# Atom-by-Atom Analysis by Aberration-Corrected STEM*

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in collaboration with
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*and*

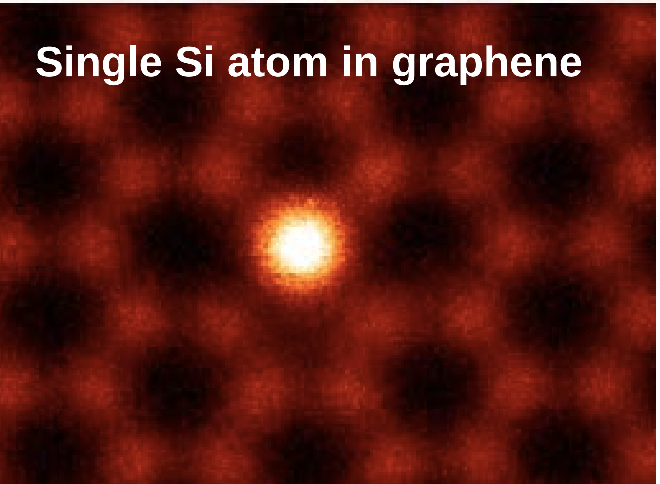
Phil Batson, Mick Brown, Ray Carpeneter, Matt Chisholm, Christian Colliex,
Lena Fitting, Juan Carlos Idrobo, Vladimir Kolarik, David Muller, Julia Mundy,
Valeria Nicolosi, Steve Pennycook, Tim Pennycook, Quentin Ramasse,
Kazu Suenaga, Wu Zhou, and many others

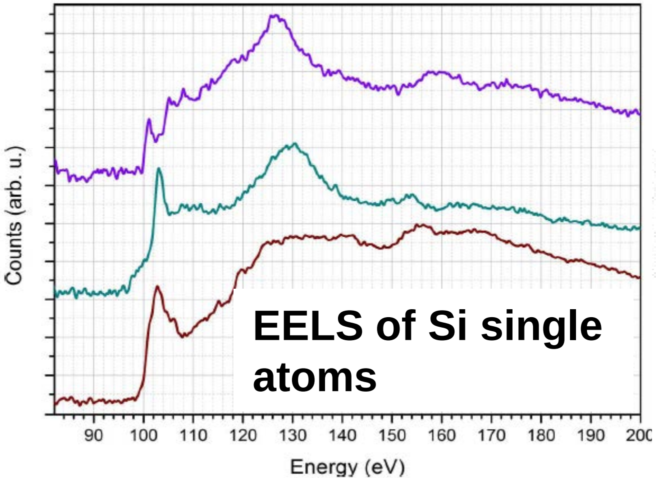
**scanning transmission electron microscopy*

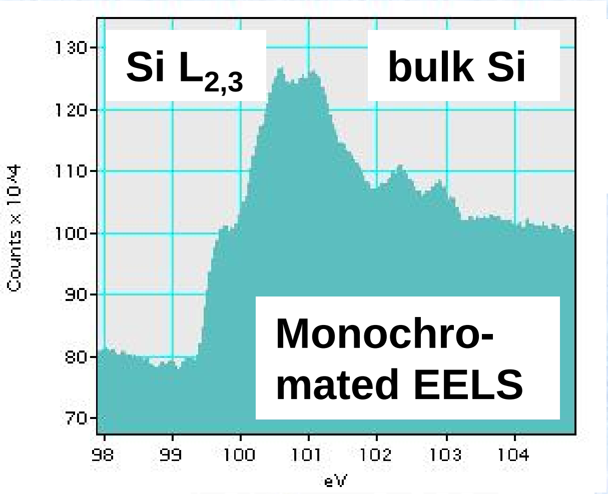
***FCMN, 2013-03-26***

# Talk outline

- Aberration-corrected STEM: a tool for probing atoms
- Imaging and analyzing single atoms
- New monochromator (MC) for meV-resolution spectroscopy
- First results from the MC EELS system
- Summary





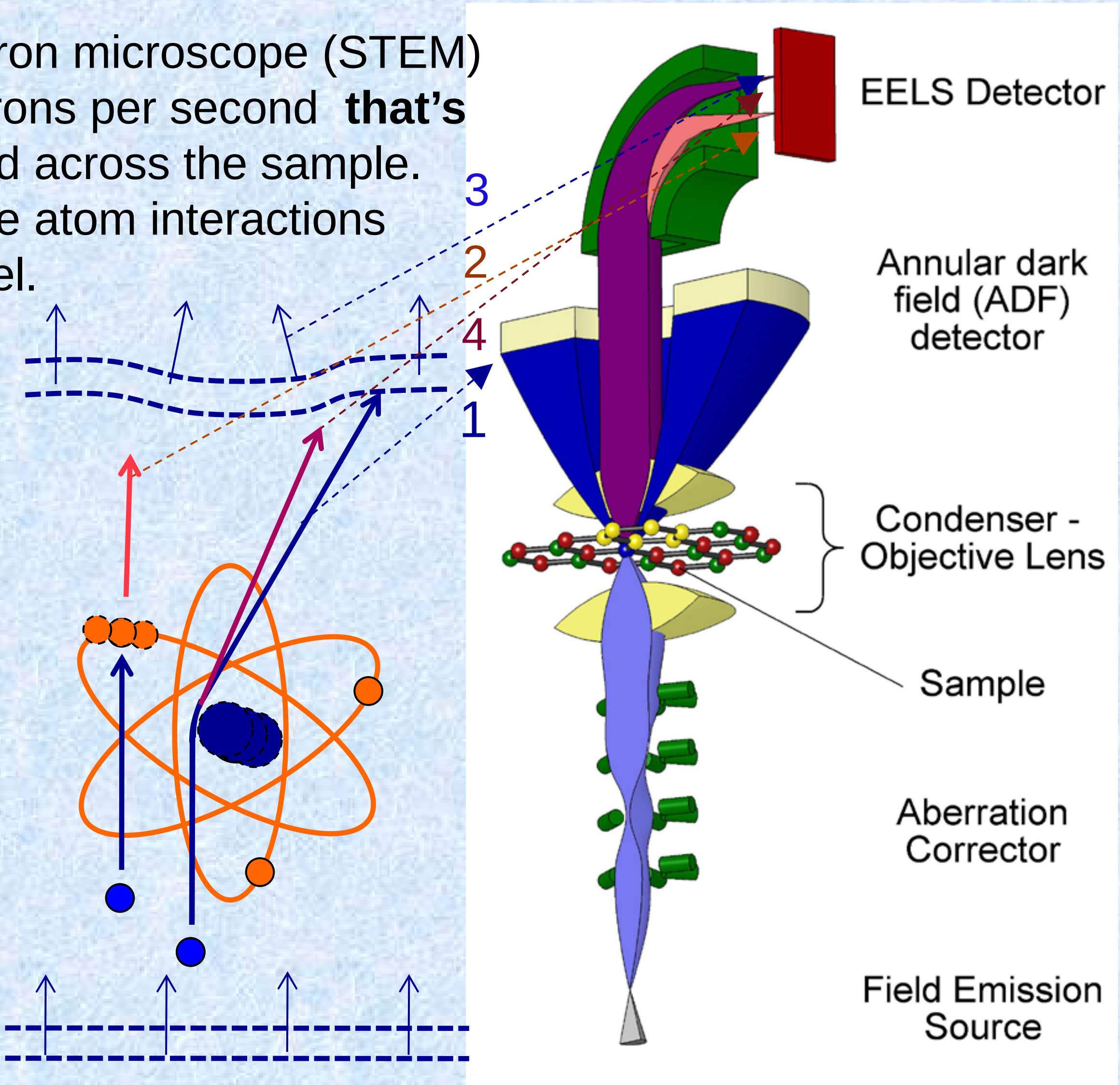


# STEM - an instrument for imaging and analyzing atoms

In the scanning transmission electron microscope (STEM) an electron probe with $\sim 10^{10}$ electrons per second **that's smaller than one atom** is scanned across the sample. Many types of fast electron – single atom interactions can be detected, typically in parallel.

Key **primary** signals and *detectors*:

1) **Elastic scattering** from the atomic nucleus (Rutherford scattering): *high angle ADF*
2) **Inelastic scattering** from electrons: *electron energy loss spectrometer* (*EELS*)
3) **e- wavefront reconstruction** (holography): *2D camera*
4) **Inelastic scattering from the nucleus**: *high resolution EELS*



# STEM - an instrument for imaging and analyzing atoms

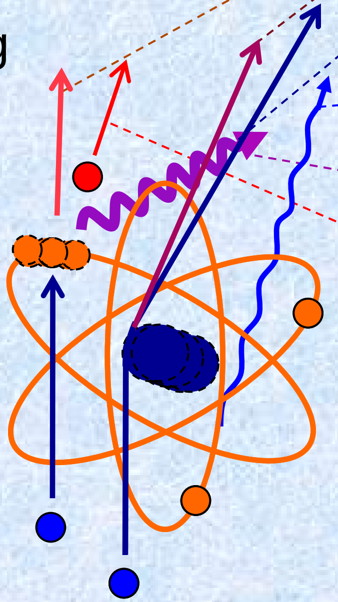
An electron probe with ~$10^{10}$ electron per second **that's smaller than an atom** is formed and scanned across the sample.
Many types of fast electron – single atom interactions can be detected, typically in parallel.

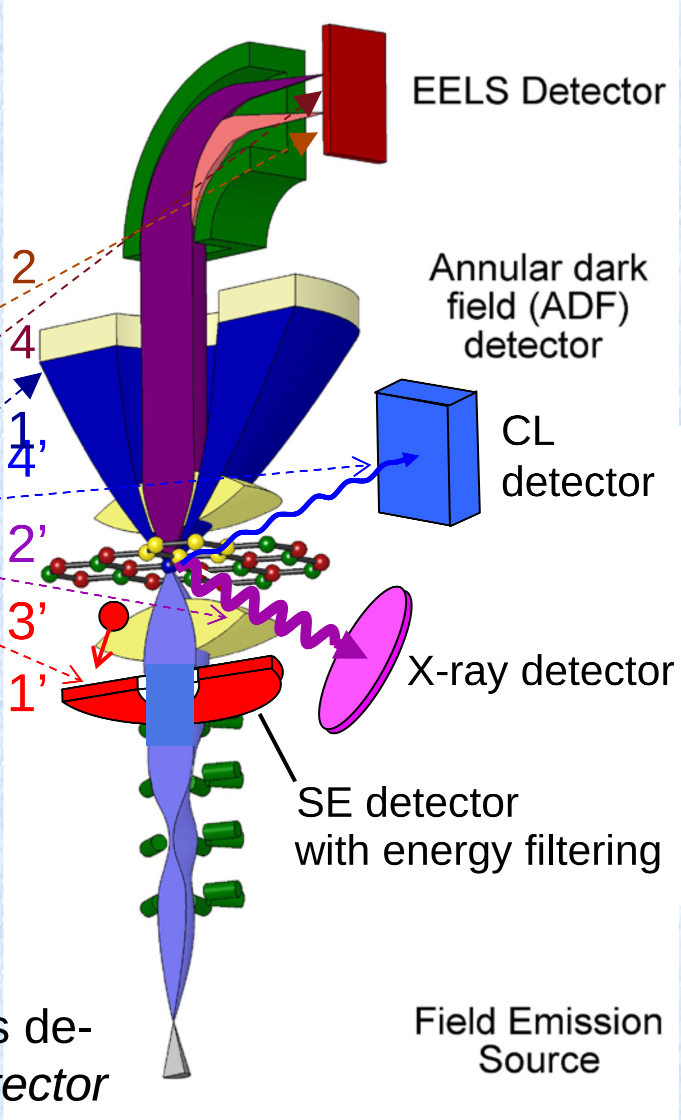
Key **secondary** signals and *detectors*:

1') **Secondary electrons (SE)** arising from various scattering processes: *low-energy electron detector*

2') **X-rays** arising from de-excitation of inner shell hole: *X-ray spectrometer (EDXS, WDS)*

3') **Auger electrons** arising from de-excitation of inner shell hole: *low-energy electron detector*





4') **Optical, infrared + UV photons** arising from various de-excitation processes: *cathodoluminescence (CL) detector*

There are many signals, and they can mostly be detected in parallel.

nion

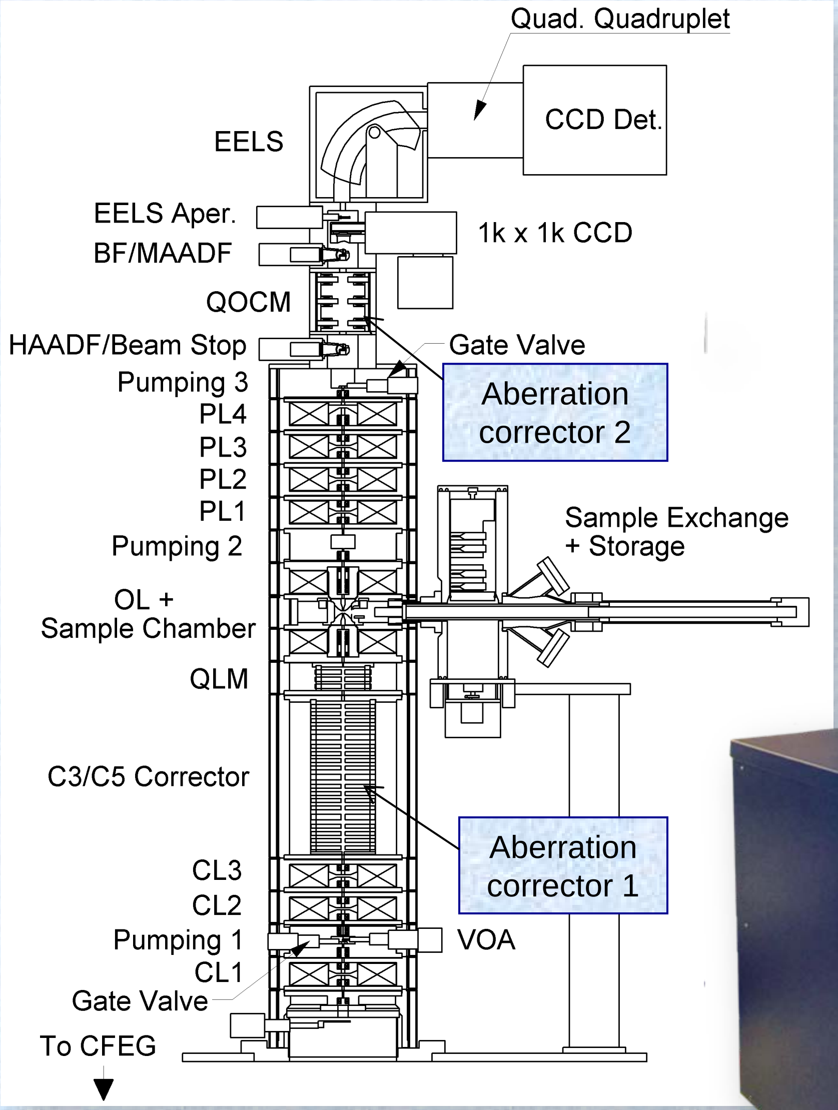
# Many signals, one microscope: Nion UltraSTEM™

Fully modular (all lenses, the corrector, etc., are independent modules, with identical mechanical interfaces) and thus very flexible.

UHV at the sample:
*no contamination*

ultra-high stability:
*no probe jitter*

ultra-bright gun (true CFEG – not Schottky):
*fast imaging (single atoms imaged at TV rate) and analysis*

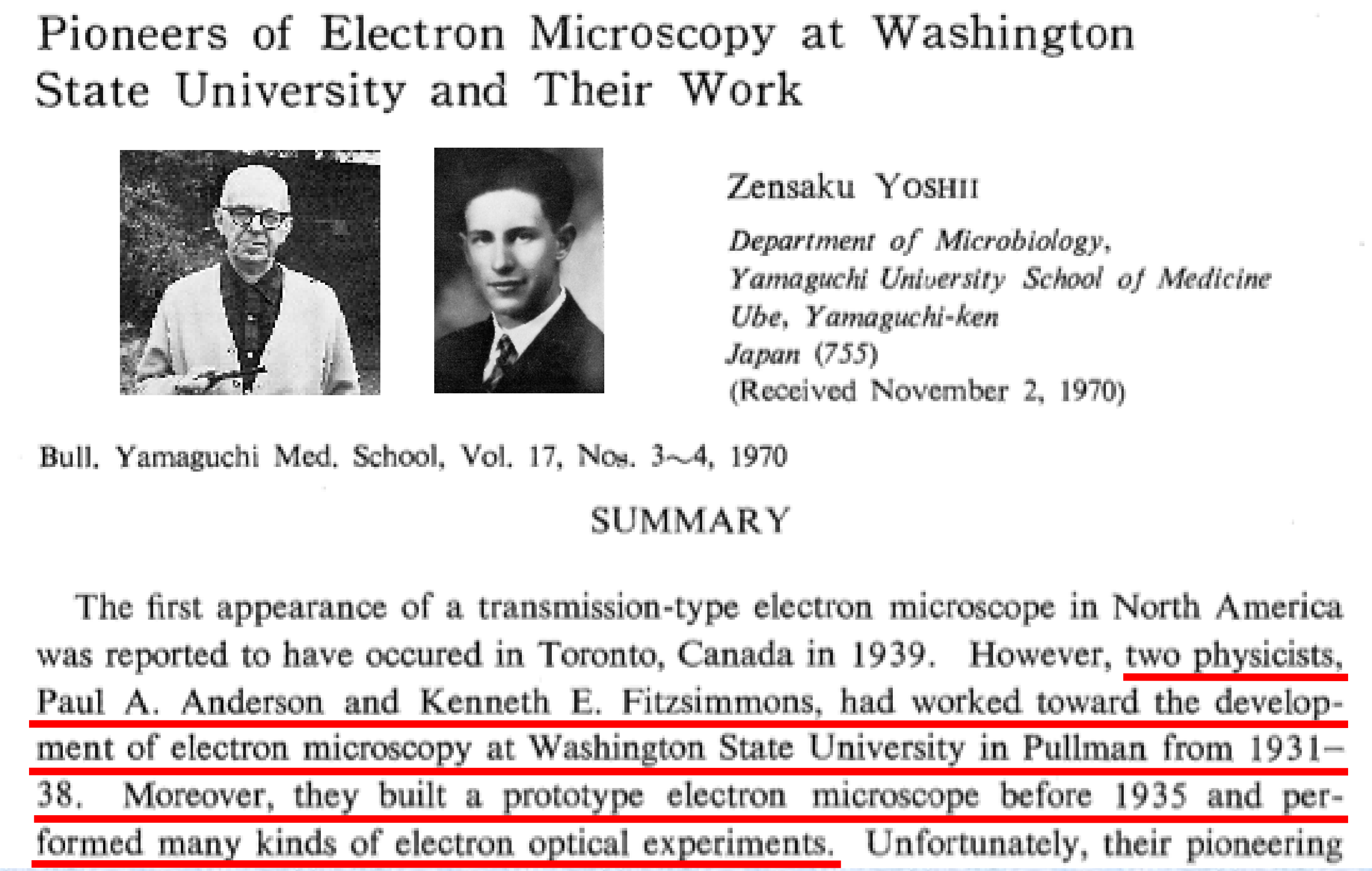


UltraSTEM200*

Described in: *Krivanek et al. Ultramicroscopy* ***108*** *(2008) 179-195 and Dellby et al. EPJAP 2011.* More info at www.nion.com.

*instrument shown:
CNRS Orsay, France

# Washington state, USA: 1st EM outside of Europe…



## Pioneers of Electron Microscopy at Washington State University and Their Work

Zensaku Yoshii

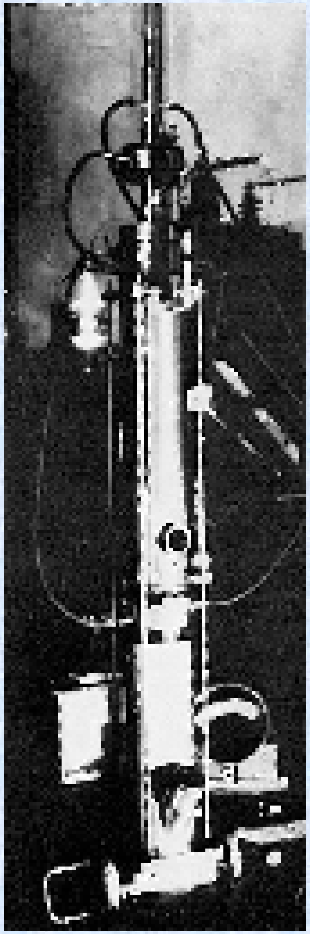
*Department of Microbiology,*
*Yamaguchi University School of Medicine*
*Ube, Yamaguchi-ken*
*Japan* (755)

(Received November 2, 1970)

Bull. Yamaguchi Med. School, Vol. 17, Nos. 3～4, 1970

### SUMMARY

The first appearance of a transmission-type electron microscope in North America was reported to have occured in Toronto, Canada in 1939. However, two physicists, Paul A. Anderson and Kenneth E. Fitzsimmons, had worked toward the development of electron microscopy at Washington State University in Pullman from 1931–38. Moreover, they built a prototype electron microscope before 1935 and performed many kinds of electron optical experiments. Unfortunately, their pioneering



Washington State EM history continued:

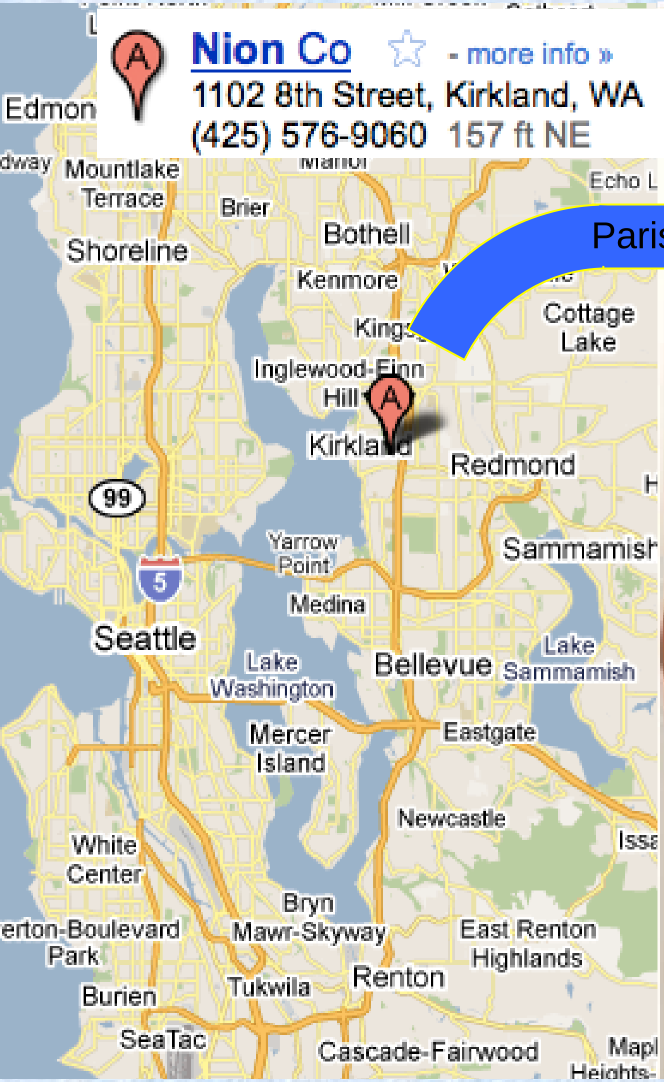
1998: Nion Co. started (in Kirkland, WA).

2000: Nion builds the first commercial EM aberration corrector in the world.

2008: Nion builds a whole STEM.

2012: Nion builds a monochromated STEM able to do 30 meV resolution EELS.

# Washington state, USA: $1^{st}$ EM outside of Europe…



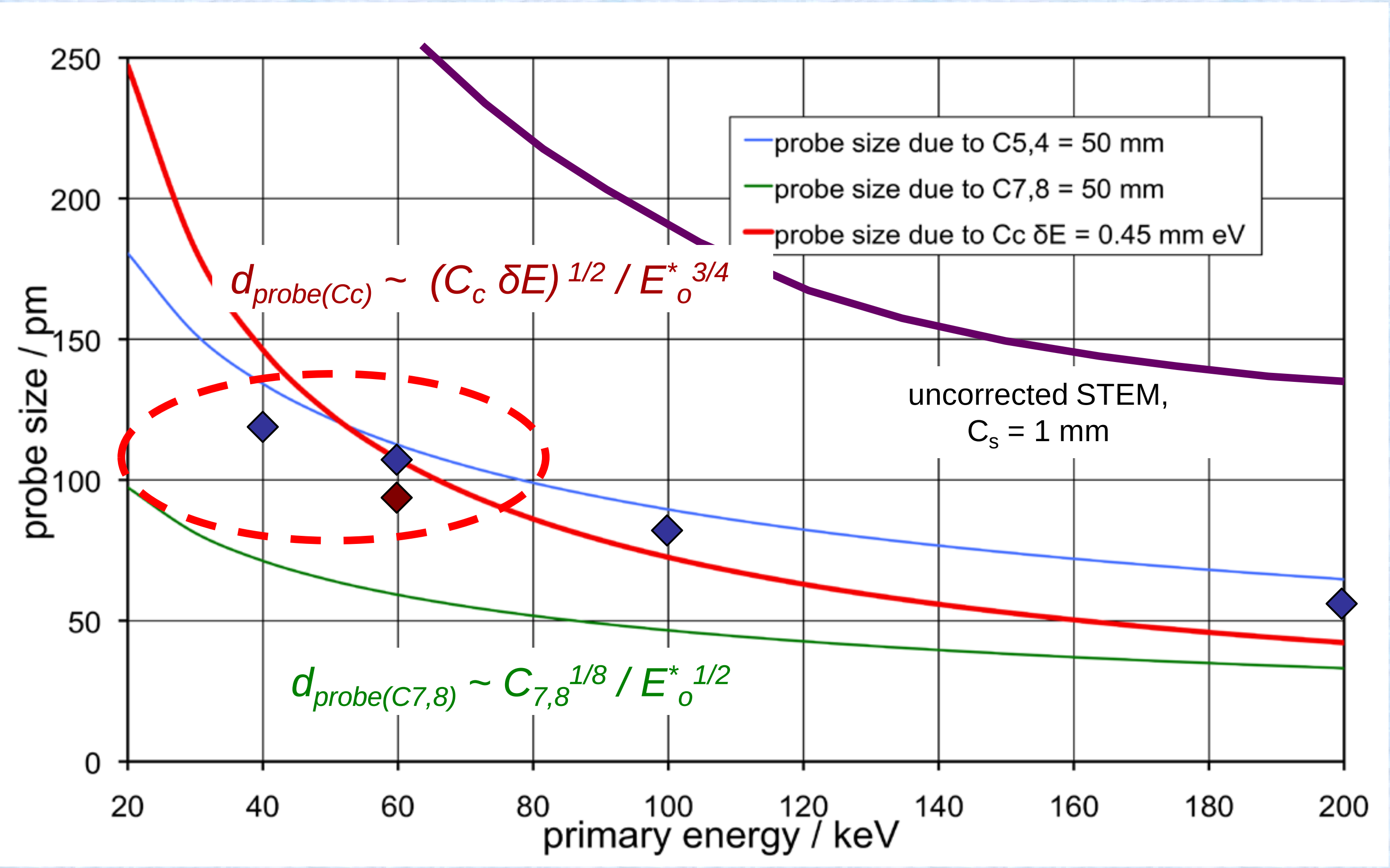
**Nion Co** - more info »
1102 8th Street, Kirkland, WA
(425) 576-9060 157 ft NE

Paris, France

Members of the Orsay group and Nion's Niklas Dellby with Orsay's Nion UltraSTEM™ 200.
from left: Niklas Dellby, Christian Colliex, Odile Stephan, Katia March, Marcel Tence

…and now the supplier of advanced aberration-corrected STEMs to the world

# STEM probe size in the aberration-corrected era



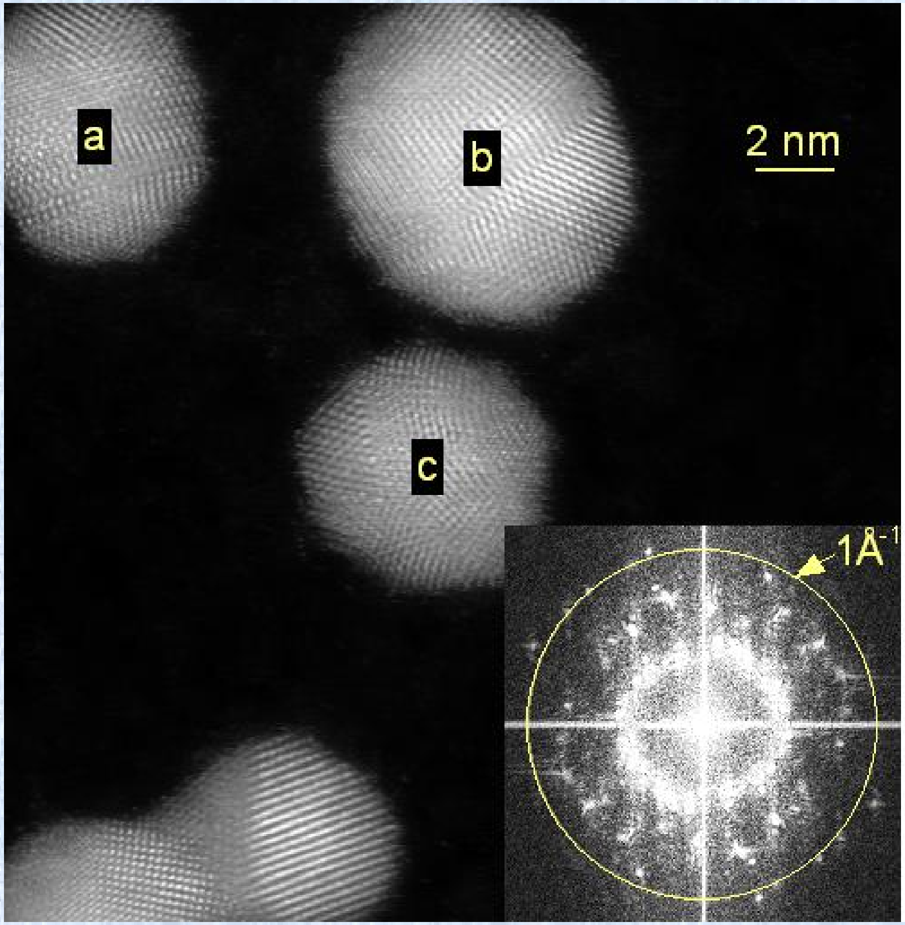
Graph shows probe size for probe current $I_p$ = 0.25 $I_c$

$I_c$ = coherent probe current (~0.1-0.4 nA for CFEG)

- ◆ resolutions reached in the Nion column at different kVs
- ◆ resolution reached with Nion MC

◯ Area of great current interest: beam energies which eliminate knock-on radiation damage.

# High stability of Nion's aberration-corrected STEM : Au particles imaged 18 hours apart



ASU Nion UltraSTEM100MC HAADF image recorded on 1/27/2013 5:52:00 PM monochromator off, 100 keV

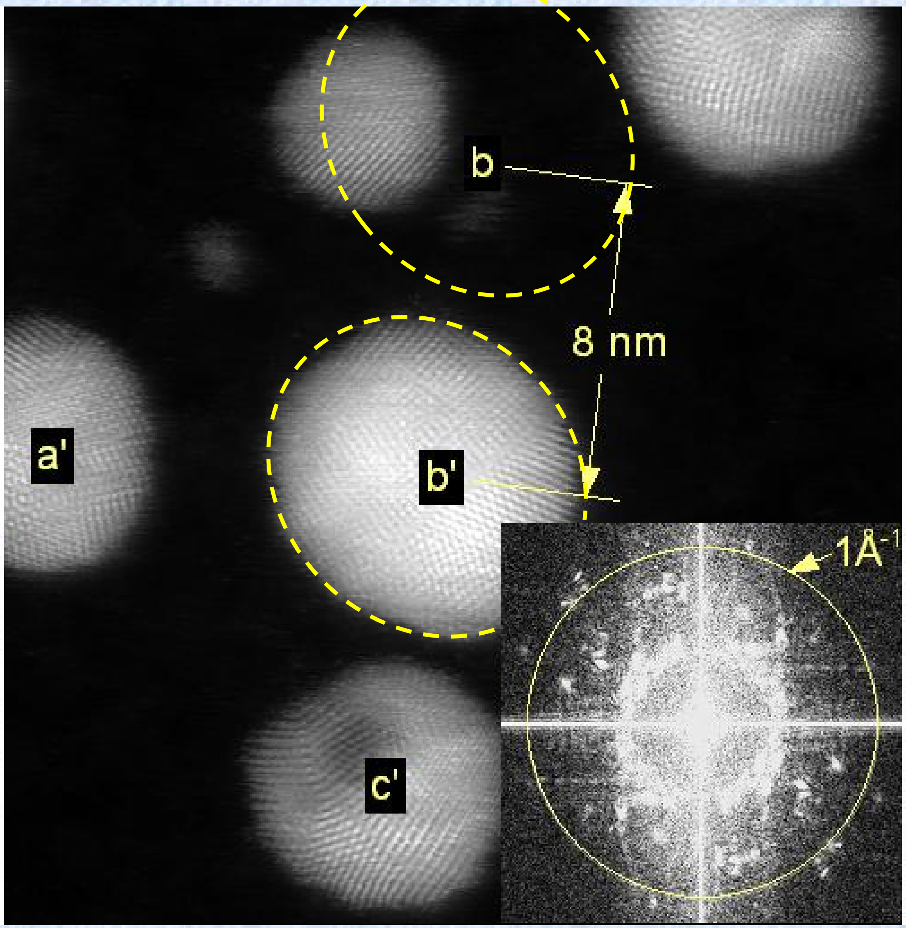
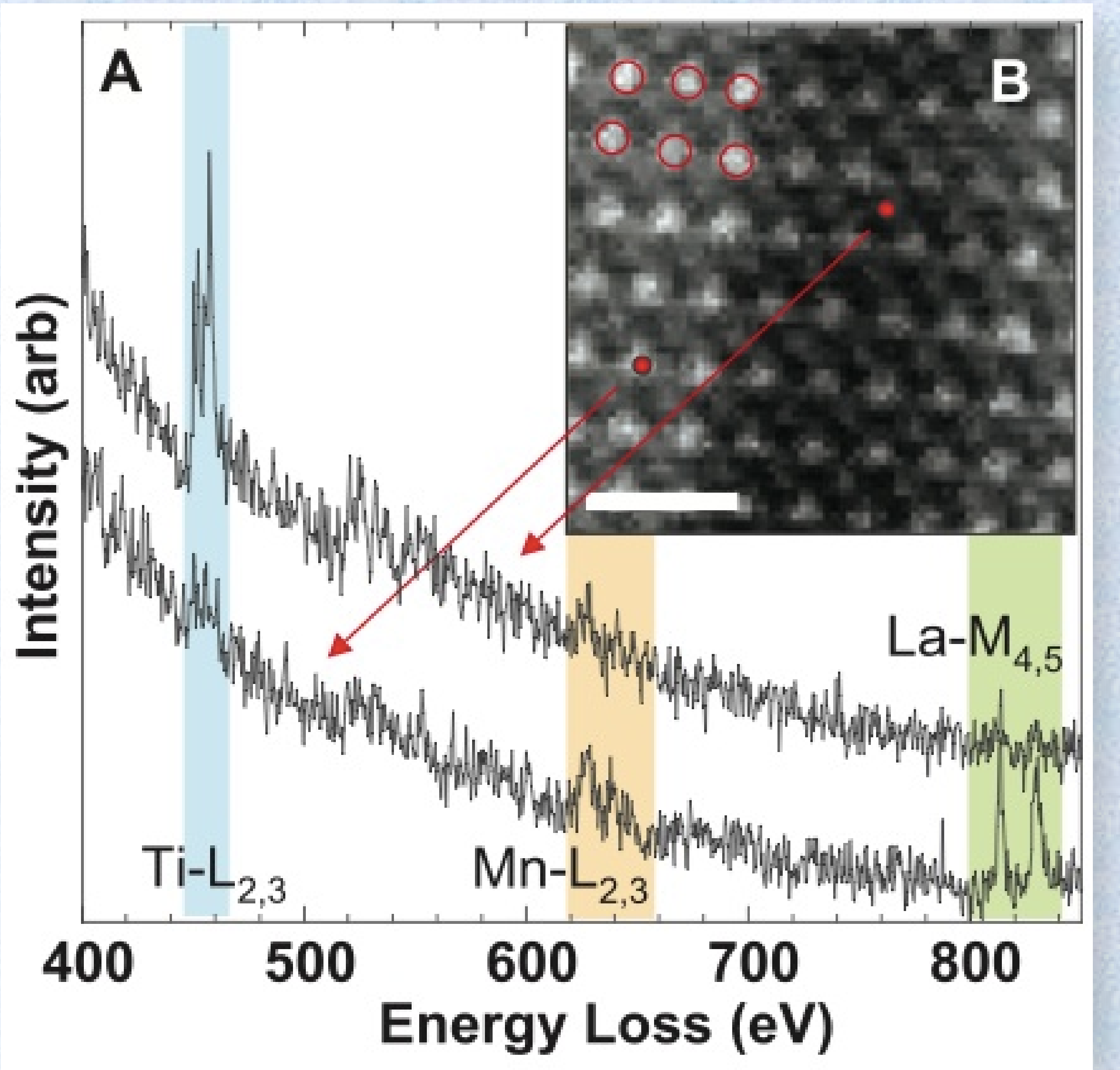


image recorded on 1/28/2013 12:02:11 PM (18 hours later), with no adjustments in between (no sample shift, no focus change)

➔ The tuned state for 1Å resolution persisted for >18 hours

# EELS atomic-resolution chemical mapping (2007)



*Muller et al., Science 319, 1073–1076 (2008)*

Electron energy loss spectra (EELS)

of $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ multilayer structure

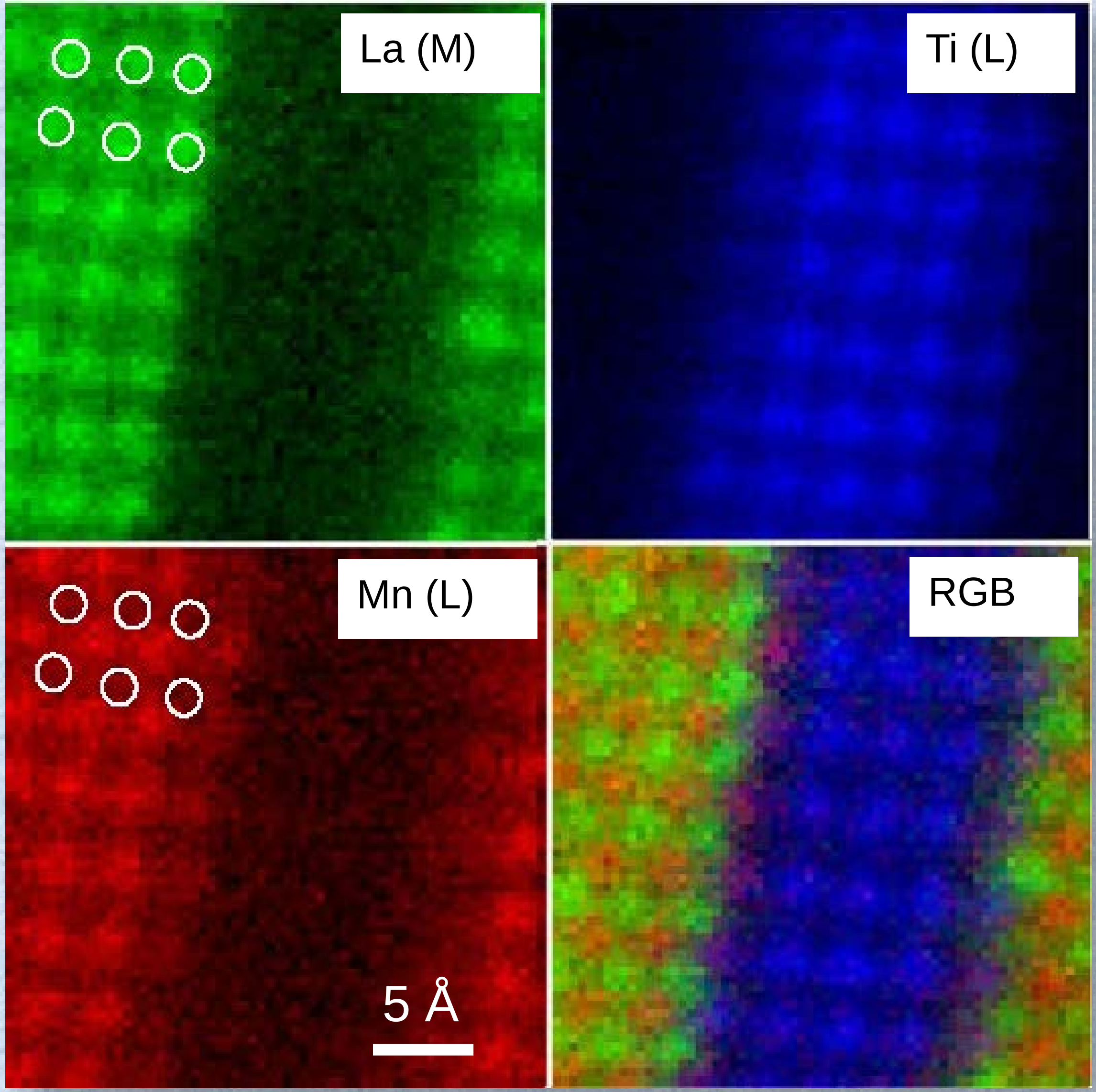
40 mr illum. half-angle
0.4 nA beam current
~1.2 Å probe
>80% efficient EELS coupling

Spectra acquired in 7 msec each from different parts of the structure.

Nion UltraSTEM100, Gatan Enfina EELS, 100 keV.

Data recorded during factory acceptance tests of Cornell UltraSTEM.

# EELS atomic-resolution chemical mapping (2007)



*Muller et al., Science 319, 1073–1076 (2008)*

## EELS chemical maps

of $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ multilayer structure

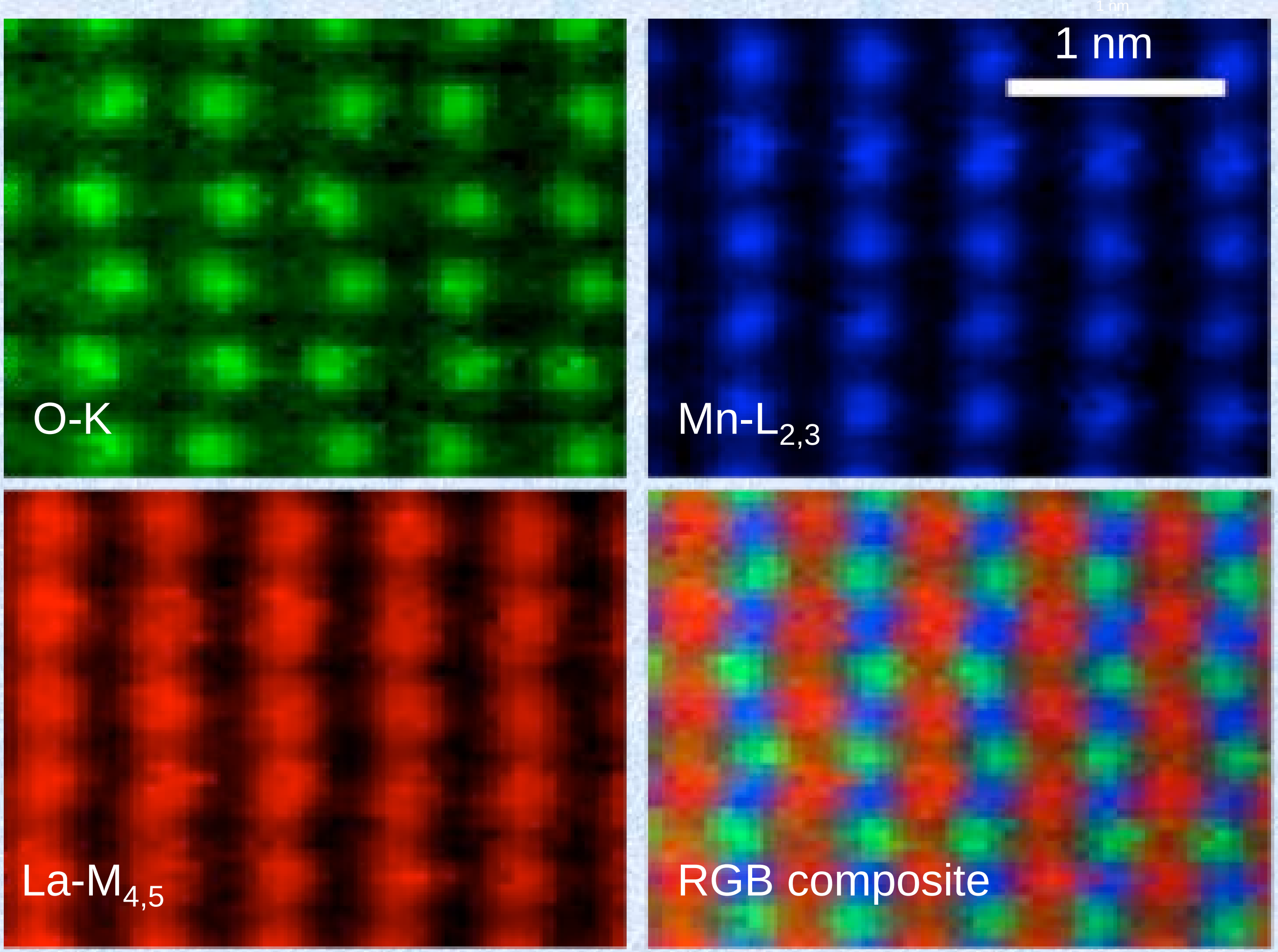
40 mr illum. half-angle
0.4 nA beam current
~1.2 Å probe
>80% efficient EELS coupling

64x64x1340 voxel spectrum-image
7 msec per pixel, i.e. 29 sec total acquisition time
10 sec additional processing time

i.e., <1 min total time

Nion UltraSTEM100, Gatan Enfina EELS, 100 keV

# Imaging different chemical species separately



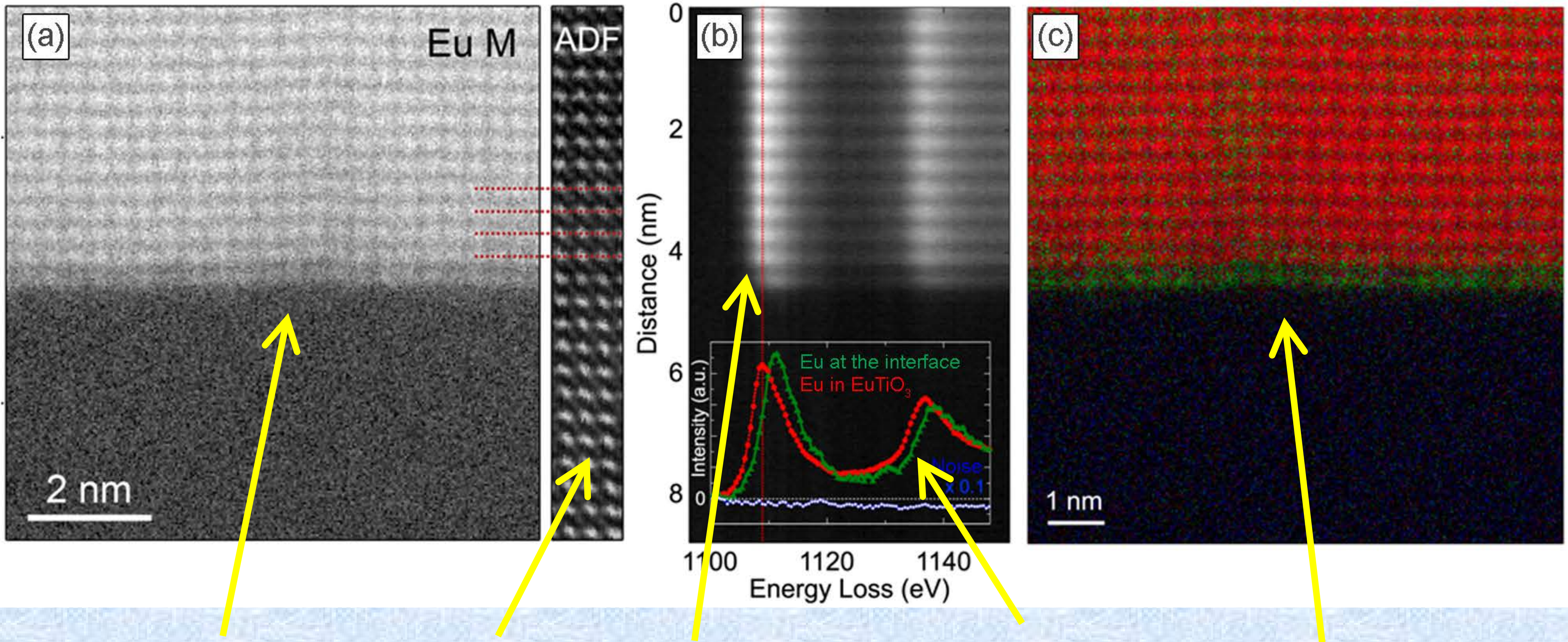
Imaging of oxygen octahedral rotations in $LaMnO_3$.

Nion UltraSTEM100, Gatan Enfina EELS, 100 keV.

Courtesy Maria Varela and Steve Pennycook, ORNL.

# Mapping oxidation states in $EuTiO_3$/$DyScO_3$

Increased Eu valence is found in a single atomic layer at the interface. UltraSTEM100, 100 kV.
*Courtesy Lena Fitting-Kourkoutis and David Muller, Cornell U. (IMC17 proceedings, 2010)*



Eu elemental map showing a reduced Eu concentration at the interface

Part of simultaneously recorded HAADF image

Evolution of the horizontally averaged Eu-M edge fine structure across the interface

The three components extracted using MCR methods

Three-component fit to the full SI demonstrating 2D mapping of oxidation state changes with atomic resolution

OCTOBER 2012 VOL 11 NO 10
www.nature.com/naturematerials

nature
materials

Oxide interfaces for the many

TUMOUR IMMUNOTHERAPY
A double attack

SEMICONDUCTING POLYMERS
One trap fits all

MECHANICAL PROPERTIES
The role of quantum effects

# nalyze…

x1k EELS spectroscopic ap of $LaMnO_3$/$SrMnO_3$ perlattice on $SrTiO_3$ bstrate.

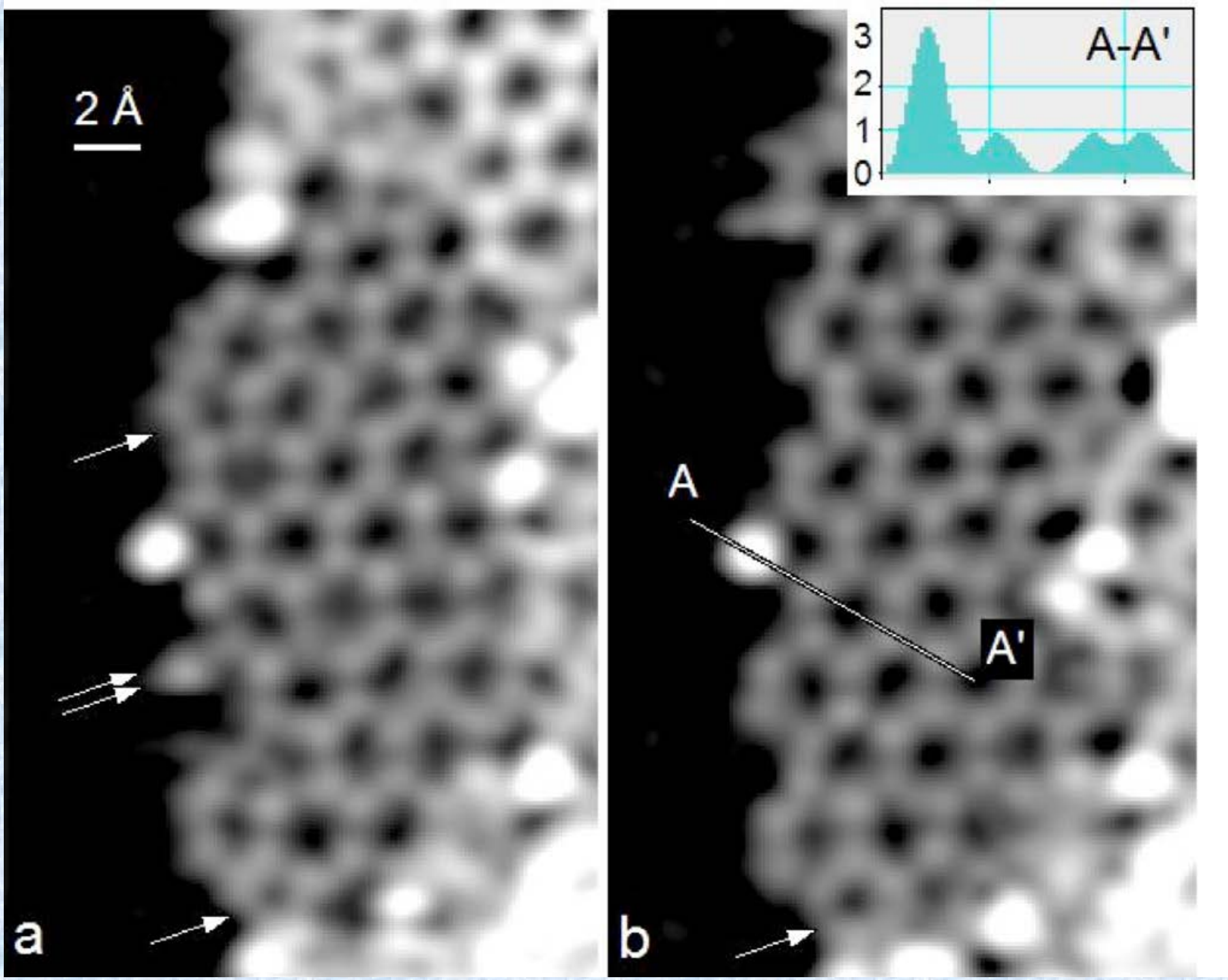
= green, Mn = red, = blue

ap size 1k x 1k (39 x 39 ), acq. time 2 ms per xel (33 min total). Probe rrent ~250 pA. No drift mpensation was used.

on UltraSTEM, Gatan antum EELS, 100 kV.

*lia Mundy, David Muller, rolina Adamo, Darrell hlom, Cornell U.; (Nature aterials **11** (2012) 55).*

# MAADF images of graphene taken 2 minutes apart



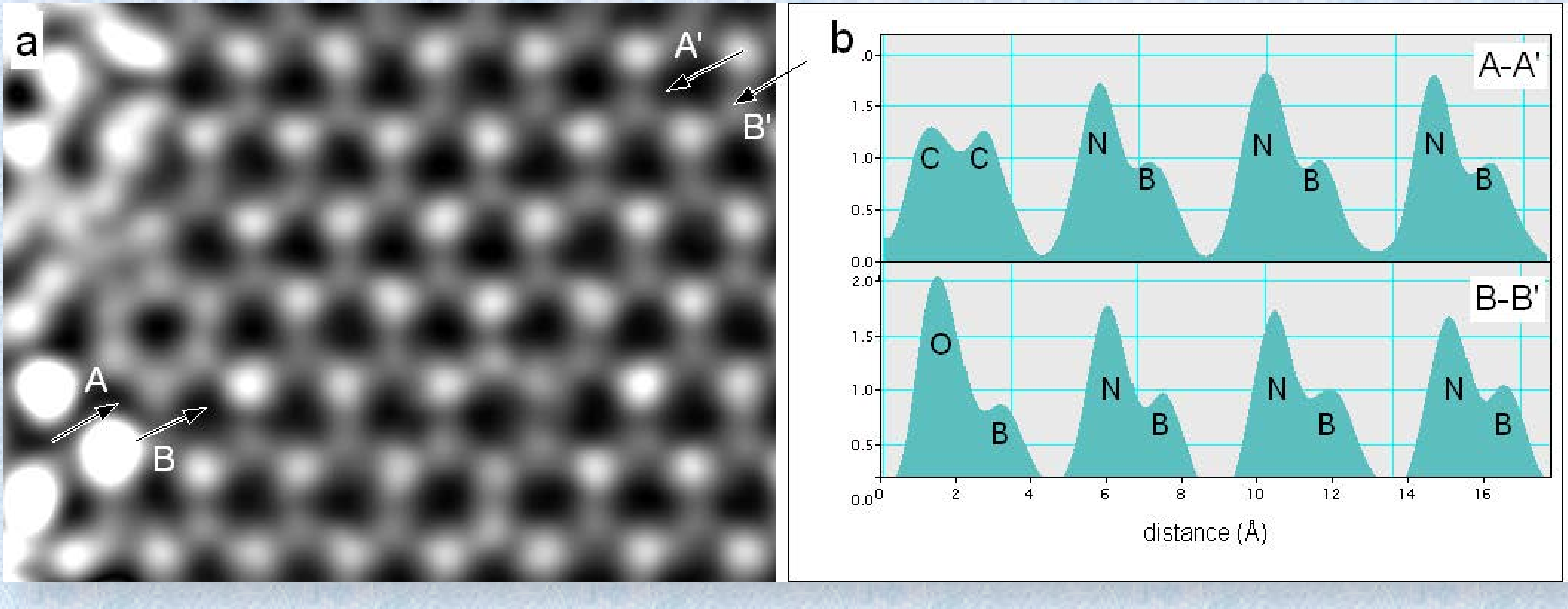
Medium angle annular dark field (MAADF) STEM images of a graphene edge, recorded 2 minutes apart. Nion UltraSTEM, 60 keV primary energy.

Configuration changes at the edge are nicely documented, a single heavier adatom (probably Si) is seen.

First images of graphene in which all individual atoms are resolved.

Images recorded in July 2009 at ORNL by olk, published in *Ultramicroscopy* ***110*** *(2010) 935-945.*

# MAADF imaging of single layer BN with impurities



60 keV MAADF image, 6 x $10^6$ e- / Å$^2$, with probe tails and high spatial frequency noise removed.

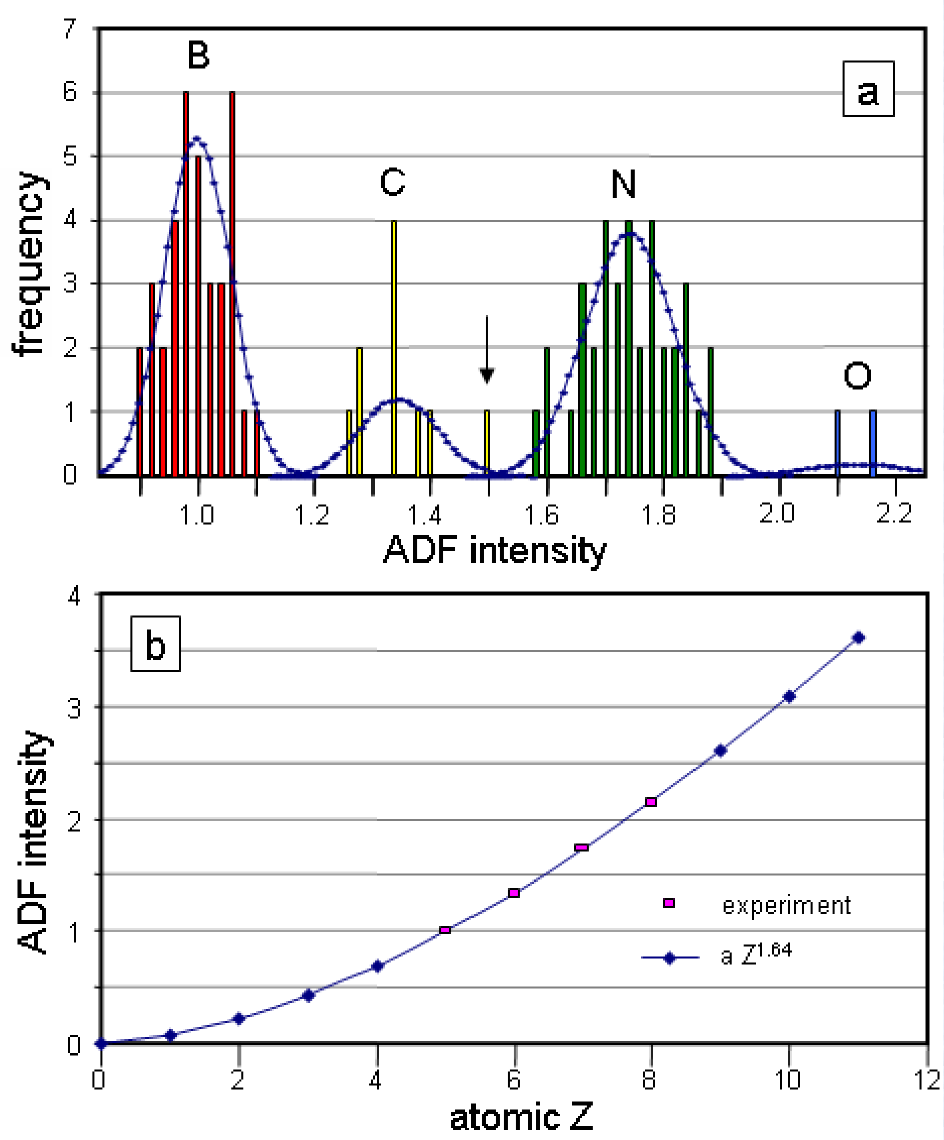
Image courtesy Matt Chisholm, ORNL, image processing by olk.

B and N atoms are readily identifiable by their MAADF intensities.

C and O substitutional impurities are identifiable in the line profiles.

*O.L. Krivanek, M.F. Chisholm et. al., Nature* ***464 (****2010 ) 571-574.*

# BN monolayer with impurities: histogram analysis

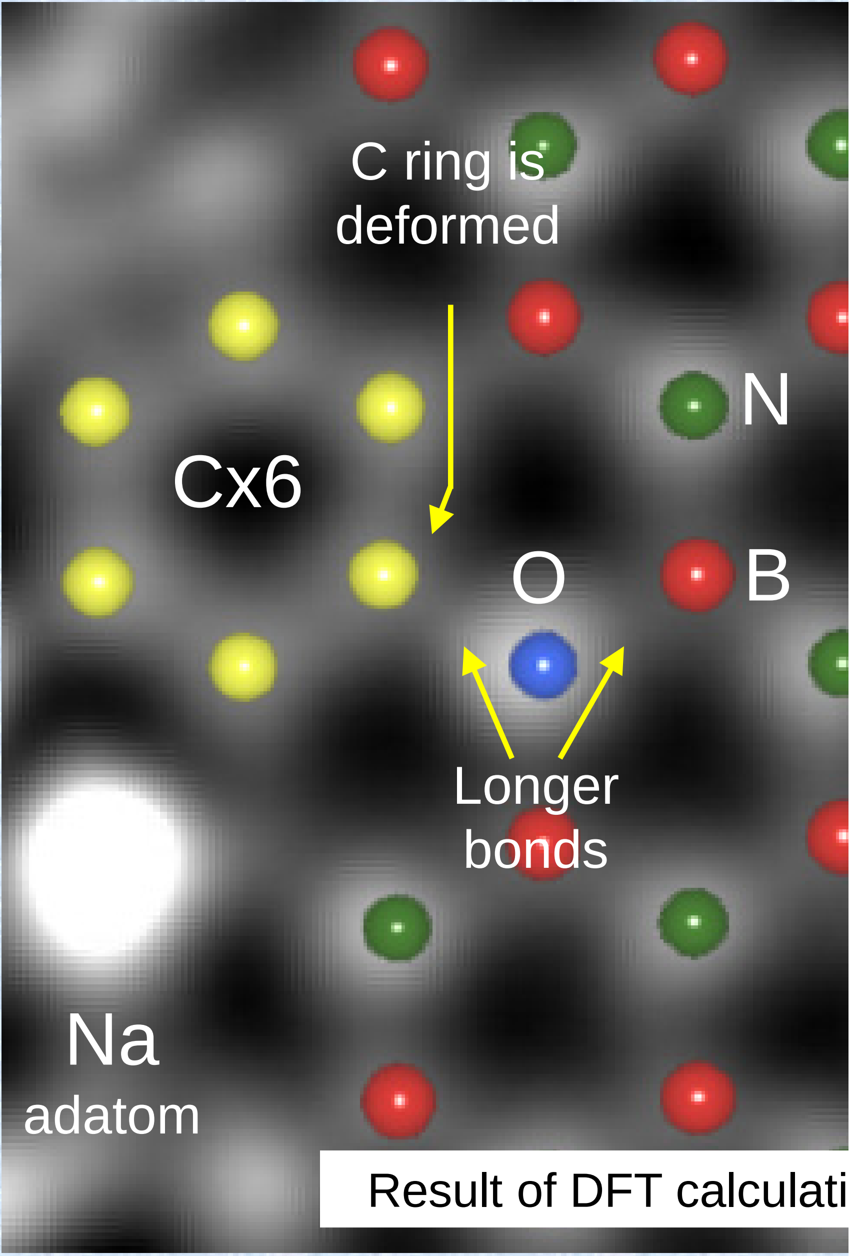


Histogram analysis of MAADF image (in which probe tails have been removed)
shows that B, C, N and O can be identified unambiguously in monolayer BN.

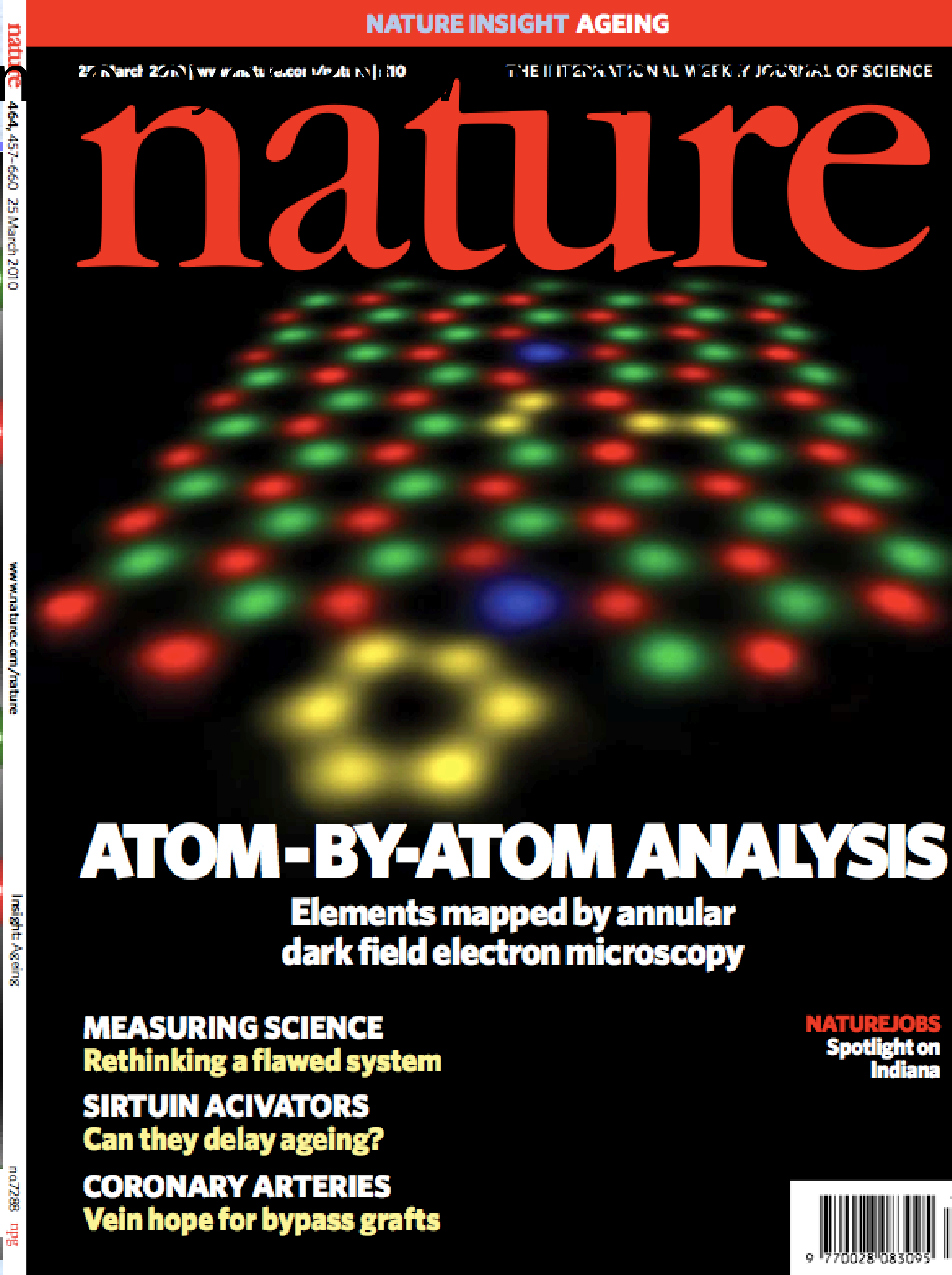
The experimentally worked out dependence of image intensity on Z goes as $Z^{1.64}$.

*O.L. Krivanek, M.F. Chisholm et. al., Nature* ***464 (****2010 ) 571-574.*

# MAADF imaging of si

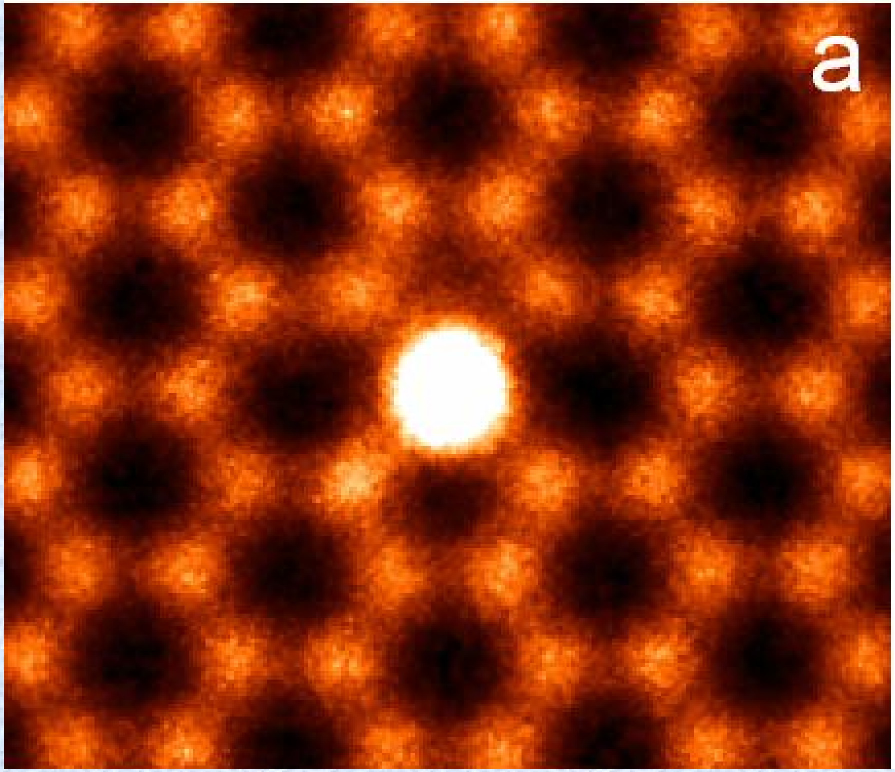


Result of DFT calculati

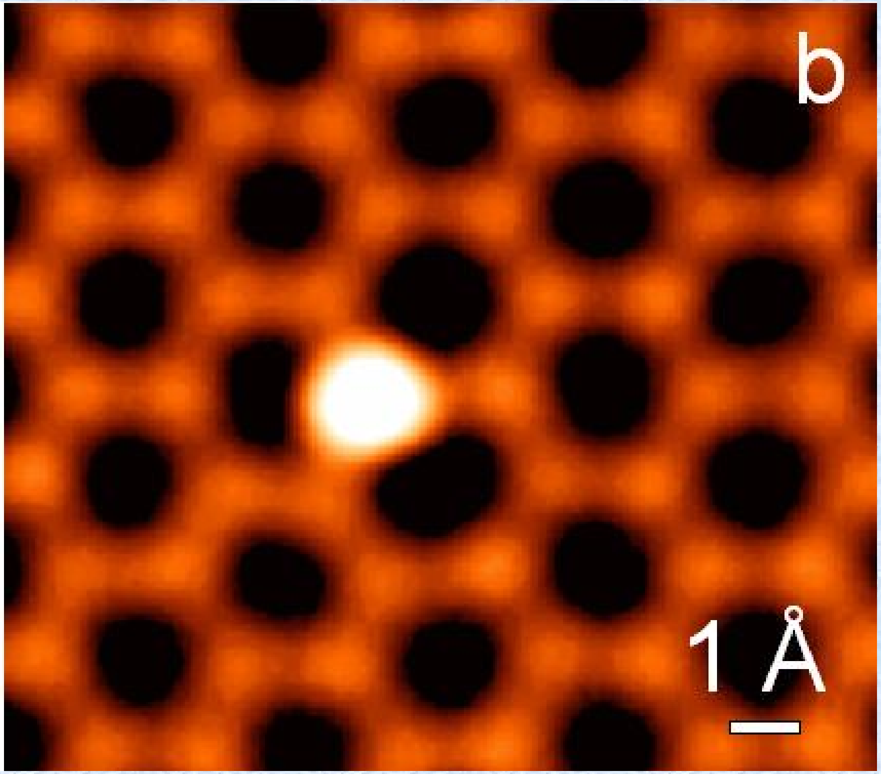


# Aberration-corrected STEM of single atoms

Si atoms in graphene can occupy two different sites.



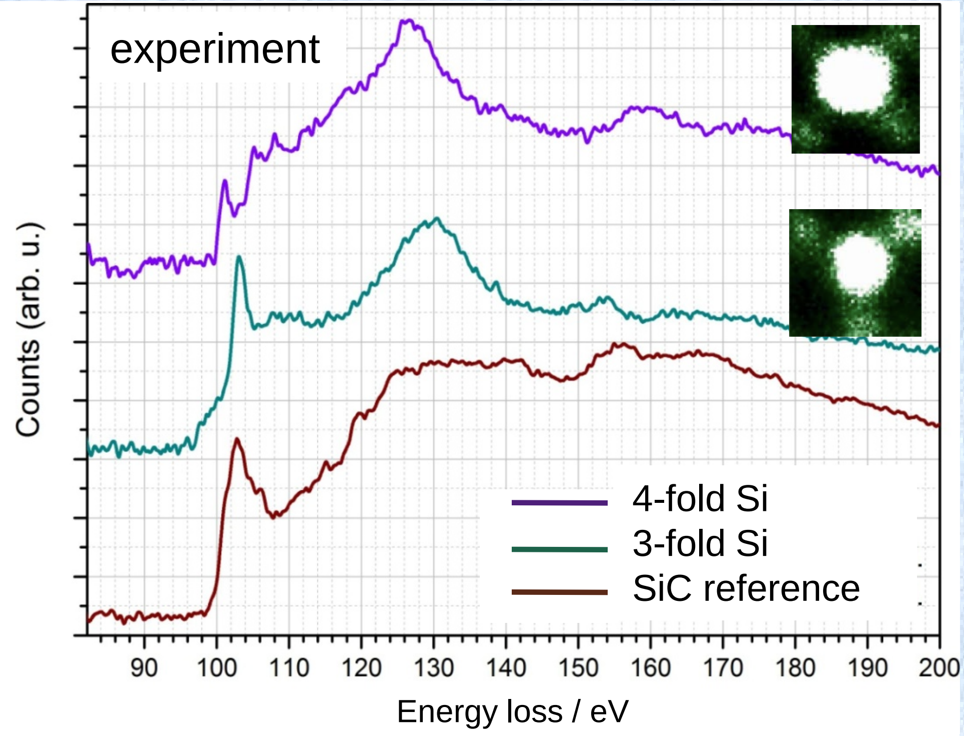
4-fold: Si substitutes for 2 C atoms
Courtesy Wu Zhou

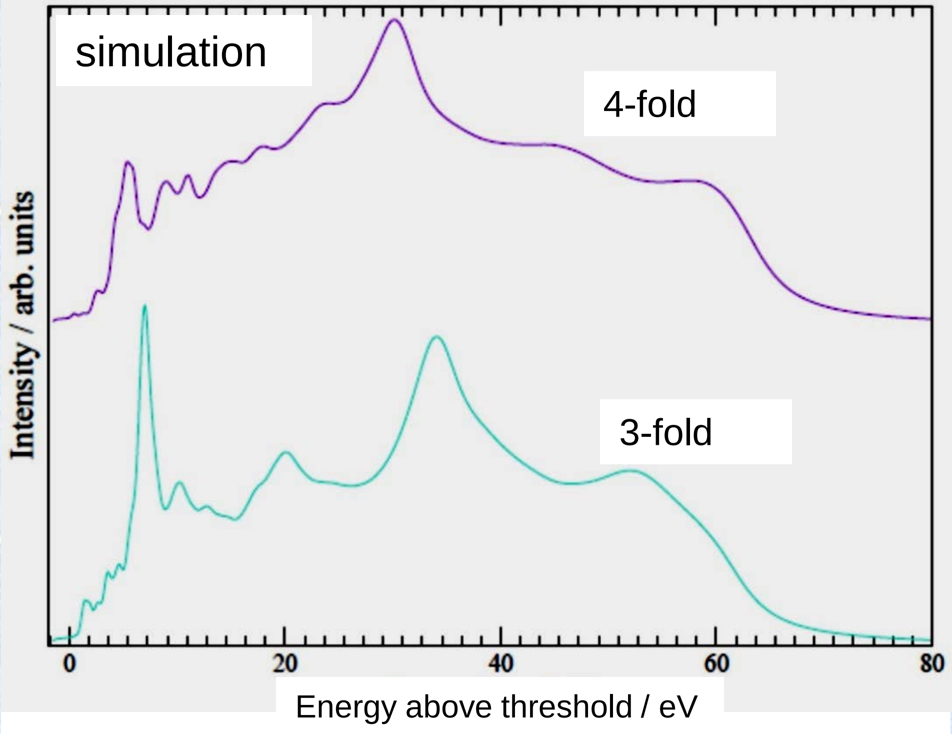


3-fold: Si substitutes for a single C atom
Courtesy Matt Chisholm

*Can we study the bonding environment of a single atom?*

# Probing the bonding of individual atoms by EELS

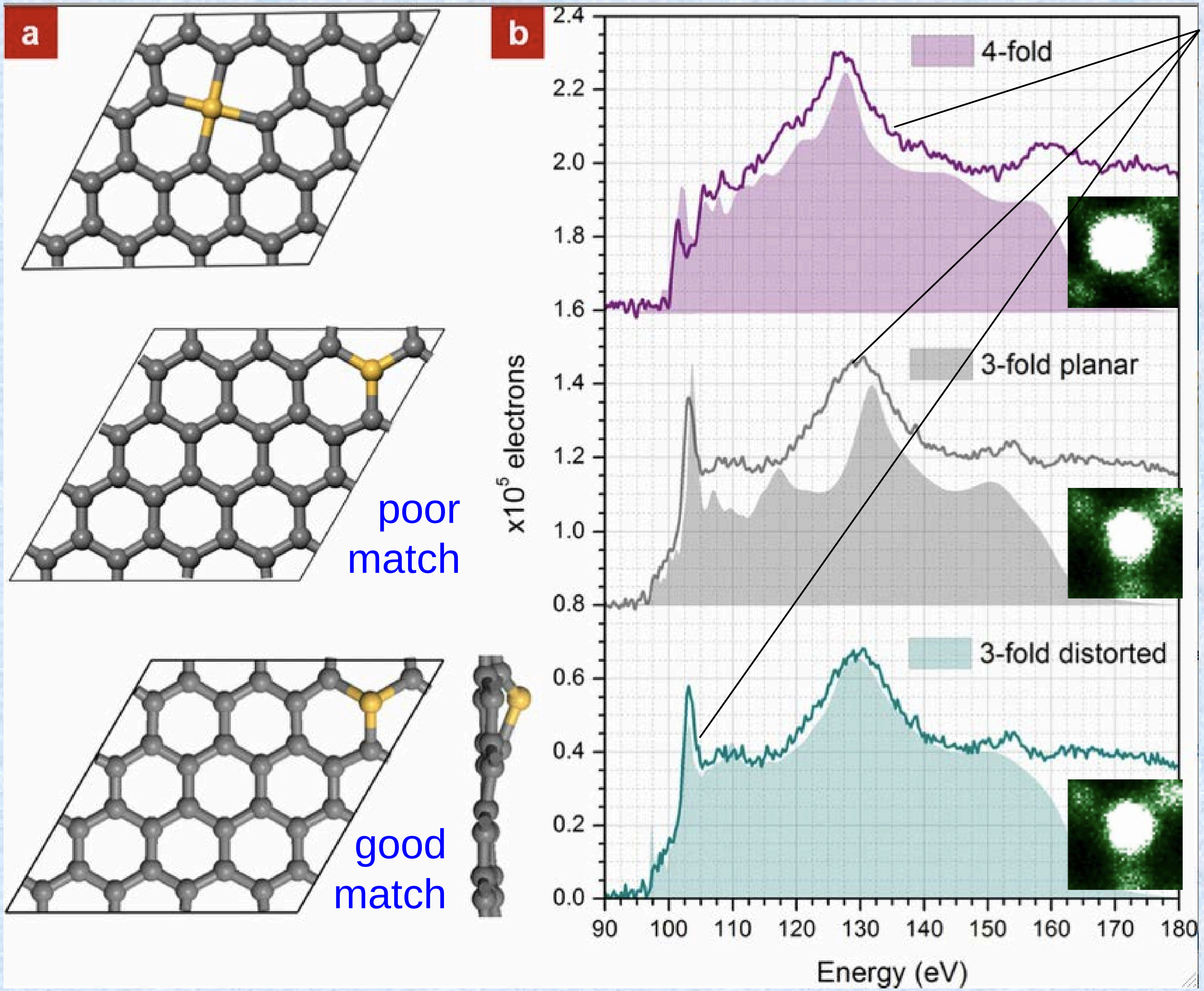




- EELS spectra at high signal/noise: 200s acquisition, following the single atom with a sub-scan window, 0.09s/frame, ~20 s directly over the atom. 60kV, 50 pA, 31mrad convergence, 36mrad collection, MAADF 55-190mrad
- Simulations with Castep EELS
- Nearly identical to work of Zhou et al.

*Q.M. Ramasse, C.R. Seabourne, R. Zan, D.M. Kepaptsoglou et al.,*
*Nanoletts (2013), DOI: 10.1021/nl304187e*

# Probing the bonding of individual atoms by EELS



Experimental EELS spectra at high signal/noise, compared to simulations.

about $1x10^{10}$ electrons illuminated the single Si atom!

60kV, 50 pA, tracking on, probe spent 20 secs over the Si atom

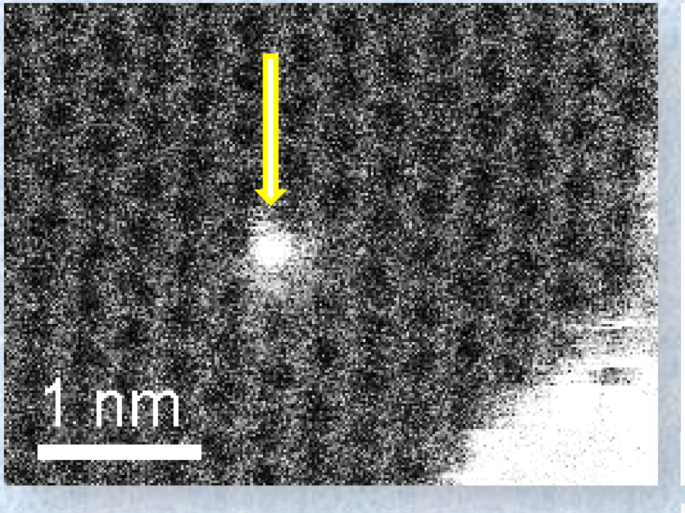
Simulations done with Castep EELS

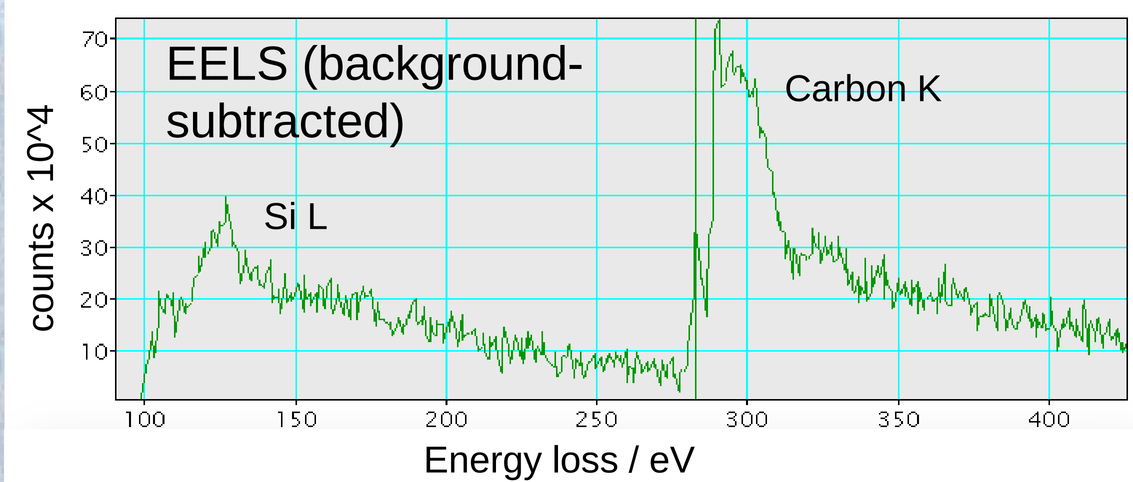
*Ramasse et al., Nano Letts (2012), DOI: 10.1021/nl304187e*

Essentially identical to results of Zhou et al., *Phys. Rev. Lett. (2012)109: 206803*

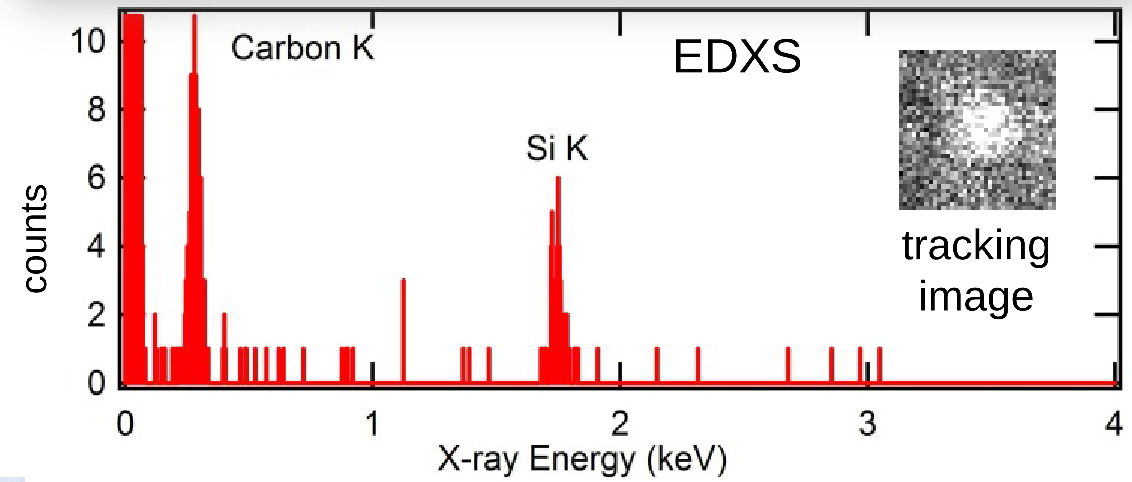
➔ ***atomic environment*** of a ***single atom*** determined by EELS

# Simultaneous EDXS and EELS from a single Si atom





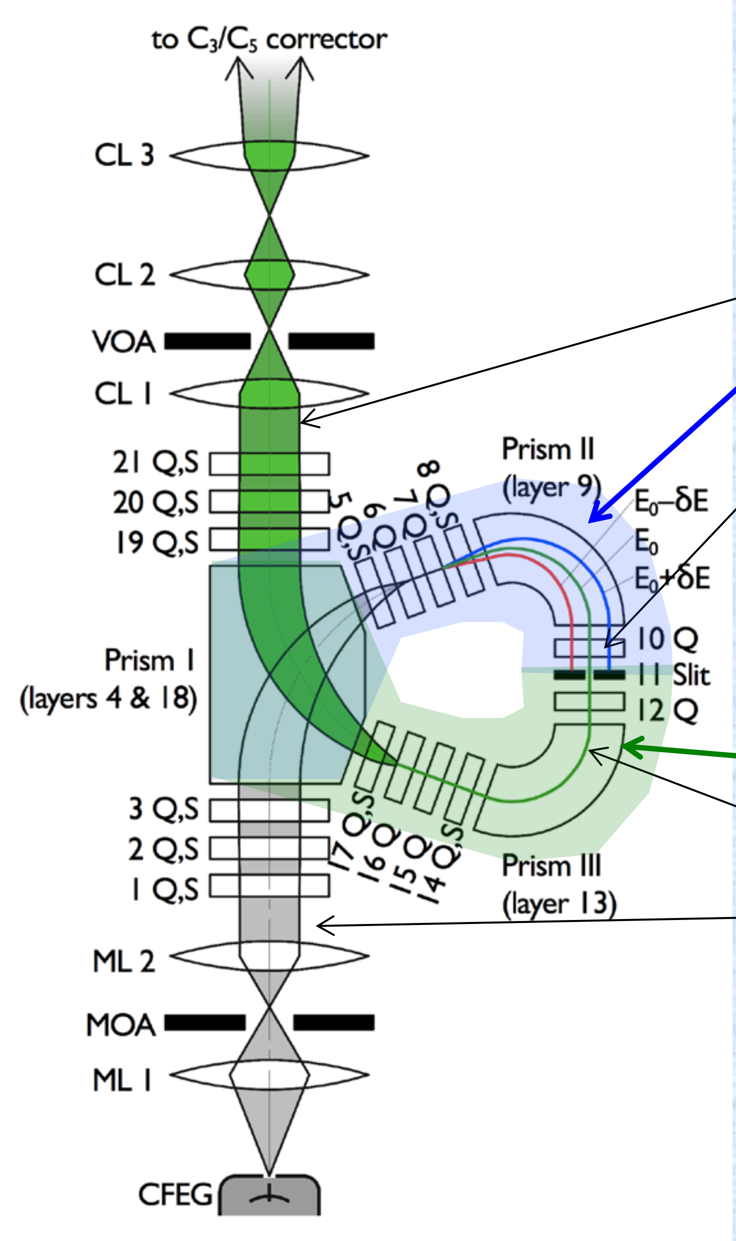
ADF image of Si atom in monolayer graphene, recorded ***after*** spectra were acquired.



EELS and EDXS recorded simultaneously while tracking the Si atom. $I_p$ = 190 pA, 224 s acquisition, of which ~10 s were spent over the Si atom.

Nion UltraSTEM100, 60 keV, Daresbury UK. Bruker SDD EDXS, Gatan Enfina EELS.
*Lovejoy et al., Appl. Phys Letts.* ***100*** *(2012) 154101*

# Nion high resolution monochromator



Full description in: Krivanek et al., Phil. Trans. Roy. Soc. **A 367** (2009) 3683, US Patent #8373137 and *Krivanek et al. Microscopy* ***62*** *(2013) 3–21.*

un-dispersed outgoing beam

EELS 1

energy-dispersed beam

Energy dispersion at slit is variable from ~ 2 µm/eV to ~ 200 µm/eV

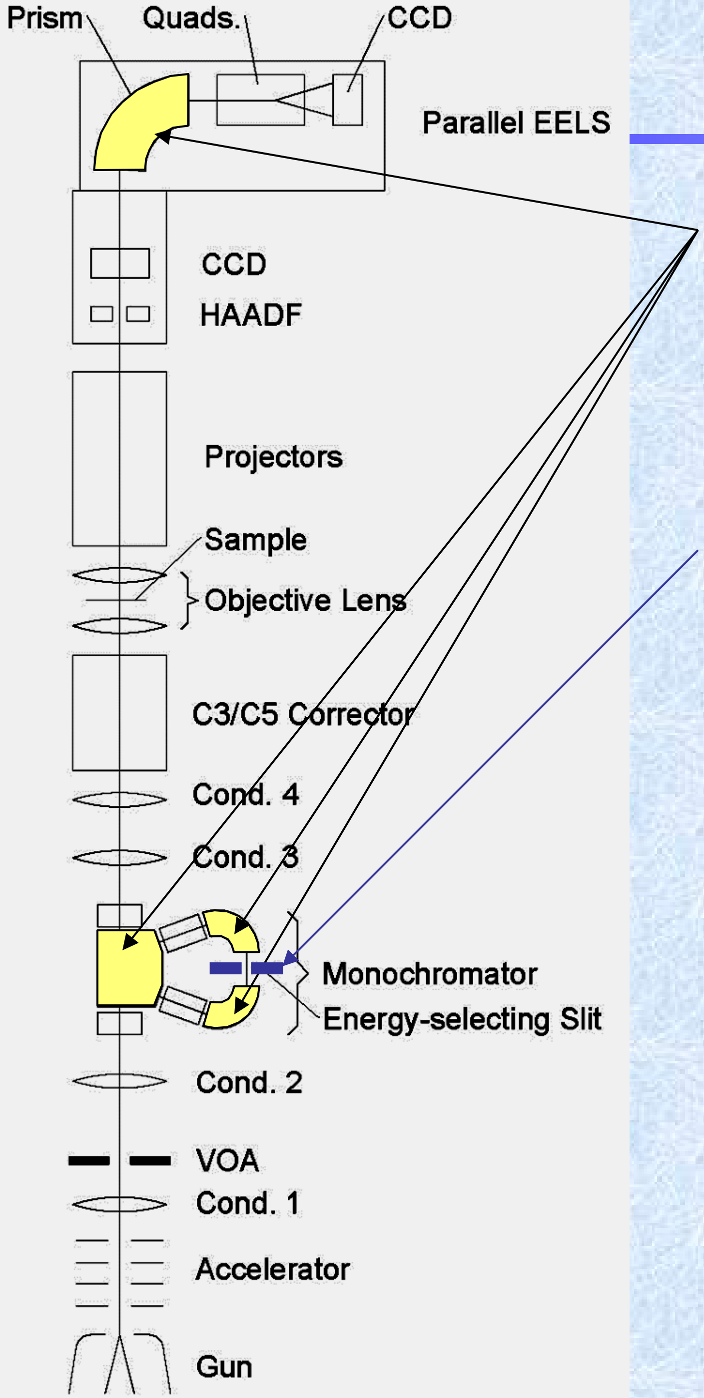
EELS 2

monochromated beam

incoming beam

The Nion monochromator is equivalent to 2 parallel EEL spectrometers arranged back-to back, with an energy-selecting slit in the mid-plane, plus (next slide):

# Two stability-enhancing schemes



A) Connect all magnetic sectors in series: an instability in their shared power supply will not shift the analyzed energy relative the selected (monochromated) energy.

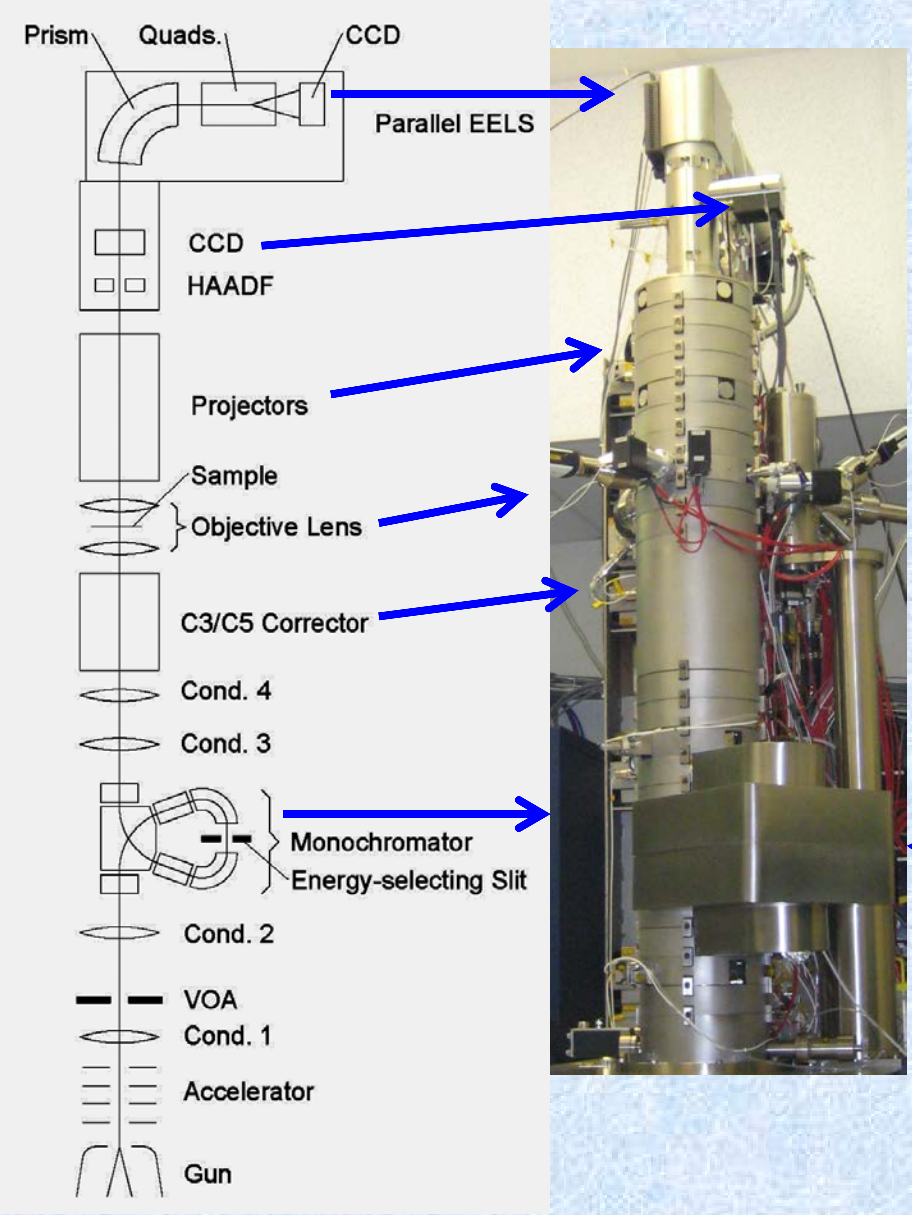
B) Sense the current falling on each of the two halves of the energy-selecting slit, use the difference in the two currents in a feedback scheme linking the HT to the prism current.

(A) and (B) plus the corrected optics of the monochromator and the spectrometer should make energy resolution < 30 meV readily possible.

< 10 meV may be doable in the future.

*(this slide was prepared in 2008!)*

# Nion monochromated system - final shape

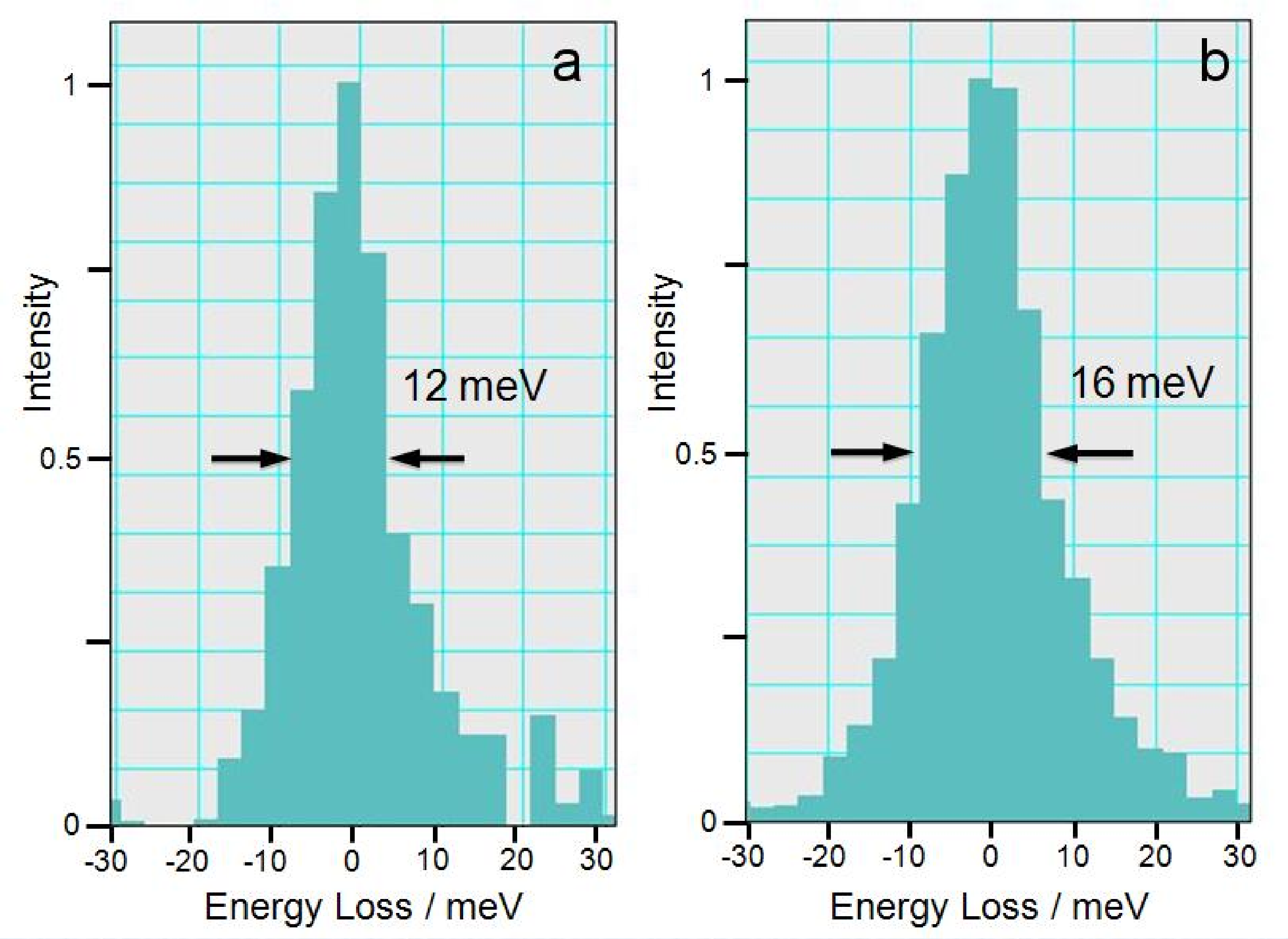


The first Nion UltraSTEM 100MC tool was delivered to Arizona State U. in January 2013, and is now working.

Future deliveries:
Rutgers U.
Daresbury SuperSTEM
U. of Paris

Monochromator
with quadruple
μ-metal shielding

# Zero loss peaks (ZLPs) acquired with the system



Spectra of the zero loss peak acquired in 2 ms (a) and 50 ms (b).

60 keV, Nion UltraSTEM™ 100MC,
Gatan Enfinium spectrometer with extra-stable multipole power supplies.

Demonstrated overall stability: about
2 parts in $10^7$

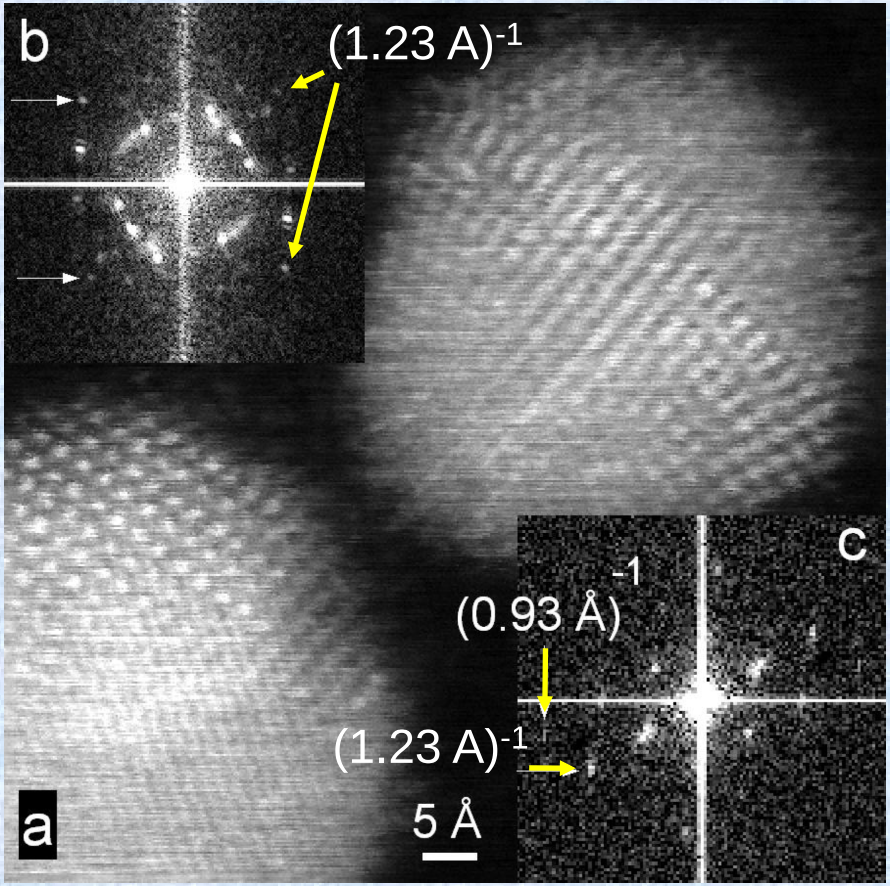
# Spatial resolution and probe current

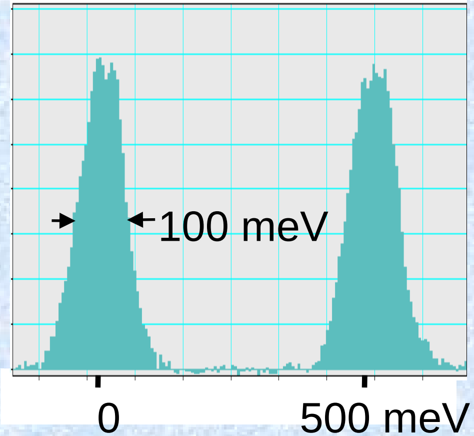
ADF images and FFTs of gold nanoparticles obtained at 60 keV.

a) Beam going through monochromator, slit out. Probe curr. ~ 120 pA.

b) FFT of (a).

c) FFT of an image of Au nanoparticles obtained with the beam going through a 100 meV wide slit. Probe curr. ~ 10 pA.

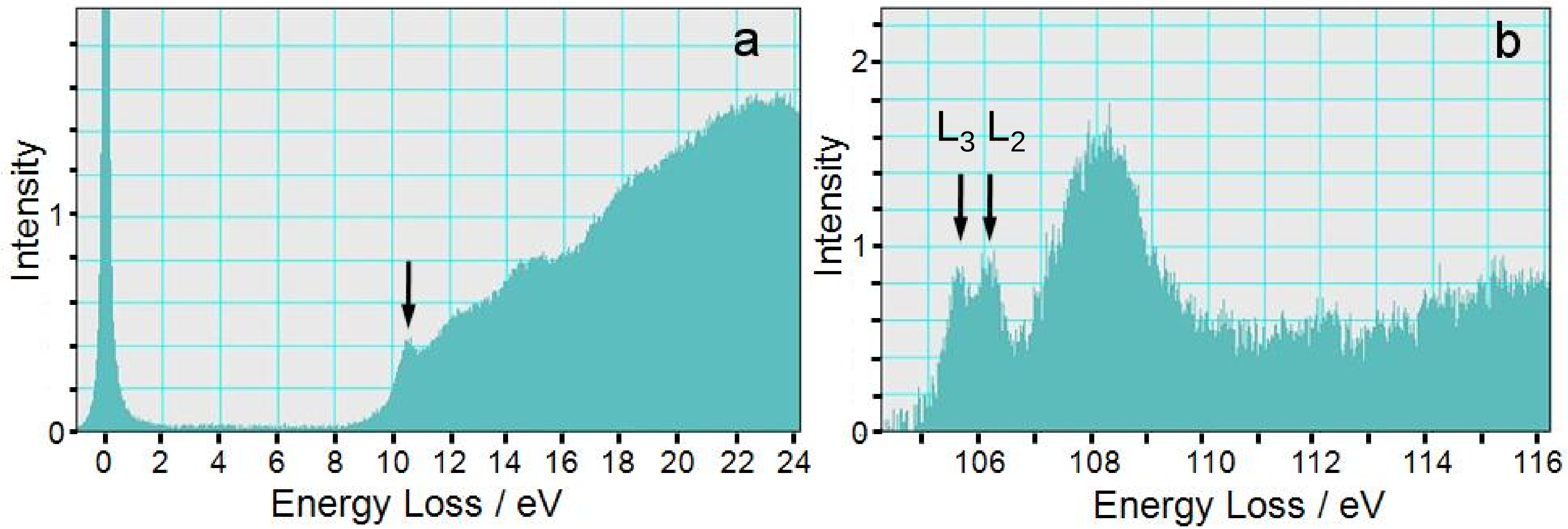




calibration ZLPs for (c): ~100 meV FWHM

➔ At 60 keV, the system is capable of giving ***equal or better spatial resolution*** with the slit in (and hence with smaller energy spread) than with the slit out (or wide open).

# Spectra from a practical sample: $SiO_2$ in a MOSFET



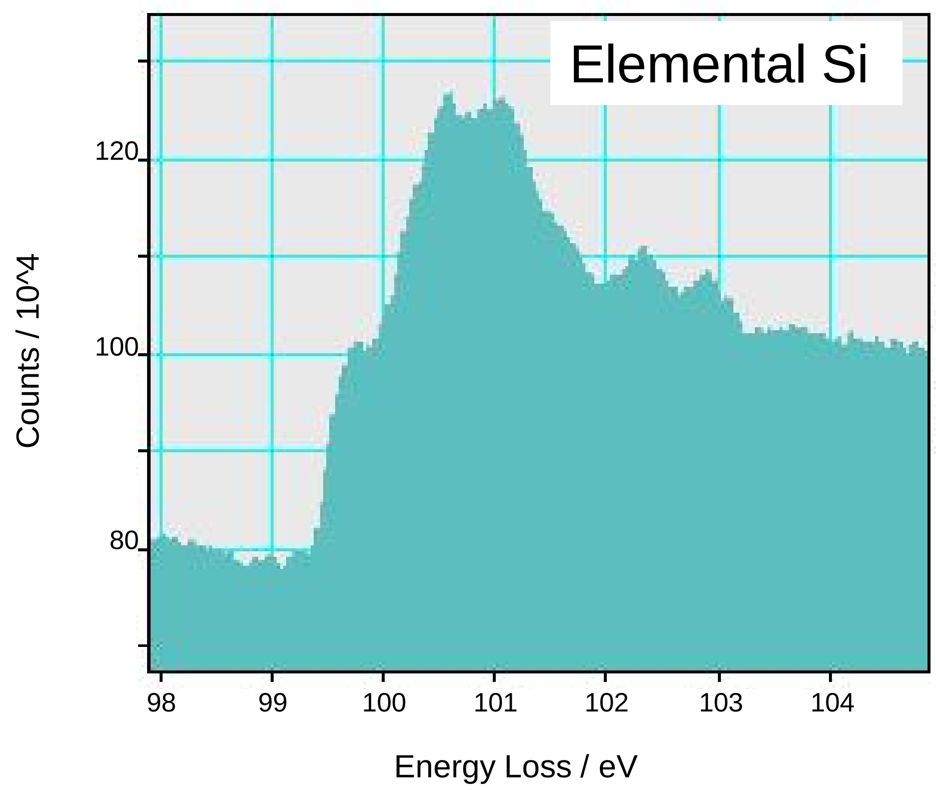
(acquisition time = 0.2 s)

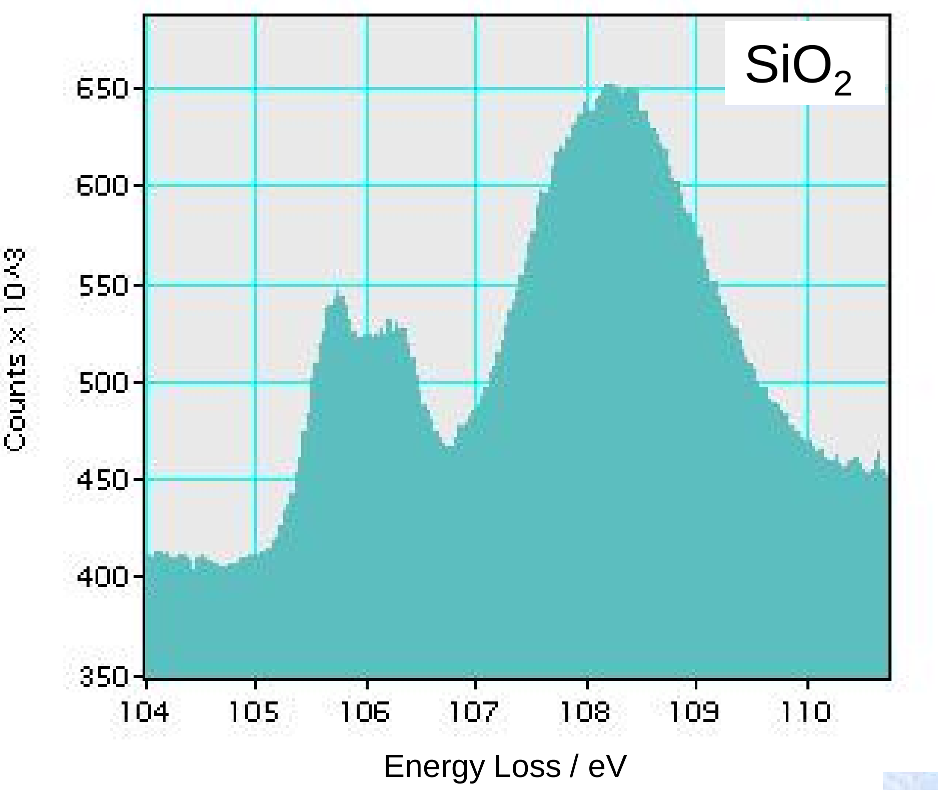
(acquisition time = 50 s)

60 keV, Gatan Enfinium EELS, coupling efficiency ~100%
FWHM of ZLP ~ 40 meV, ZLP height = 302.

The arrowed feature in (a) is probably a band edge exciton, the arrowed features in (b) correspond to resolved $L_3$-$L_2$ Si L-edge spin-orbit splitting.

# More Si $L_{2,3}$ spectra





UltraSTEM 100MC at ASU, 100 keV :
energy resolution similar or better than available at synchrotrons,
spatial resolution down to 1 Å.
More results to come shortly…

# Summary

- We are now able to perform atom-by-atom STEM analysis, because we have:
  - ultra-bright electron guns
  - aberration-corrected electron optics
  - ultra-stable electron microscopes
  - ultra-high vacuum at the sample
- A microscope capable of atom-by-atom analysis in ultra-thin samples can typically also do a very good job characterizing thicker samples.
- A new monochromator has been built at Nion. The first results show that 30 meV, 0.1 nm-level characterization of materials is now possible.
- New tools are now available but much work in developing applications remains.