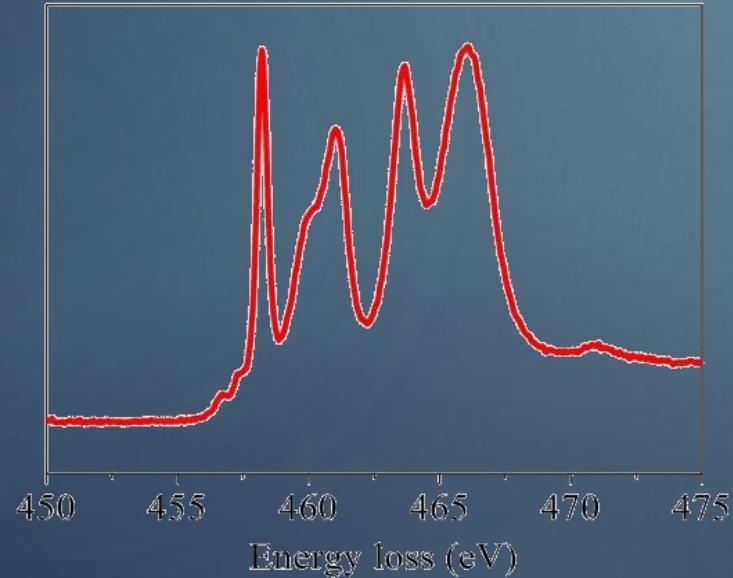
Analysis of Edge Shape



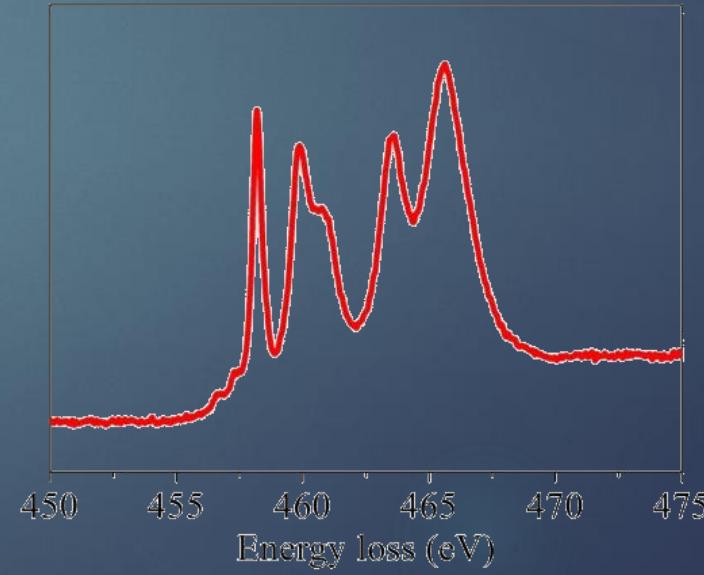
Ti -L_{2,3} ELNES of TiO₂



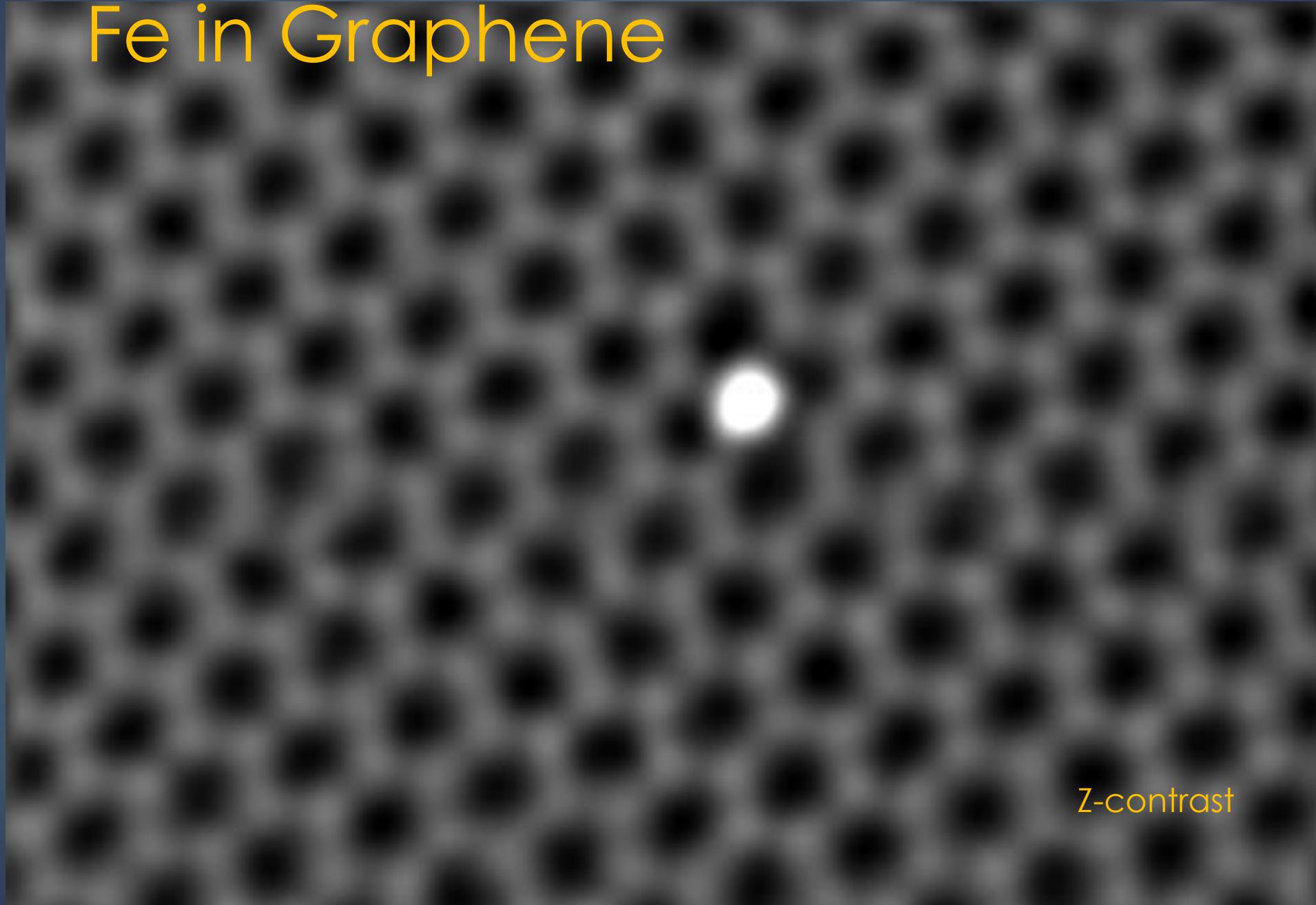
Rutile



Anatase

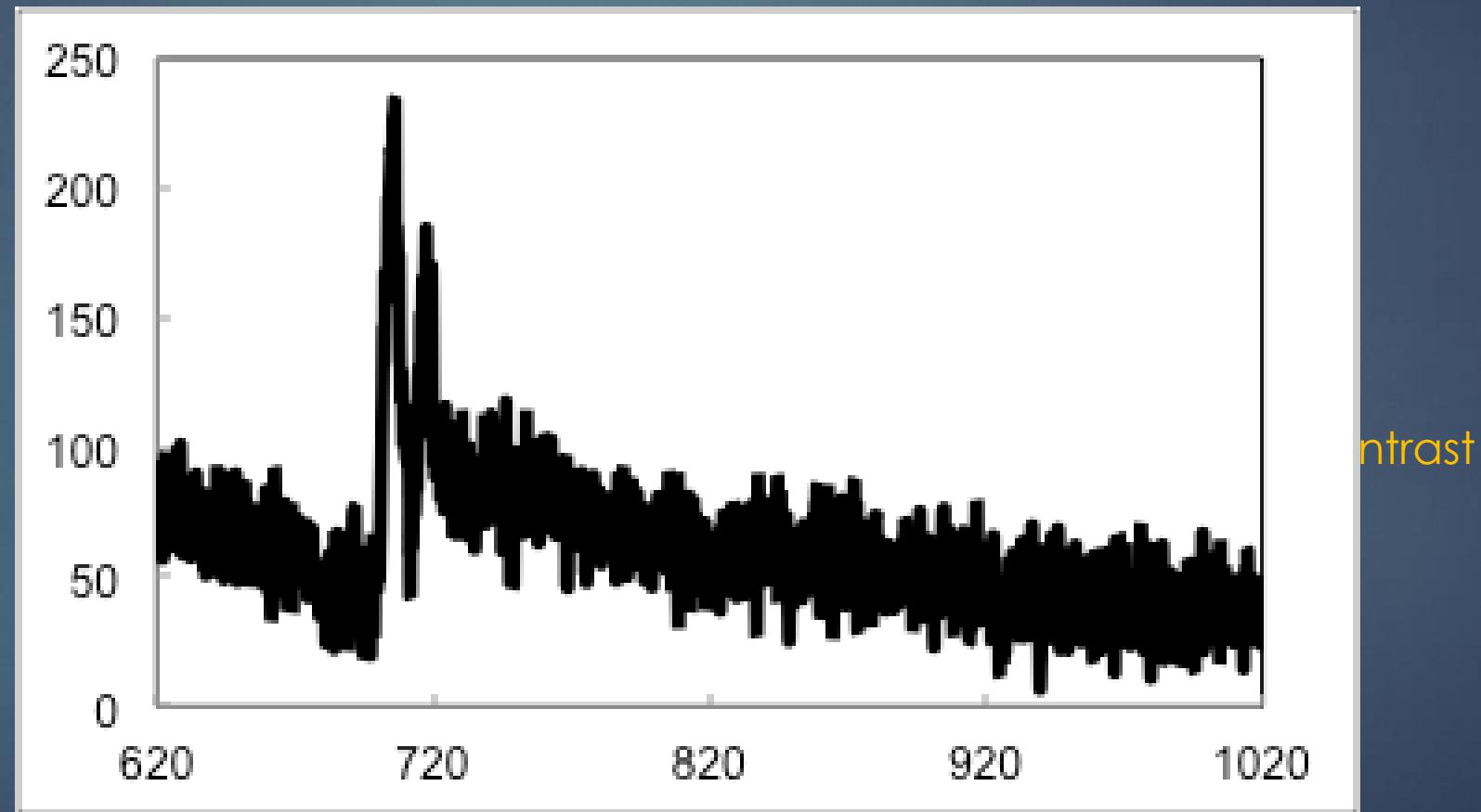


Fe in Graphene

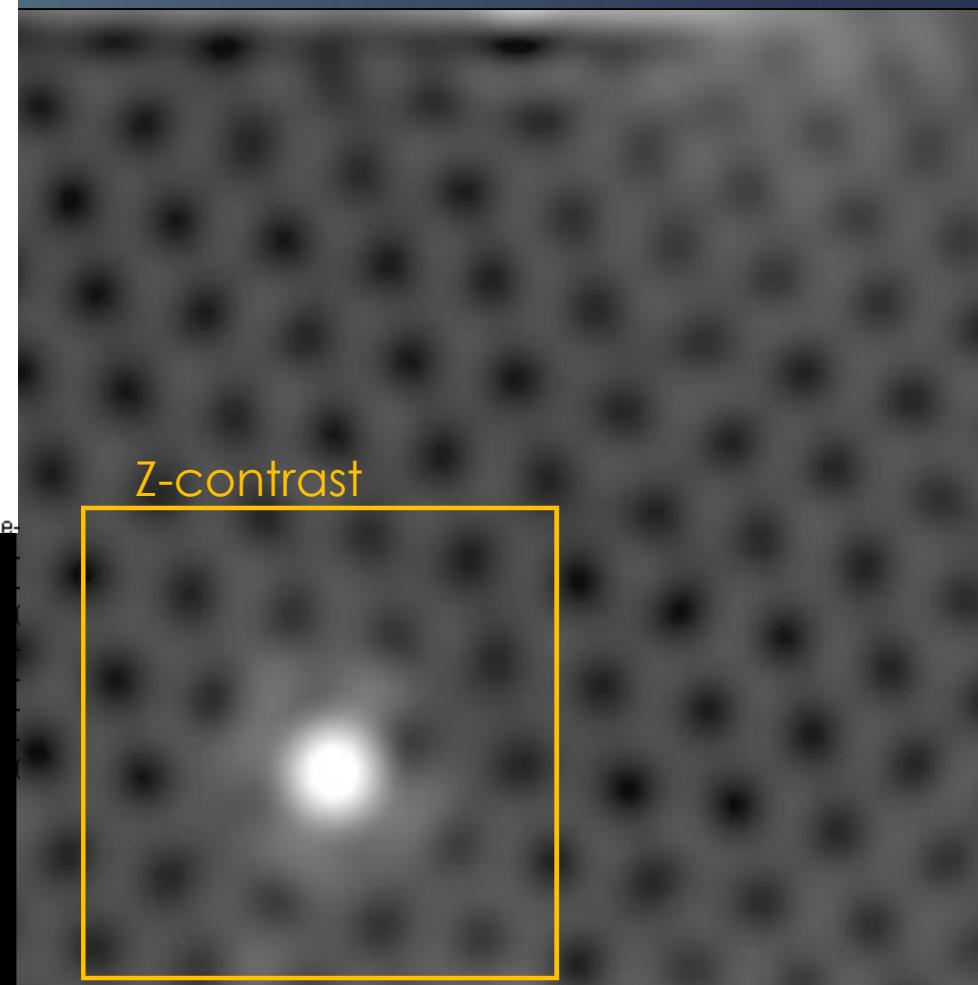
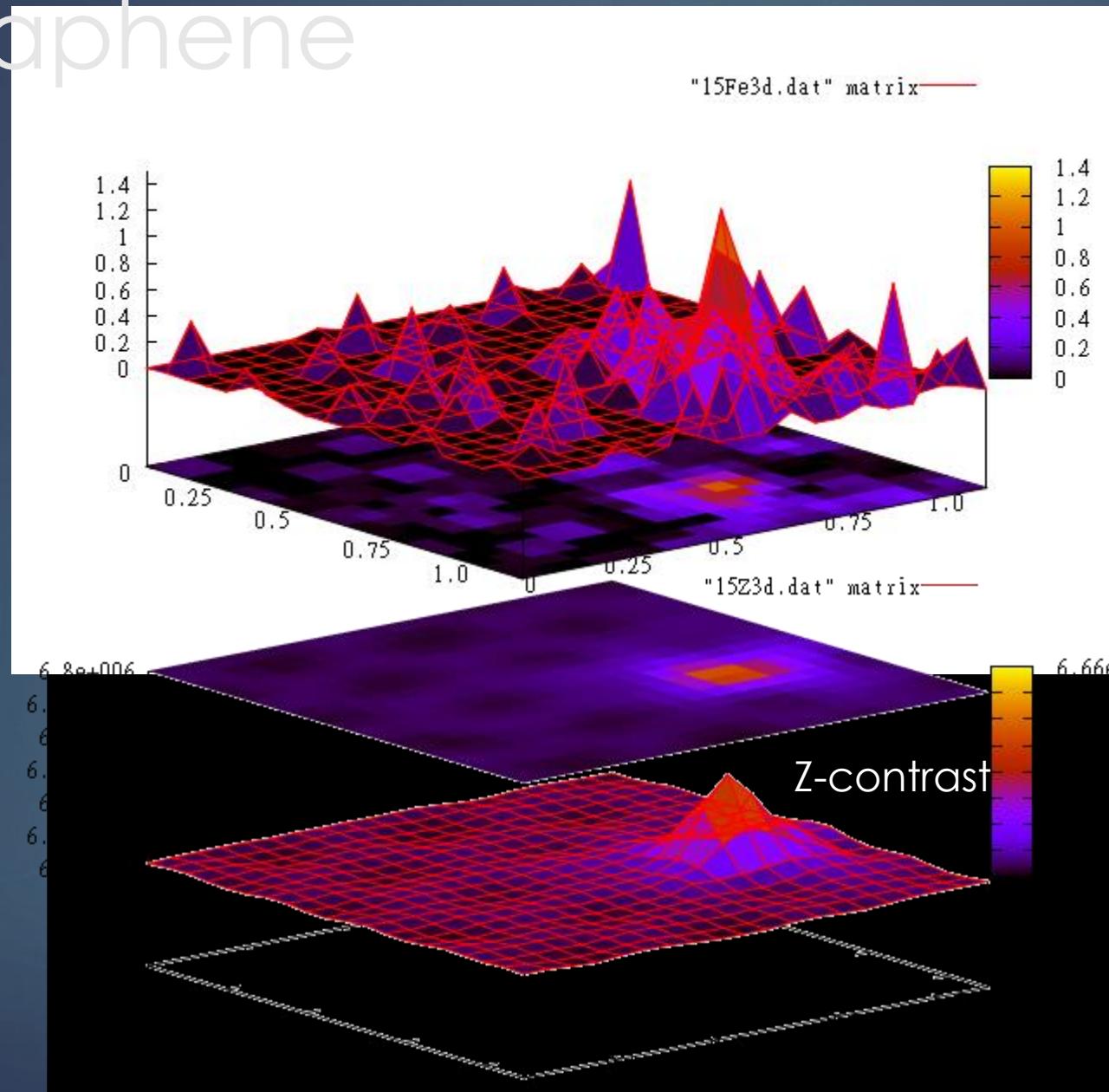


Z-contrast

Fe in Graphene



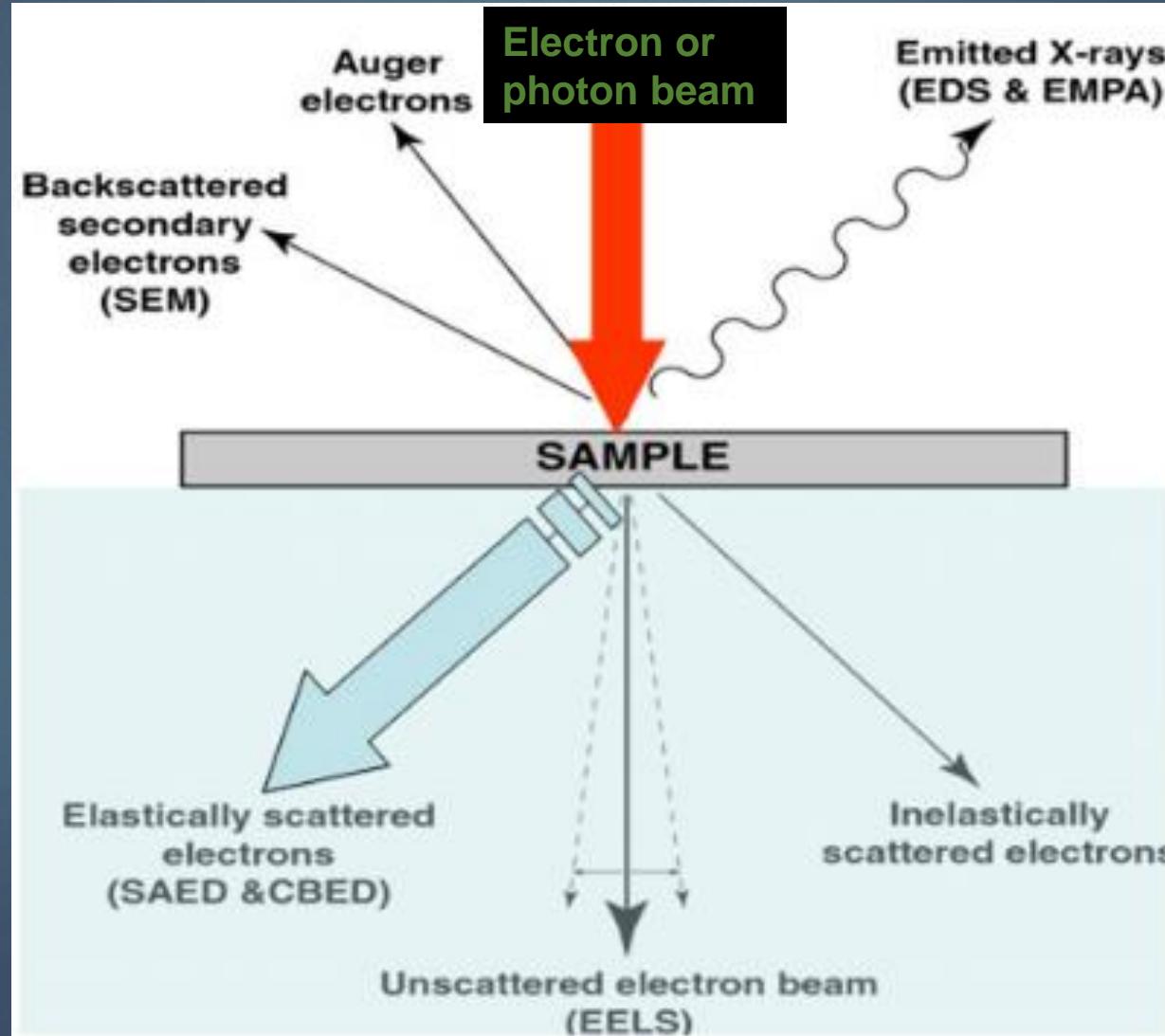
in Graphene



Summary

- ▶ EDS and EELS provide chemical composition information on the atomic scale.
- ▶ EELS is better for lighter elements while EDS is most of the times better for heavier elements.
- ▶ EELS contains additional information on bonding and optical-properties.
- ▶ Energy Filtered Imaging provides compositional overview and an additional contrast mechanism.

Shooting High-Energy Particles at Materials



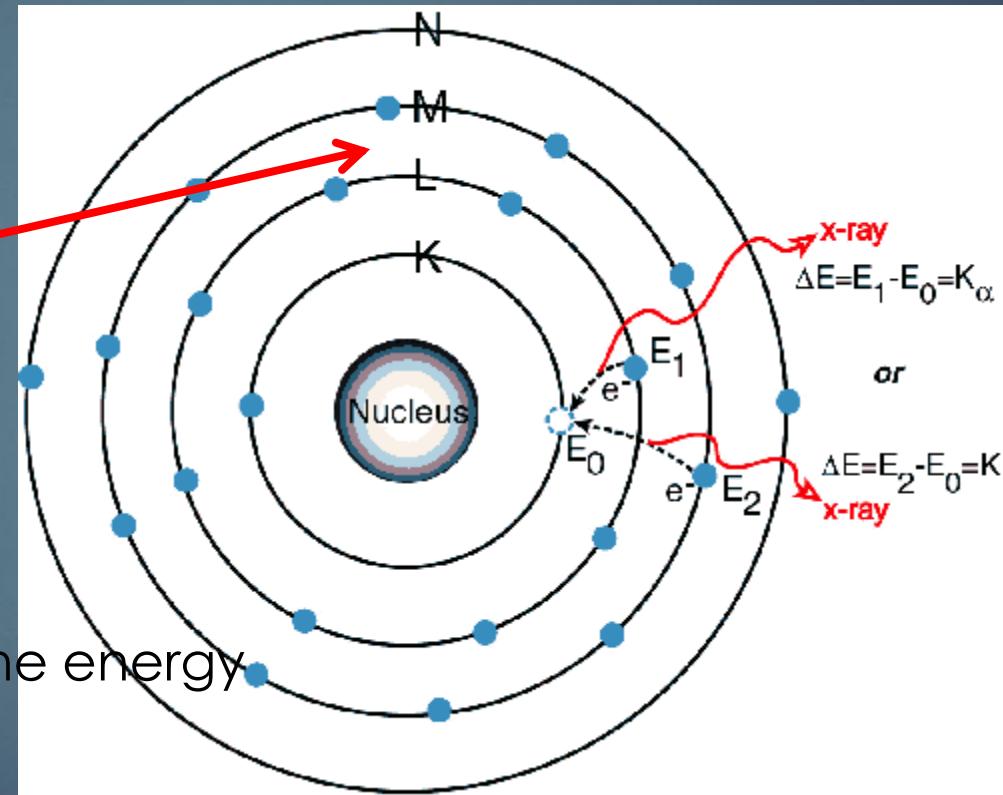
What is going on at the atomic level?

- ▶ Kick an electron out

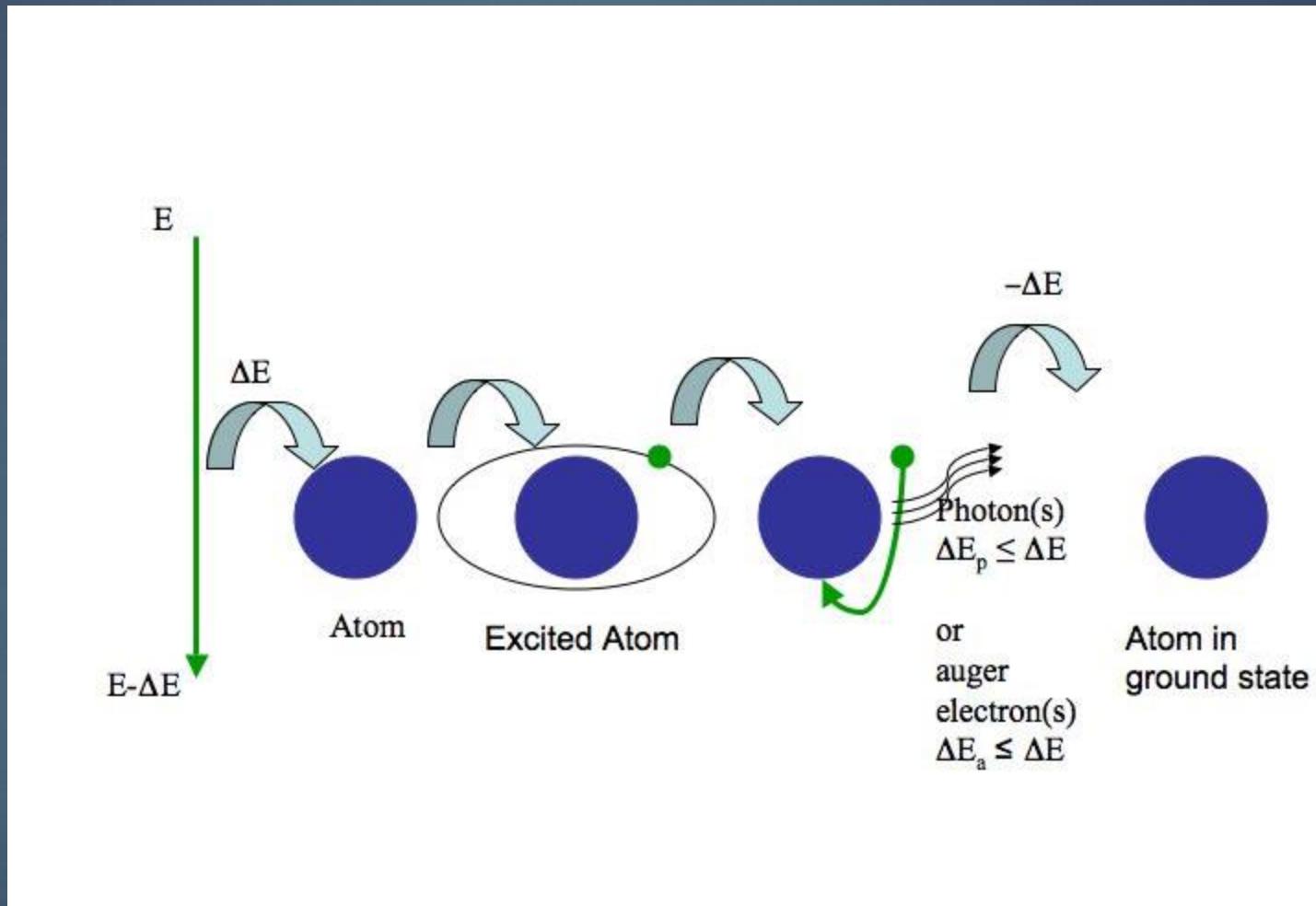
(with a high energy electron or

Energy states according to Quantum Mechanics

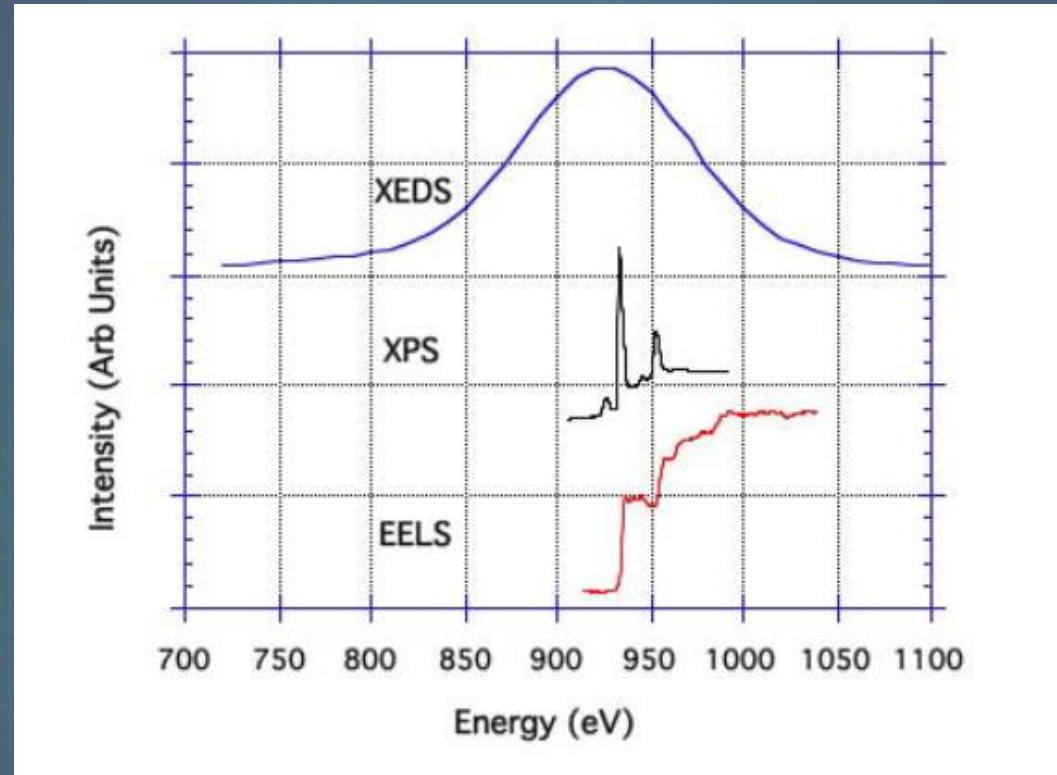
- ▶ Try to get rid of the energy



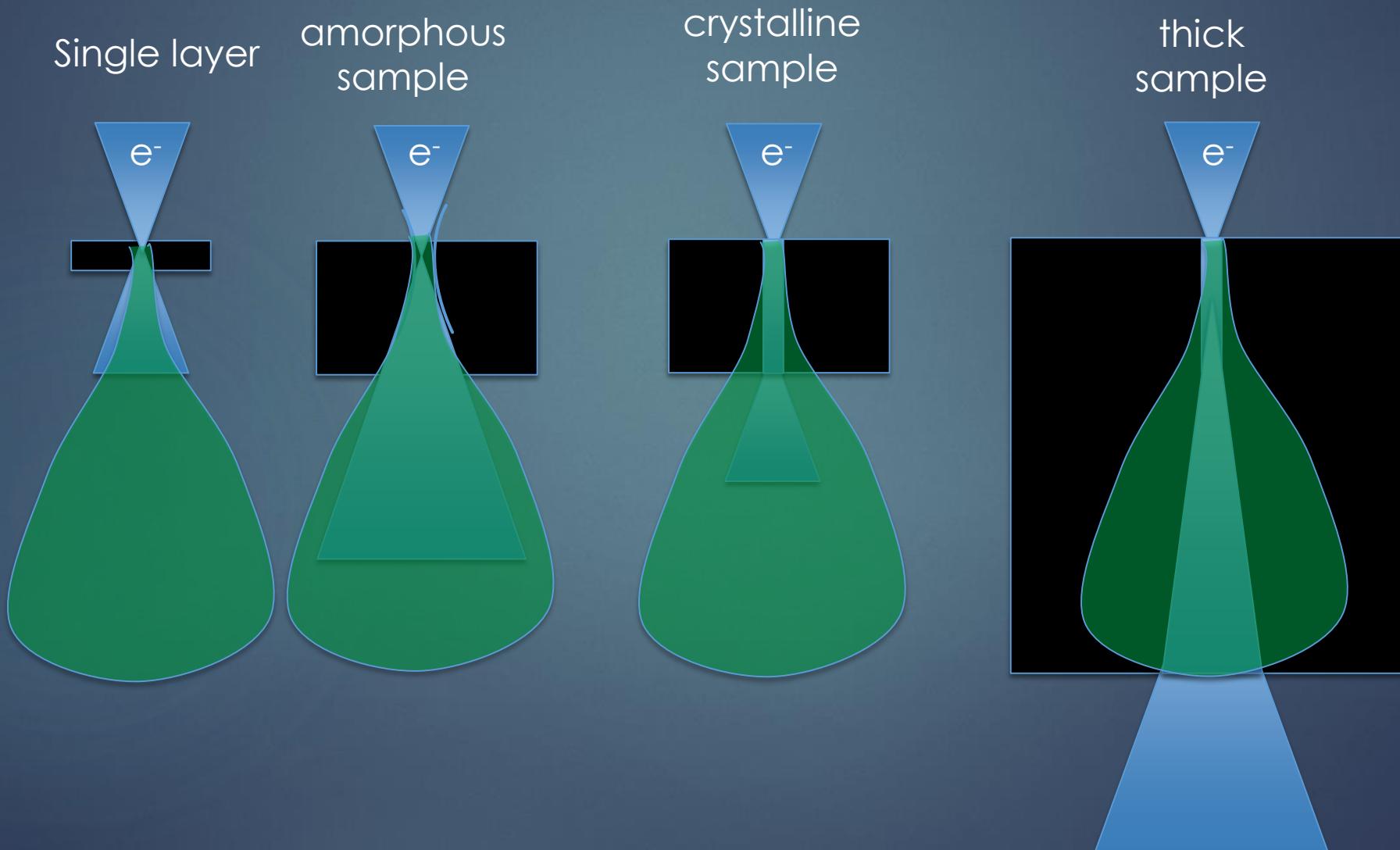
There is also a timescale involved



Energy Resolution

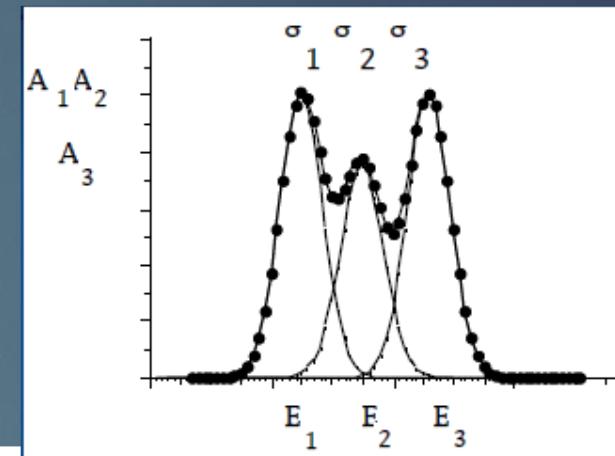
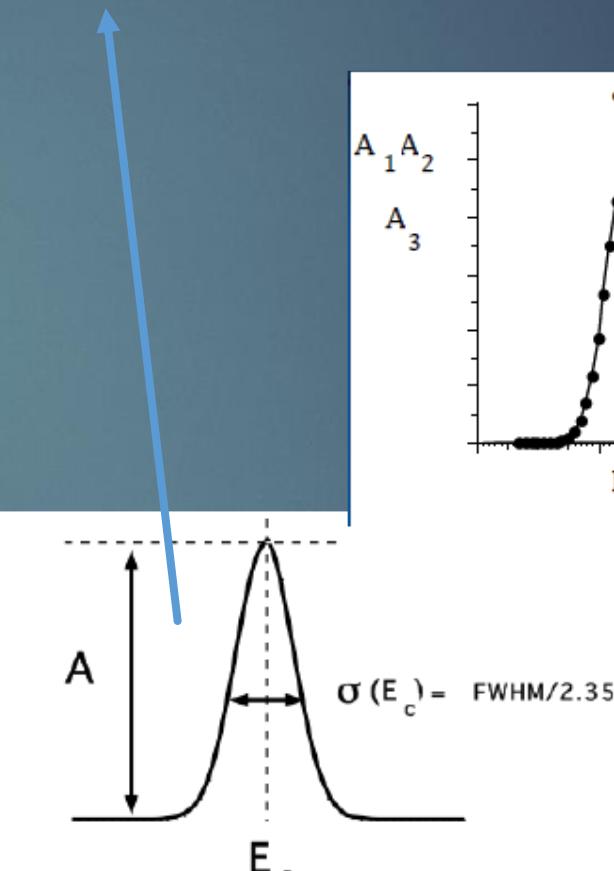
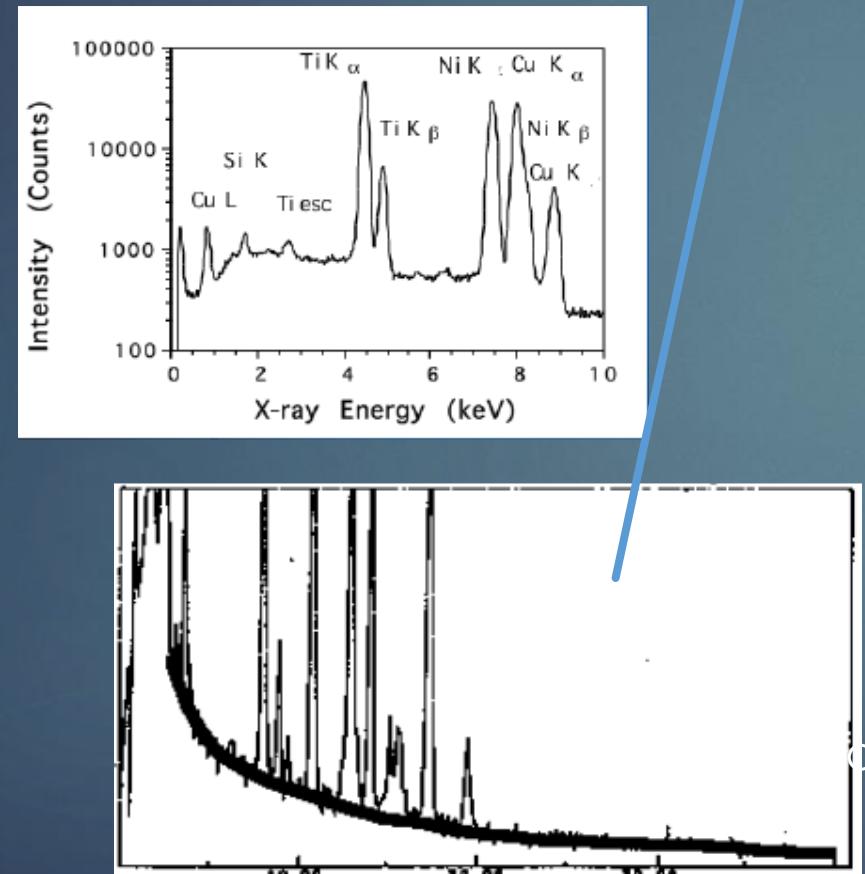


Probed Volume



Extracting I in EDS

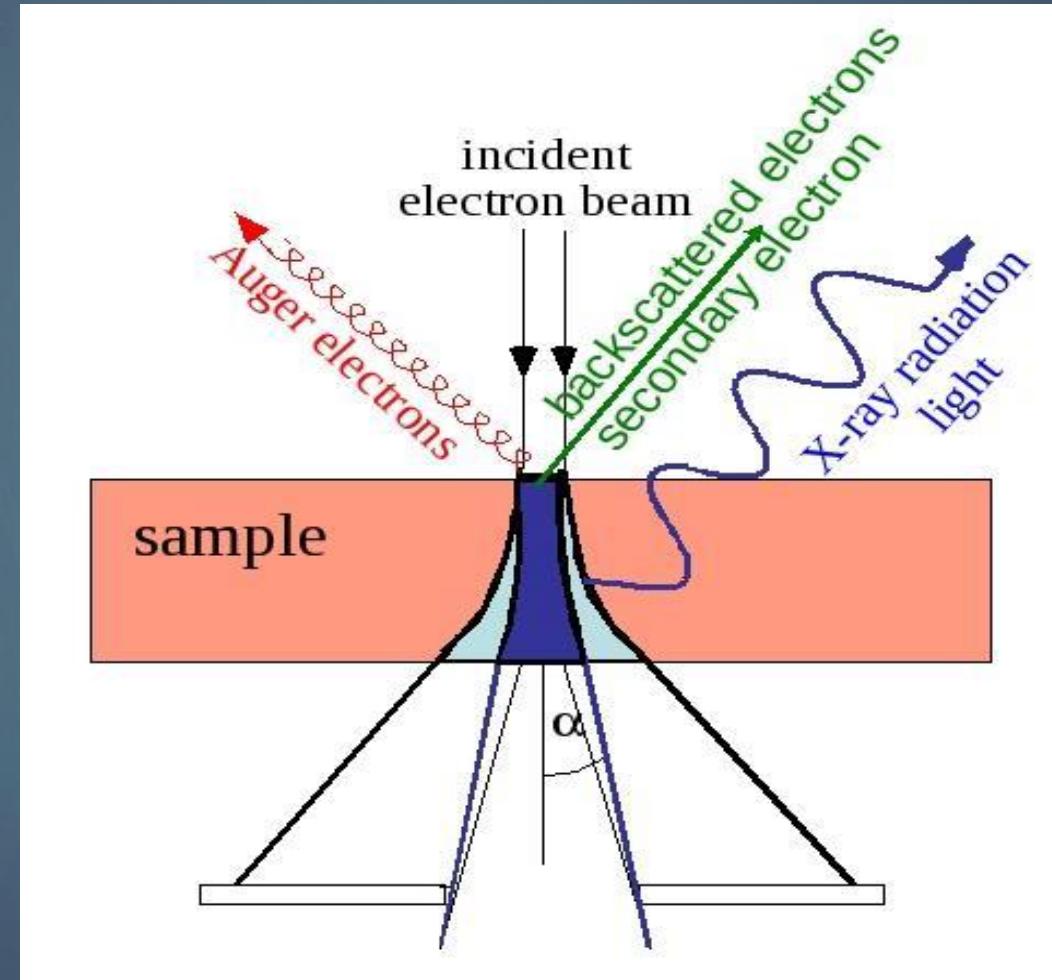
spectrum – background + Resolution Function = Signal



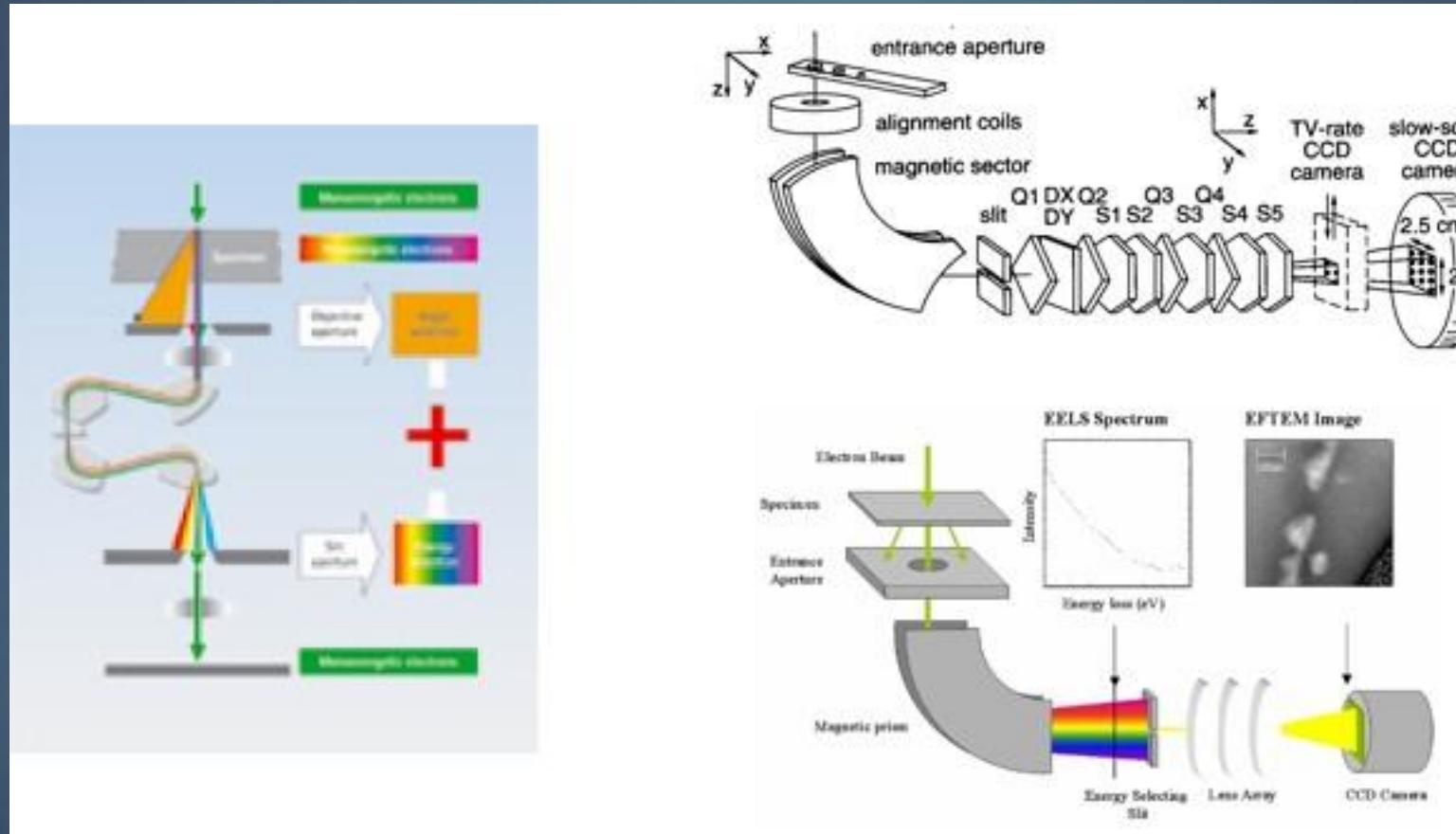
fit Gaussians to spectrum

resolution does not change with elements

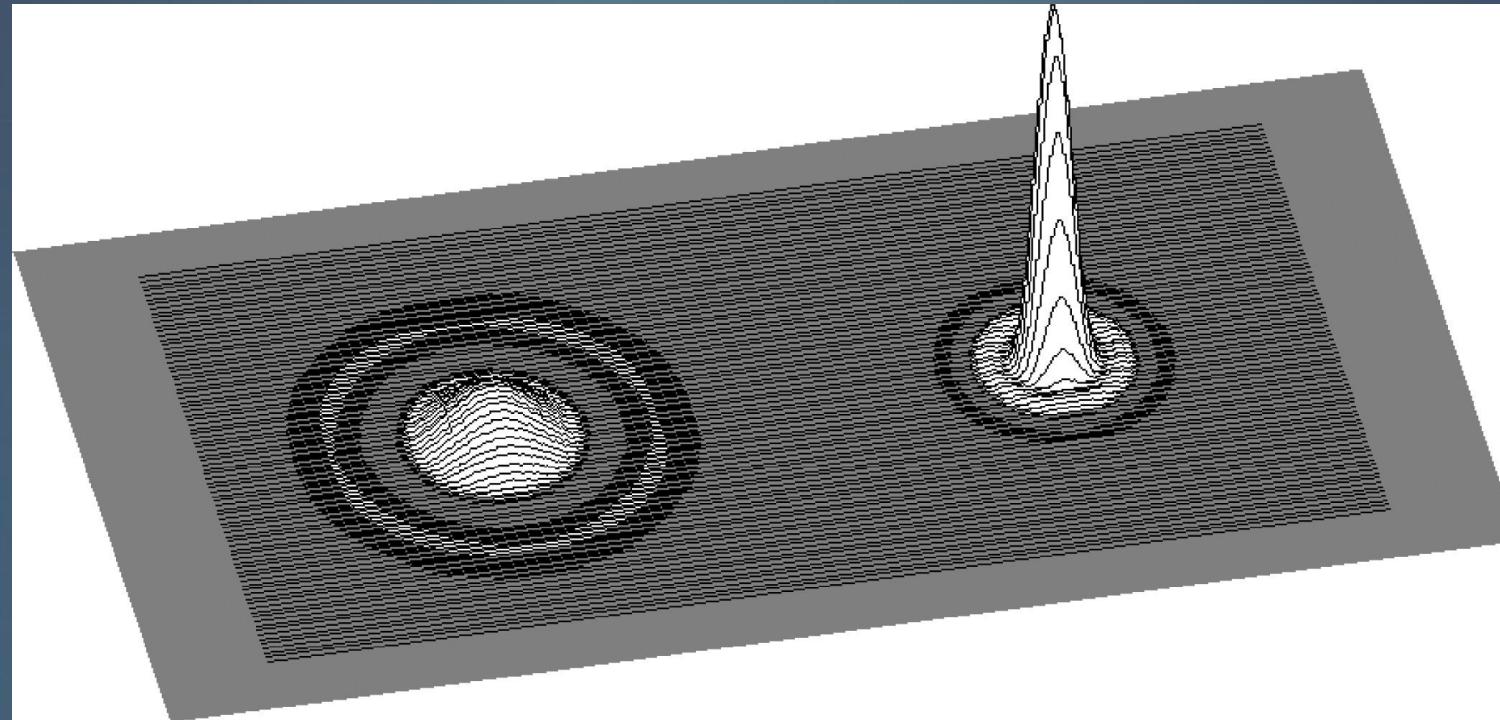
Shoot high energy electron on matter



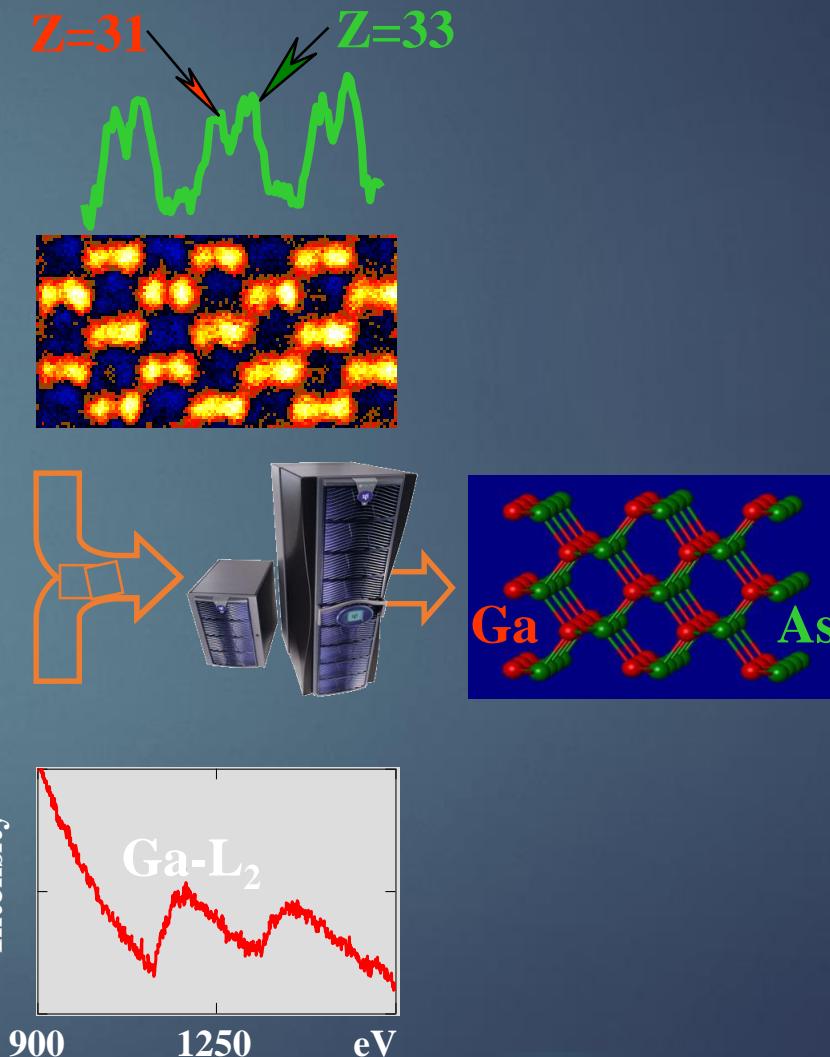
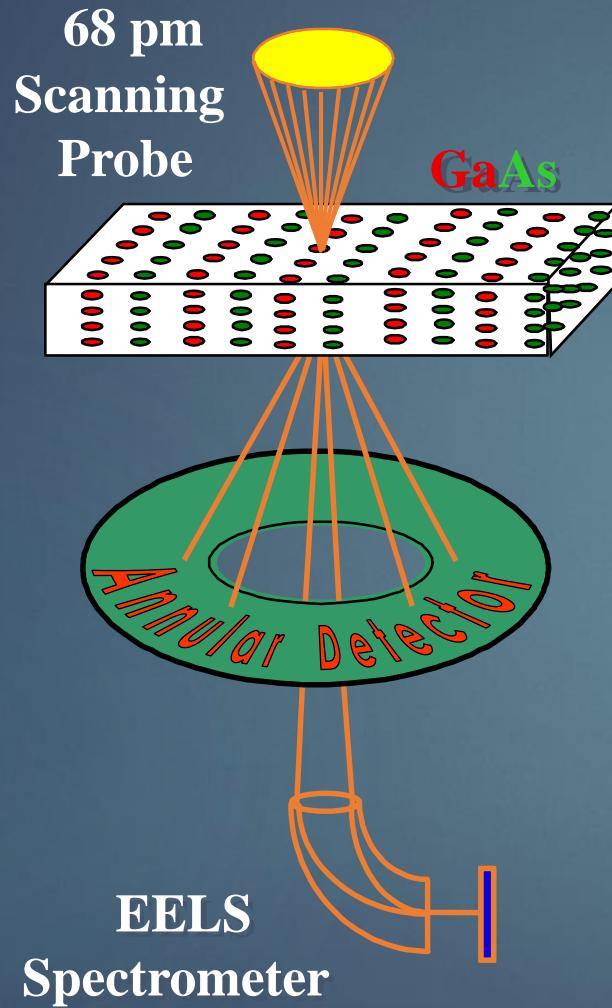
Sorting Electron by Energy



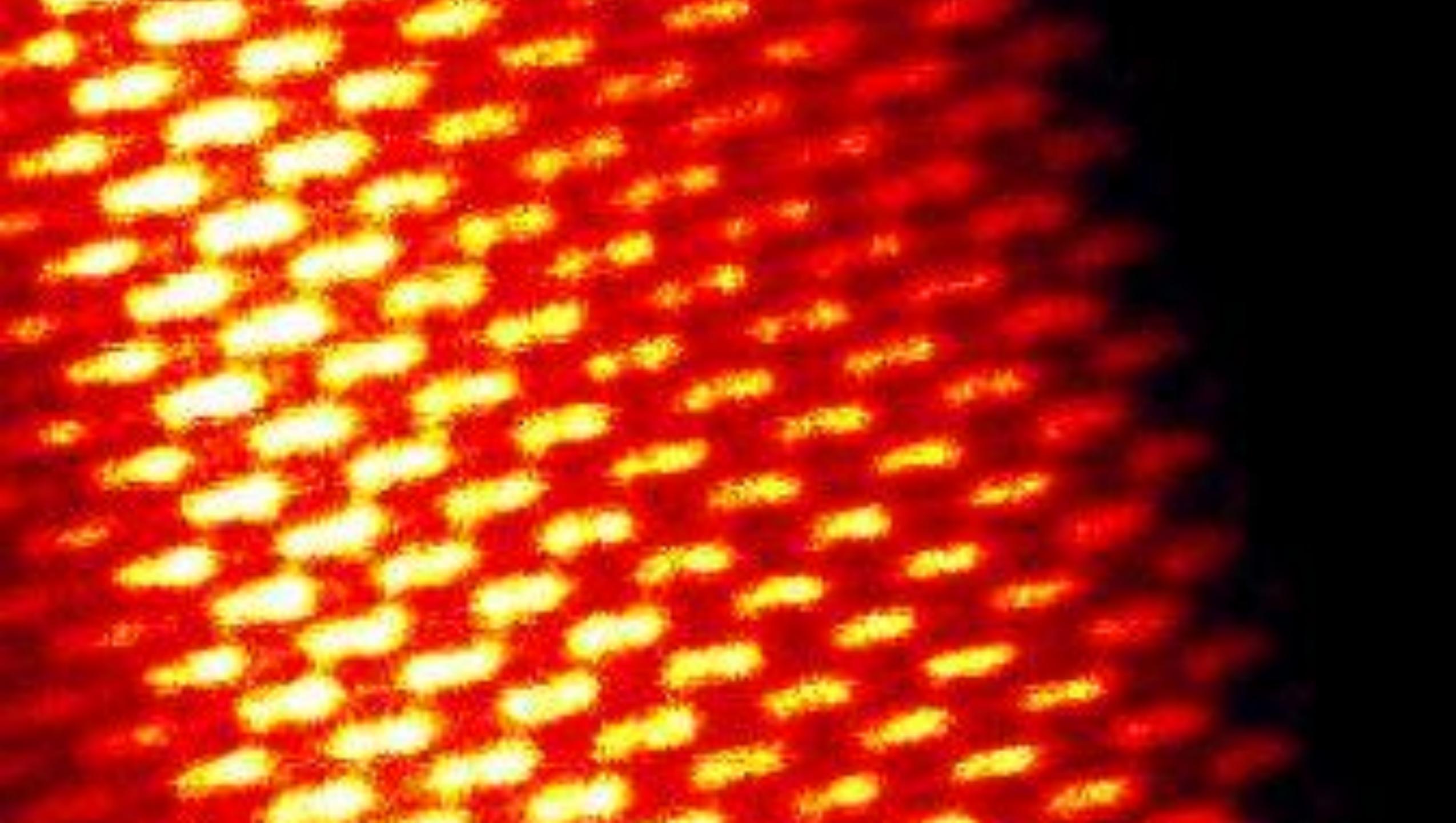
Aberration Correction



Z-Contrast Imaging



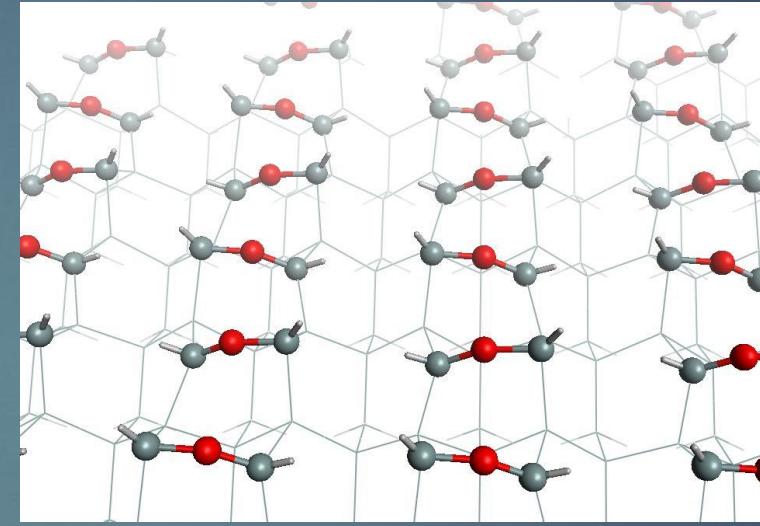
Single Silicon atoms on
graphene



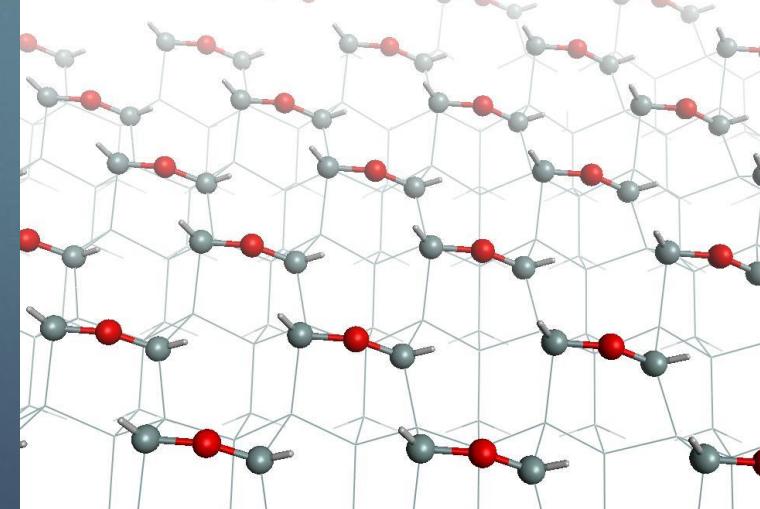
Si/SiO₂ Interface

The First Half Oxygen Layer

Rows



Checkerboard



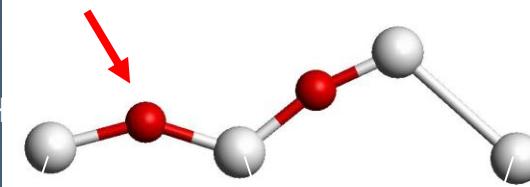
Si/SiO₂ Interface

The First Oxygen Layer

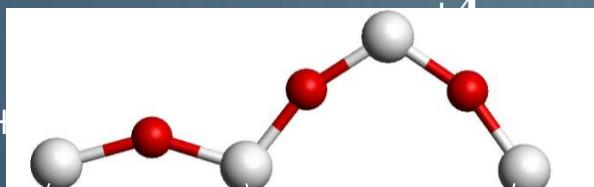
Choice of long bridges:

Quartz and Cristobalite

dimer-like



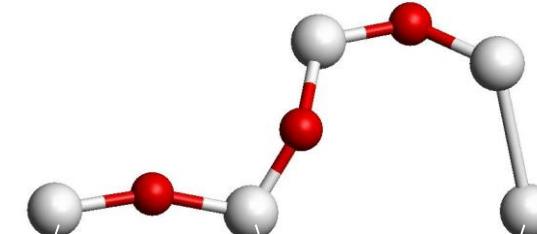
silicon



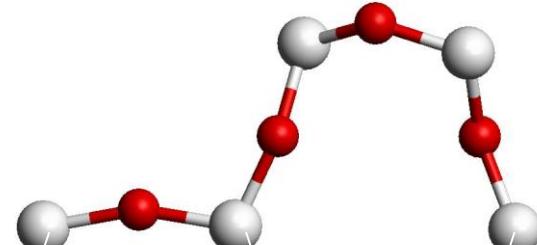
silicon

Tridymite

suboxide



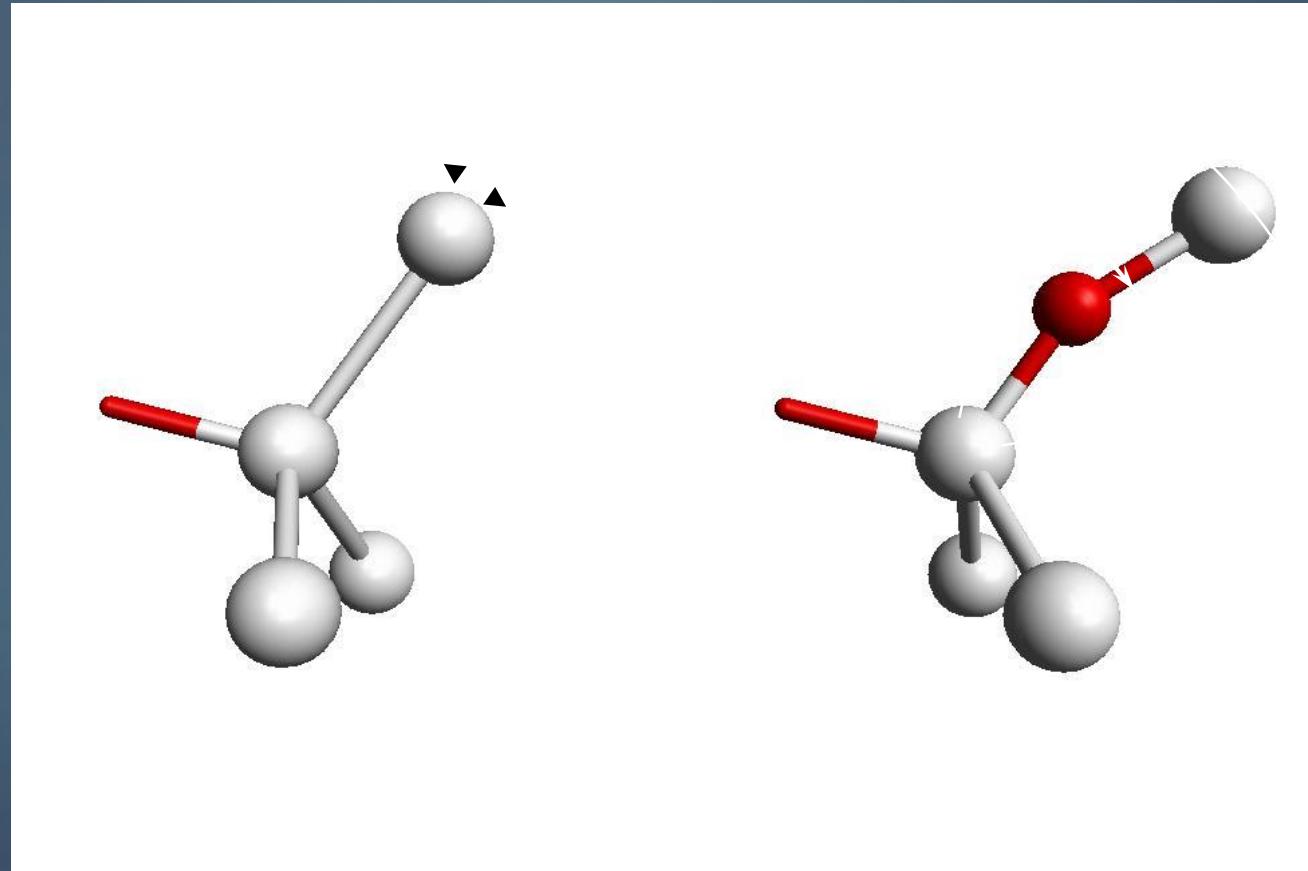
abrupt



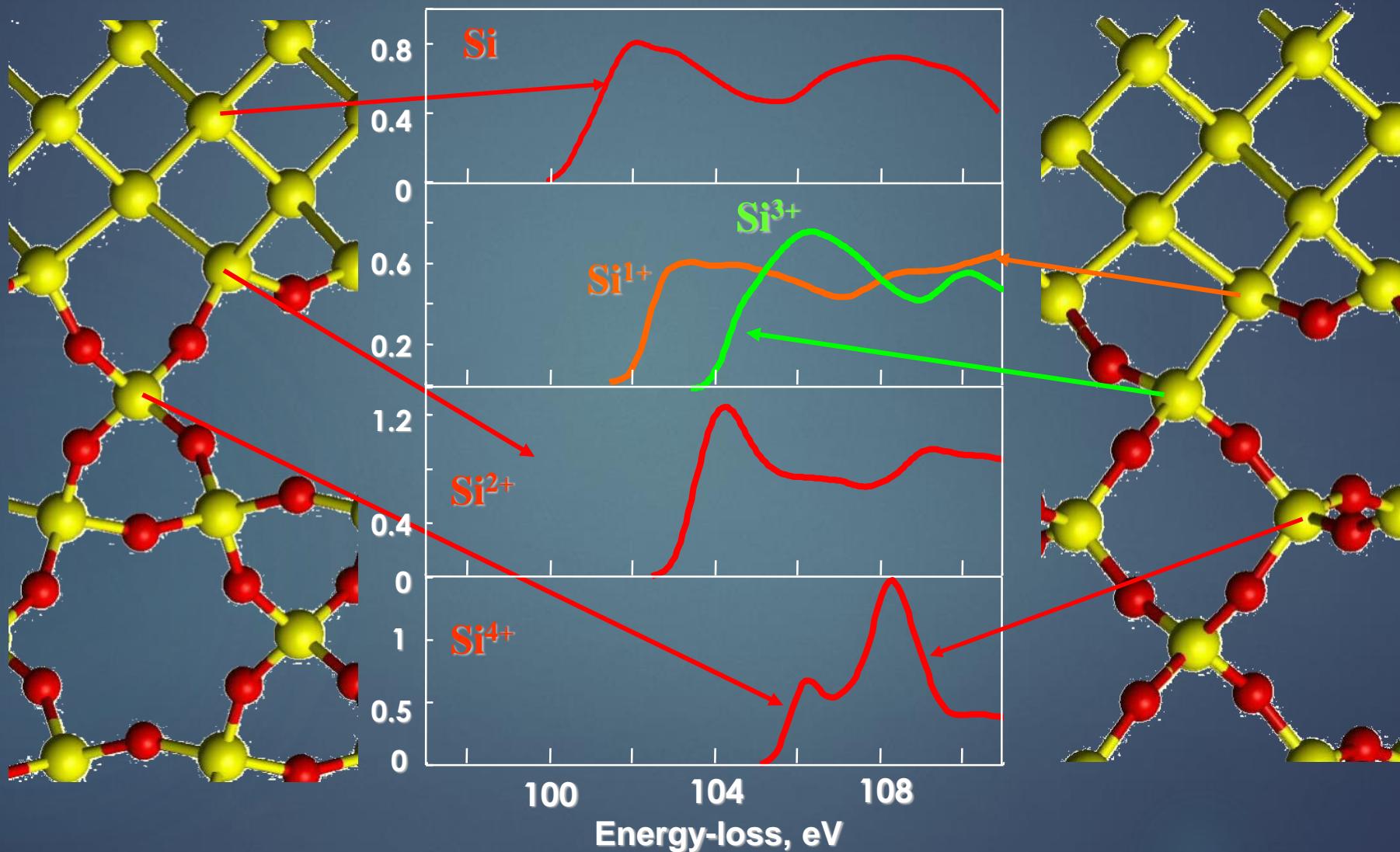
silicon

Si/SiO₂ Interface: Theoretical Results

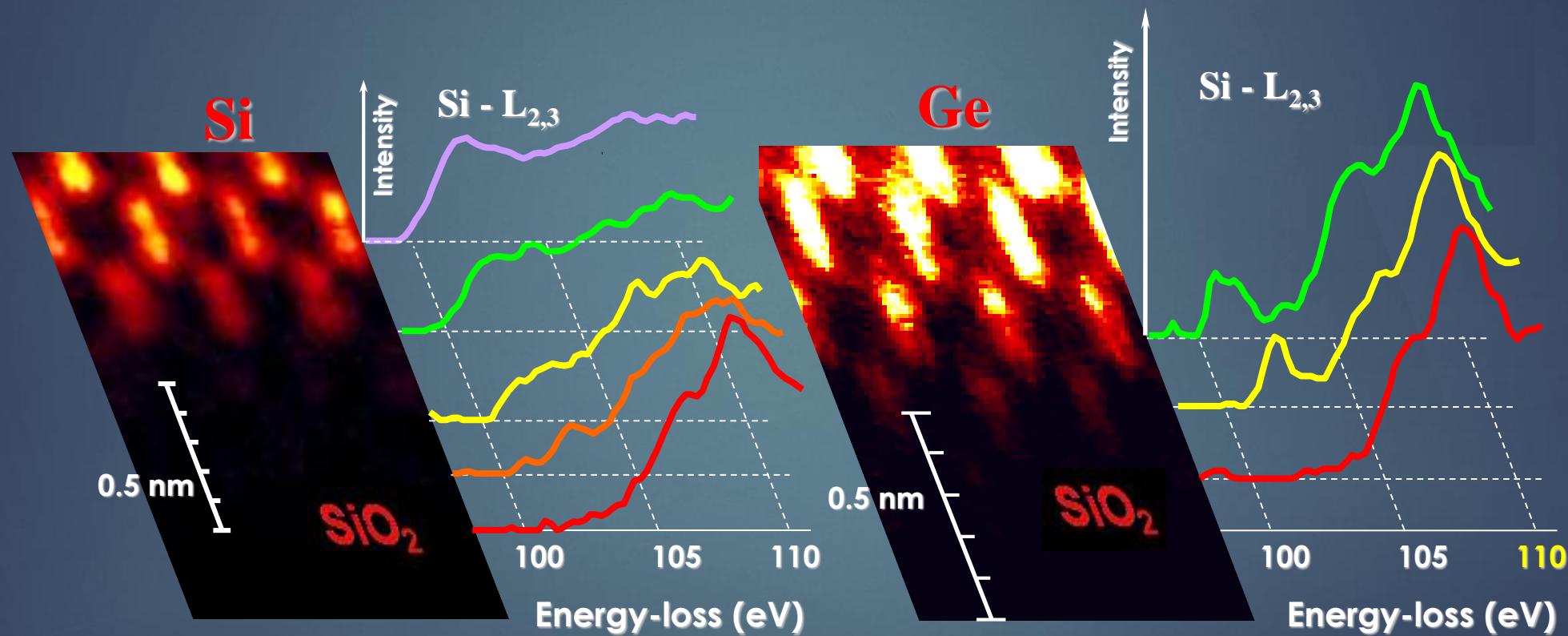
Suboxides cost energy



Calculated Si-L_{2,3} Edges at Si/SiO₂

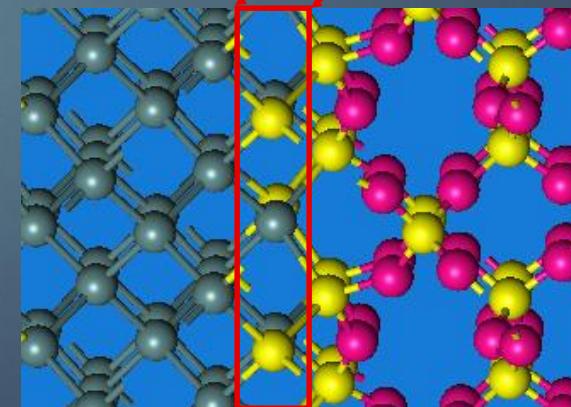
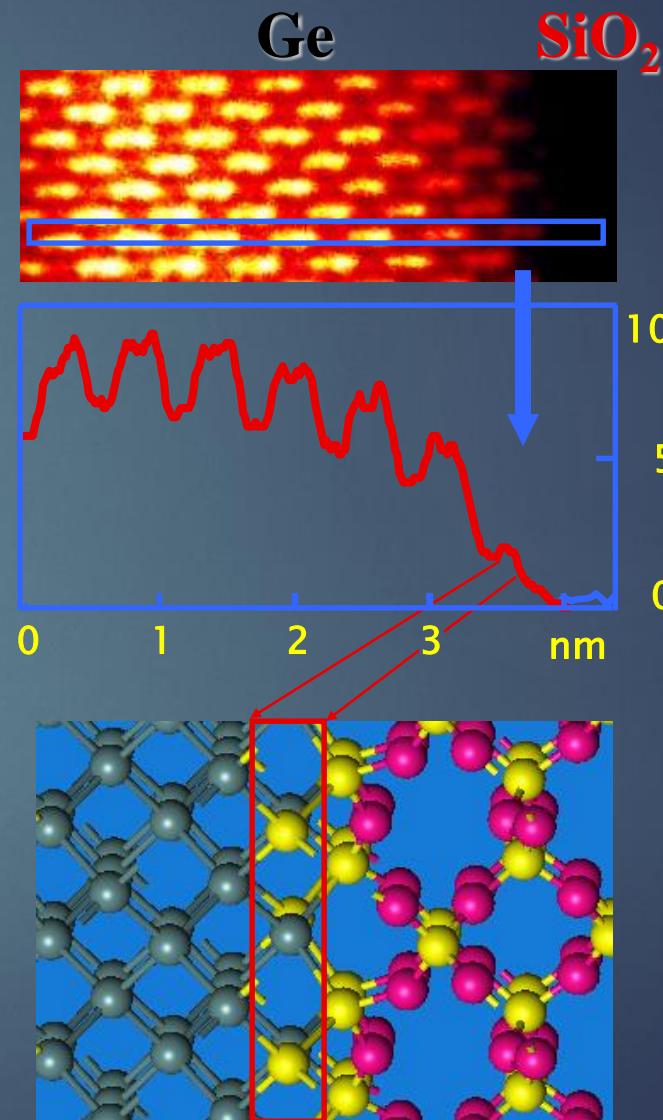


Si/SiO₂ vs. Ge/SiO₂ Atomic Resolution EELS

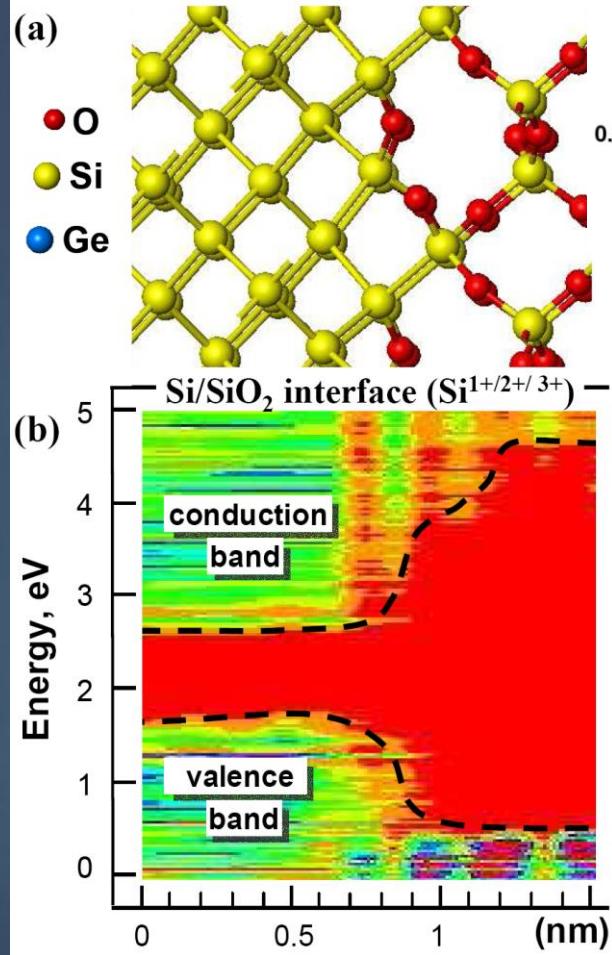


Ge/SiO₂ Interface

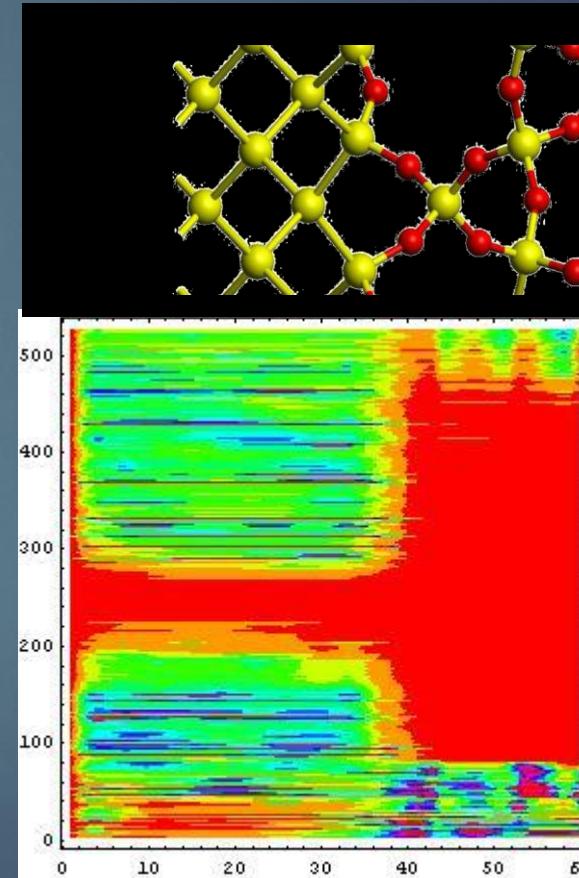
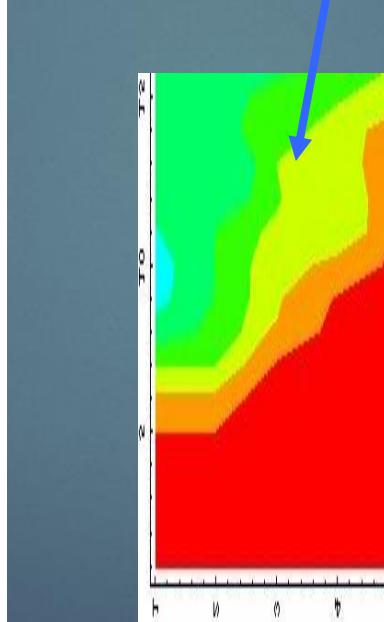
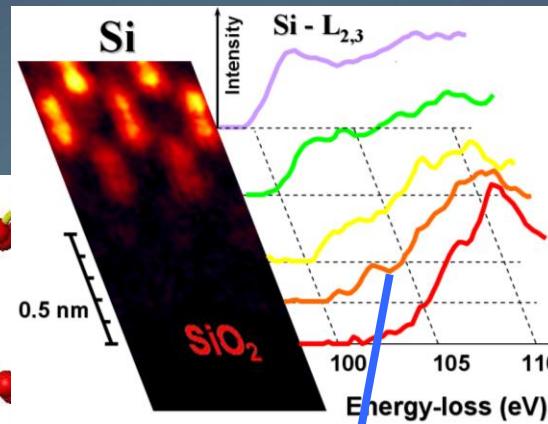
- One layer with significant Ge reduction as transition layer.
- Just one layer of Si²⁺ before stoichiometric SiO₂.
- This is consistent with atomically abrupt interface.



Relevant ?

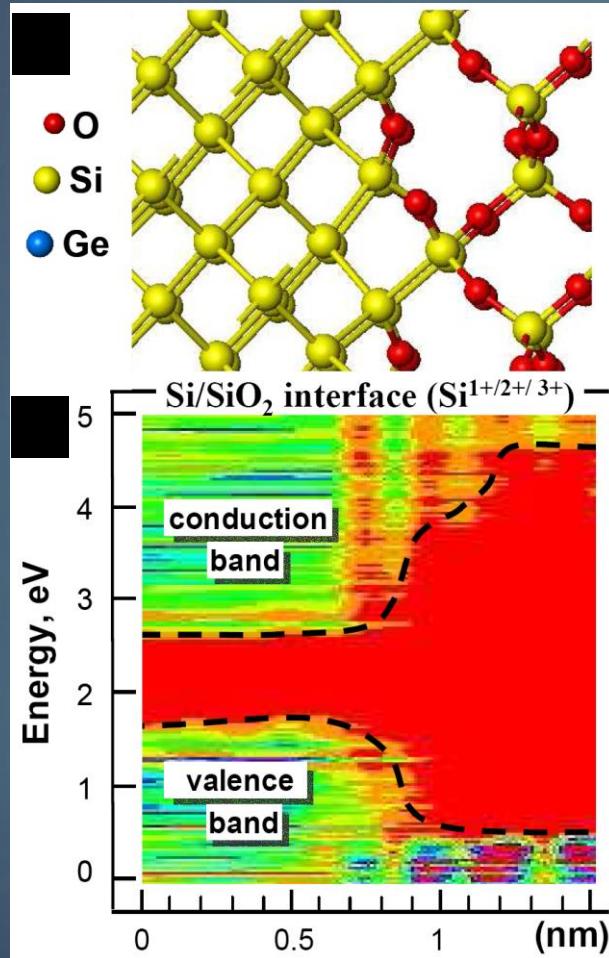


Suboxide

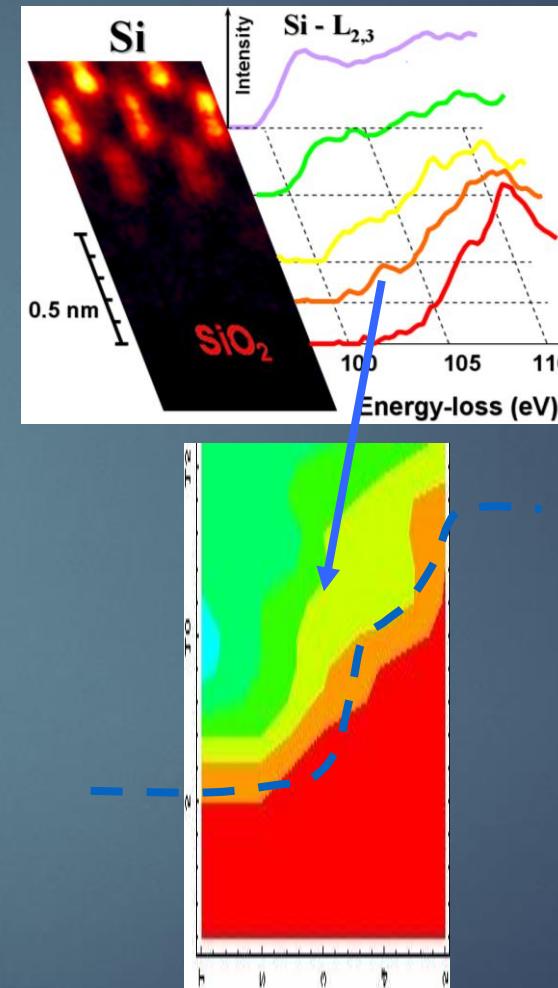


Abrupt oxide

Comparison of Experimental and Theoretical Conduction Band

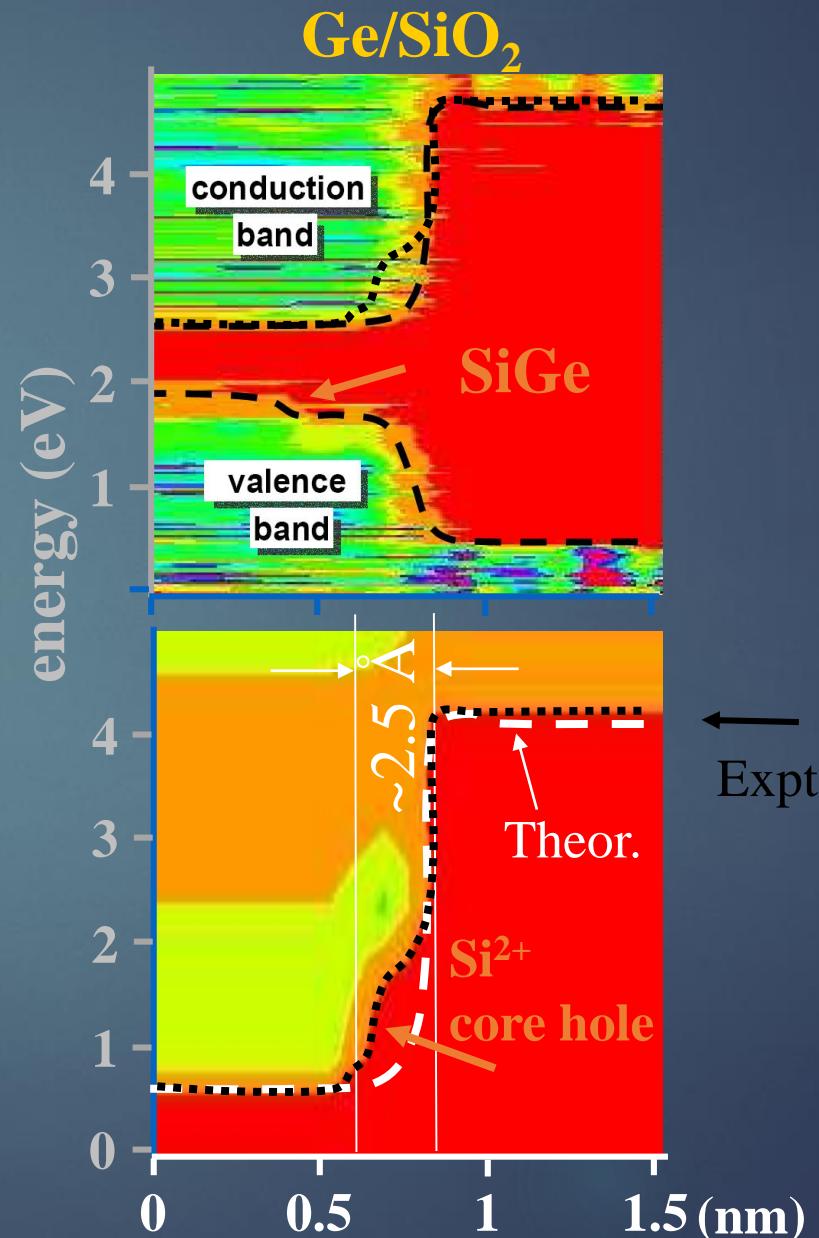
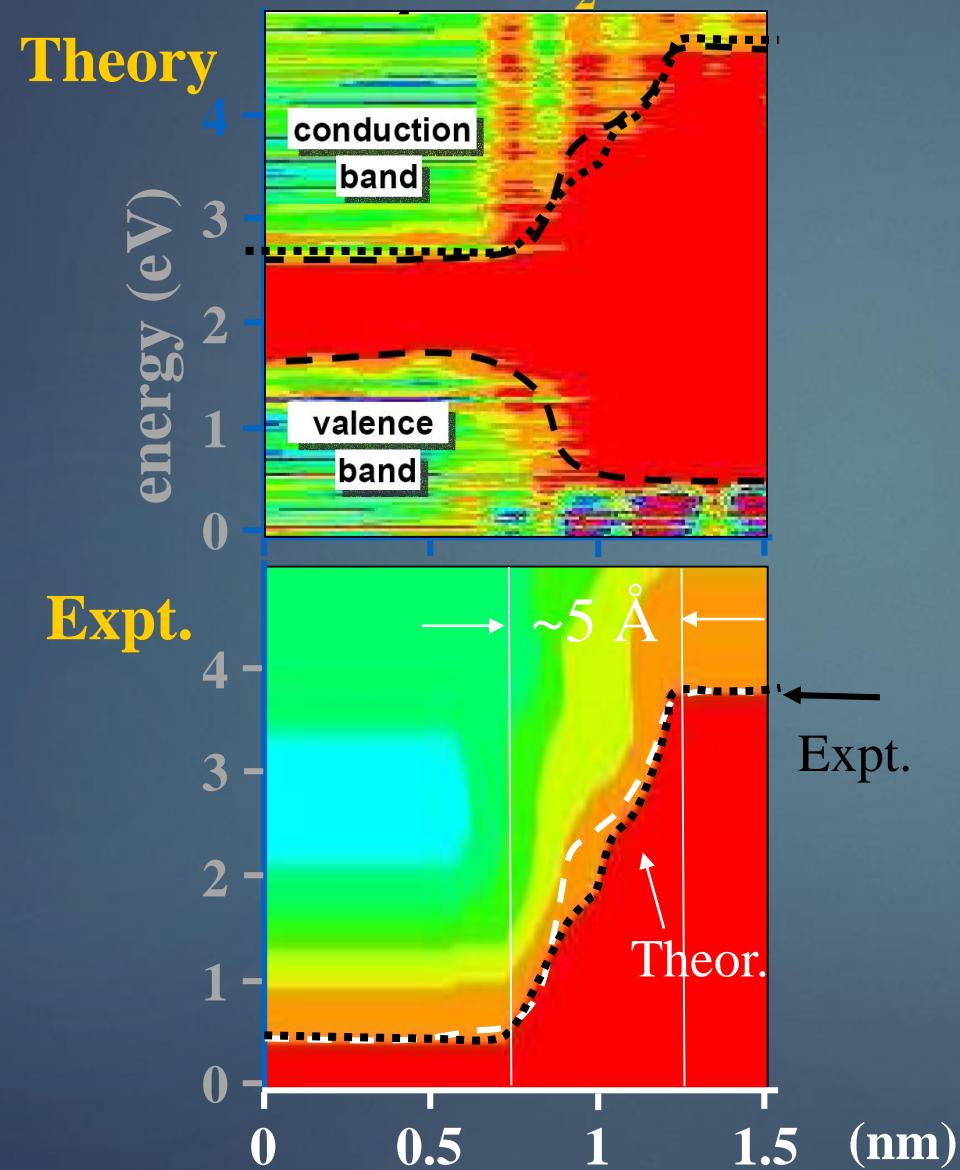


Theoretical

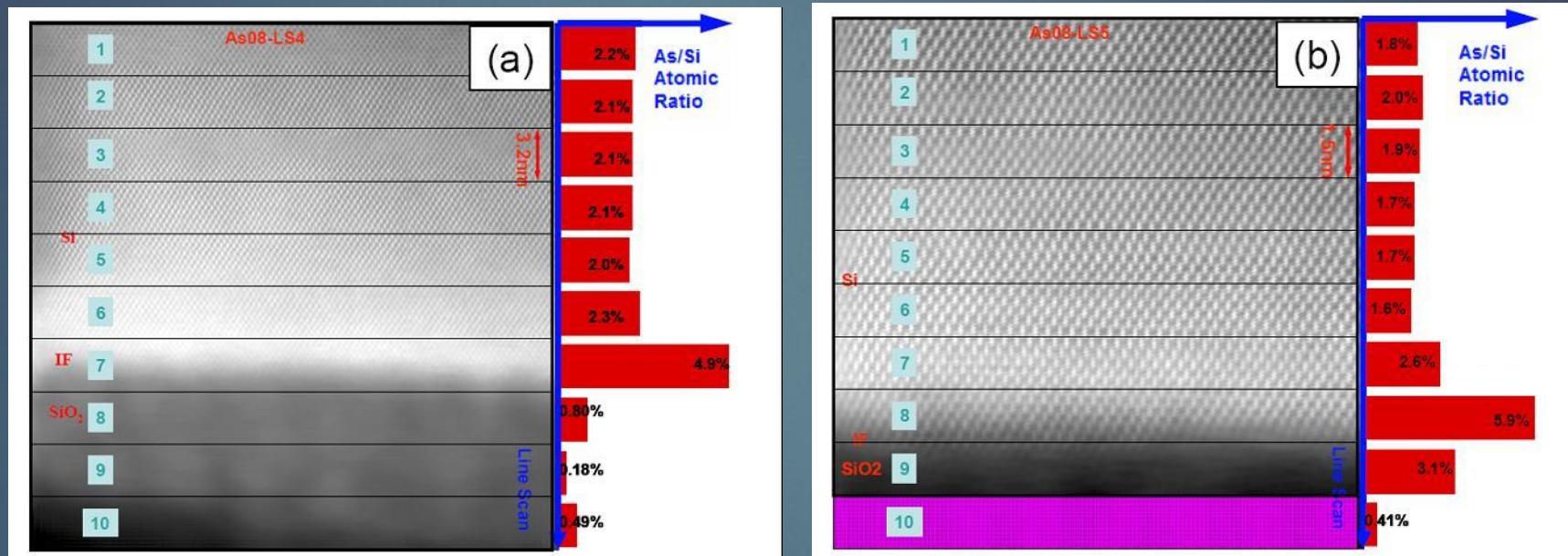


Experimental

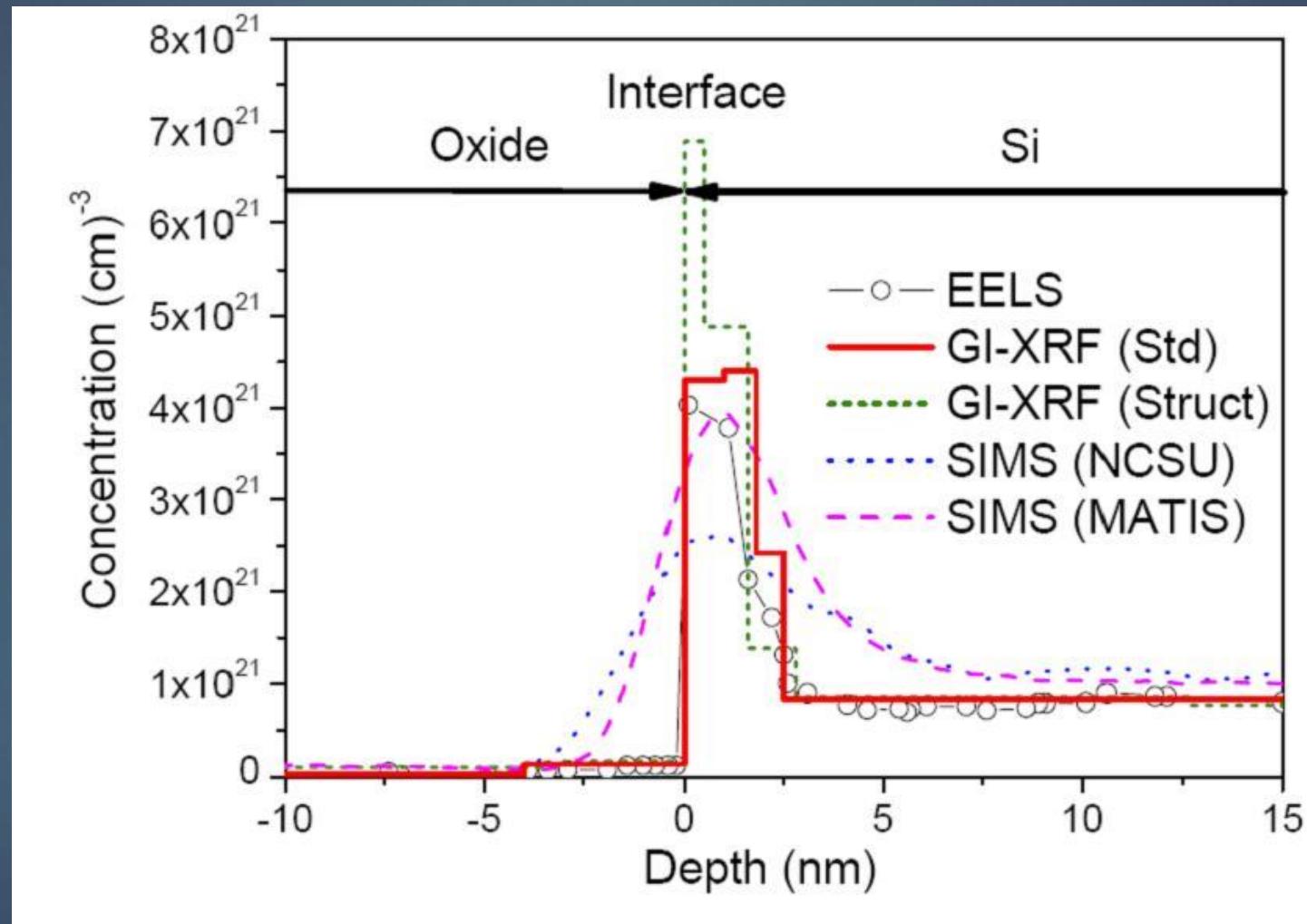
Comparison of Conduction Band Course Si/SiO_2

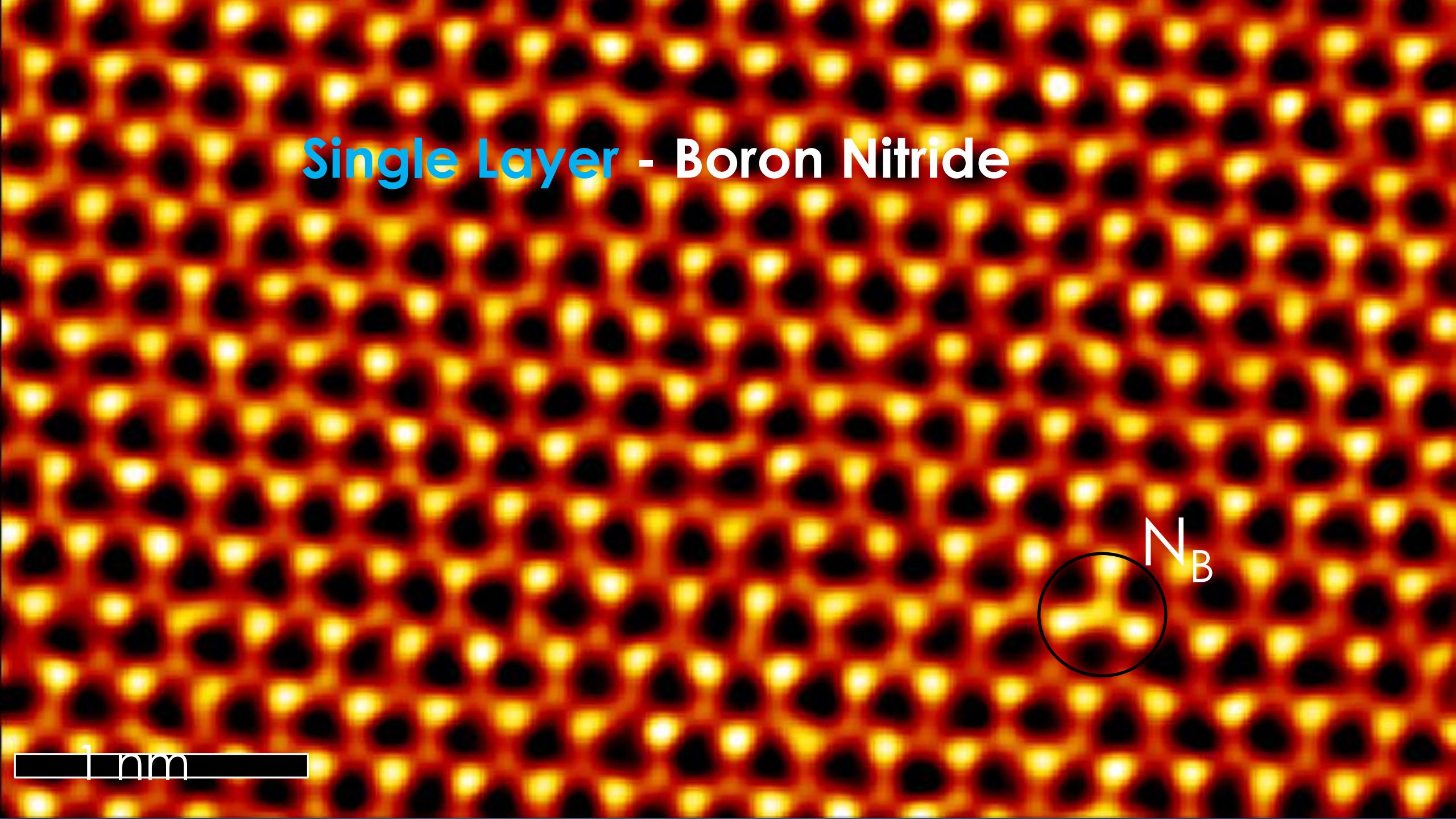


As Detection in Silicon



Arsenic Doping Profile





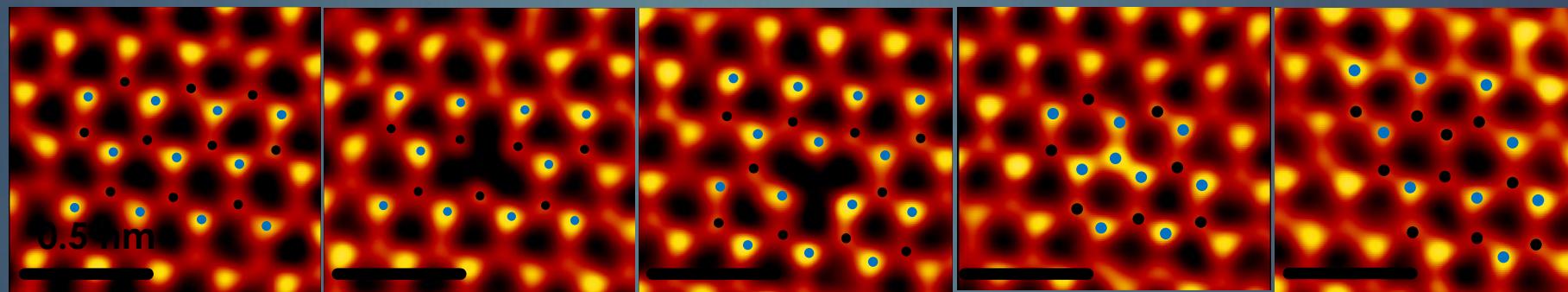
Single Layer - Boron Nitride

N_B

1 nm

Counting Point Defects in CVD-Grown BN

Perfect Atom Sites	N Vacancies	B Vacancies	N Antisites	B Antisites
303,874	68	276	228	53



$$N_N/N_B = 1.004 + \text{charge neutrality}$$

$$\triangleright E_F(1040^\circ\text{C}) = 2.59 \text{ eV}; B_N^0, N_B^0, V_B^-, V_N^+$$

$$(V_B, N_B) > (V_N, B_N)$$

Summary

- ▶ Many Instruments
- ▶ Many Techniques
- ▶ Many Possibilities

Use the cool TEMs in your neighborhood.
It is fun !