Opportunities and Challenges for DLSR enabled Scanning Probe Microscopy

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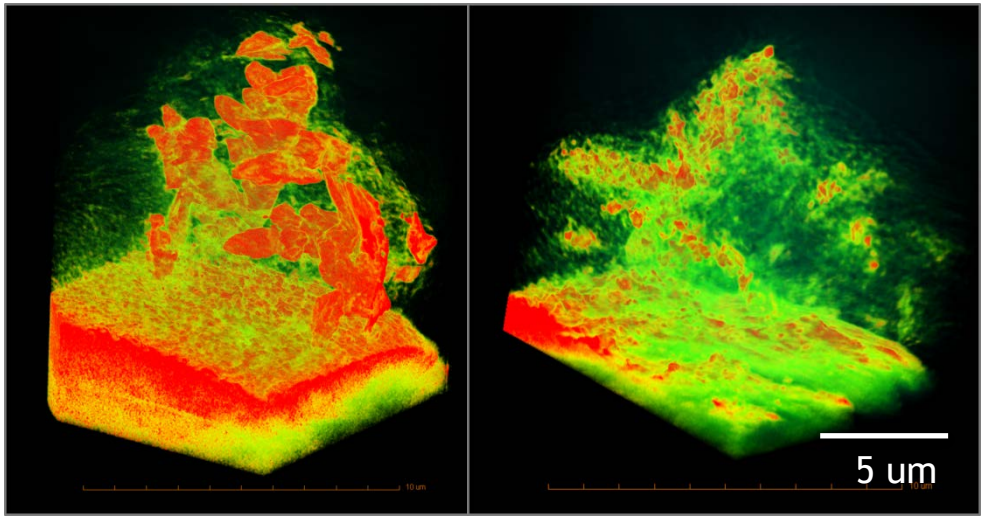
DLSR enables Next Generation Scanning Probe Microscopy

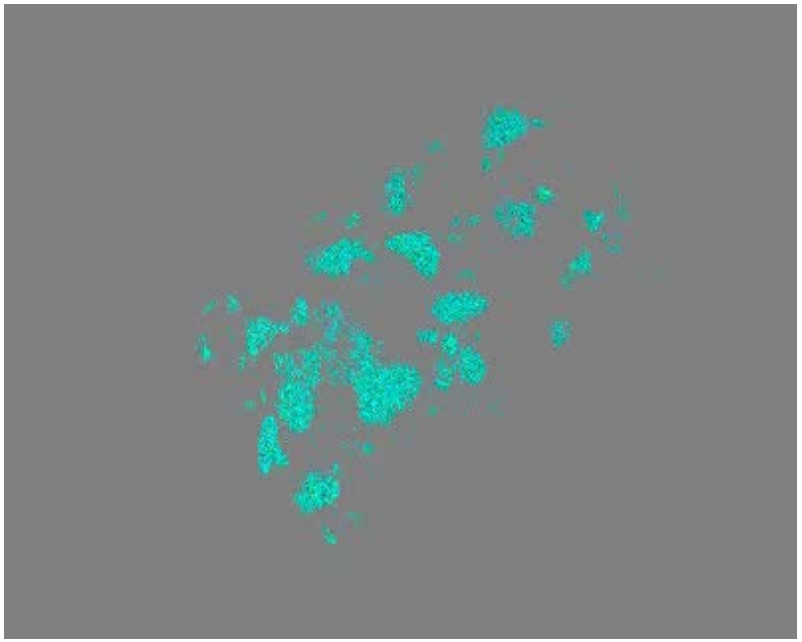
- **Insight into "Messy" Dynamics of Real-World Materials**

- **Highest spatial resolution**
  - Image processes at boundaries
- **Highest sensitivity**
  - Orders of magnitude improved sensitivity for defects, impurities, ..
- **Combined with realistic sample size**
- **And tomography**
  - **With all relevant contrast modes (phase, chemical sensitivity, XRD, …)**
- **And spectroscopy**
- **And additional relevant techniques**

Real devices and processes in real environments in real time (operando)

Imaging batteries in motion





Top image courtesy R. P. Winarski (ANL/CNM)

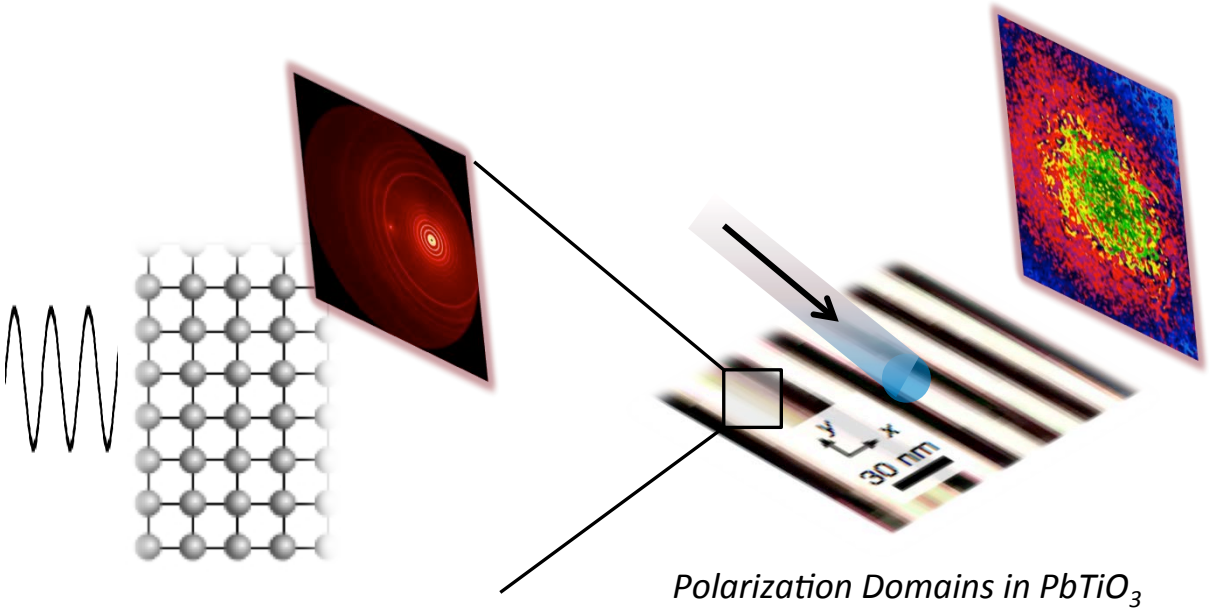
L. Trahey, D. J. Vine, *et al*

Fast, multiscale visualization with nano-beams: Uniquely enabled by DLSR and required for characterization of real systems in 3D

Atomic Scale ↕ X-Ray Wavelength

Mesoscale ↕ Focused Beam

Macroscale ↕ Scanning Image



Polarization Domains in $PbTiO_3$
Hruszkewycz *et al.*, PRL (2013)

Memory cells in EPROM chip
Science Photo Library

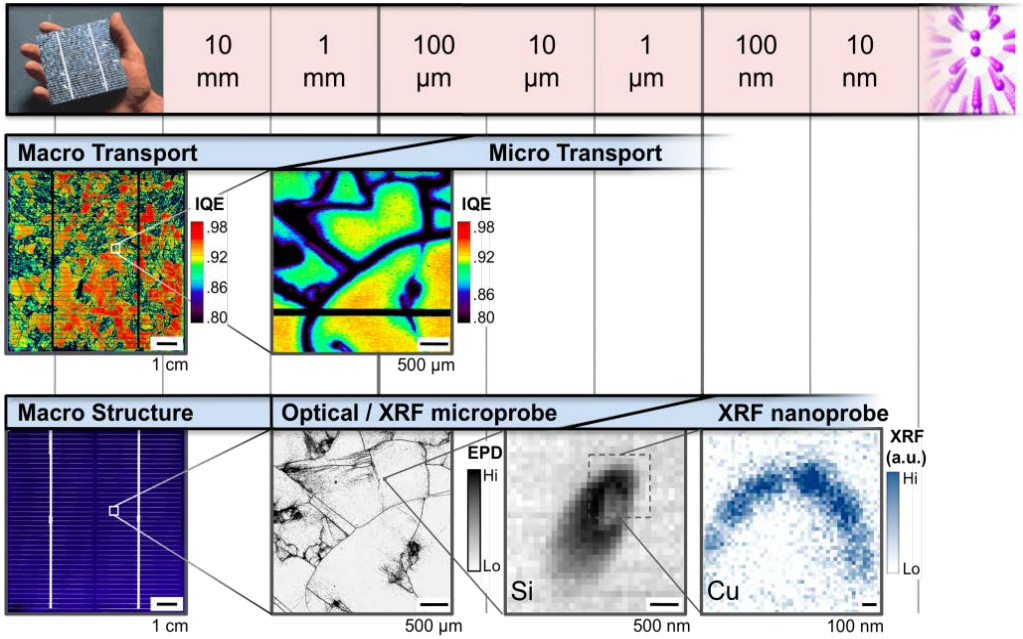
Ptychopgraphy, CDI
Diffraction, spectroscopy

Absorption, phase, XRF, XRD, ….

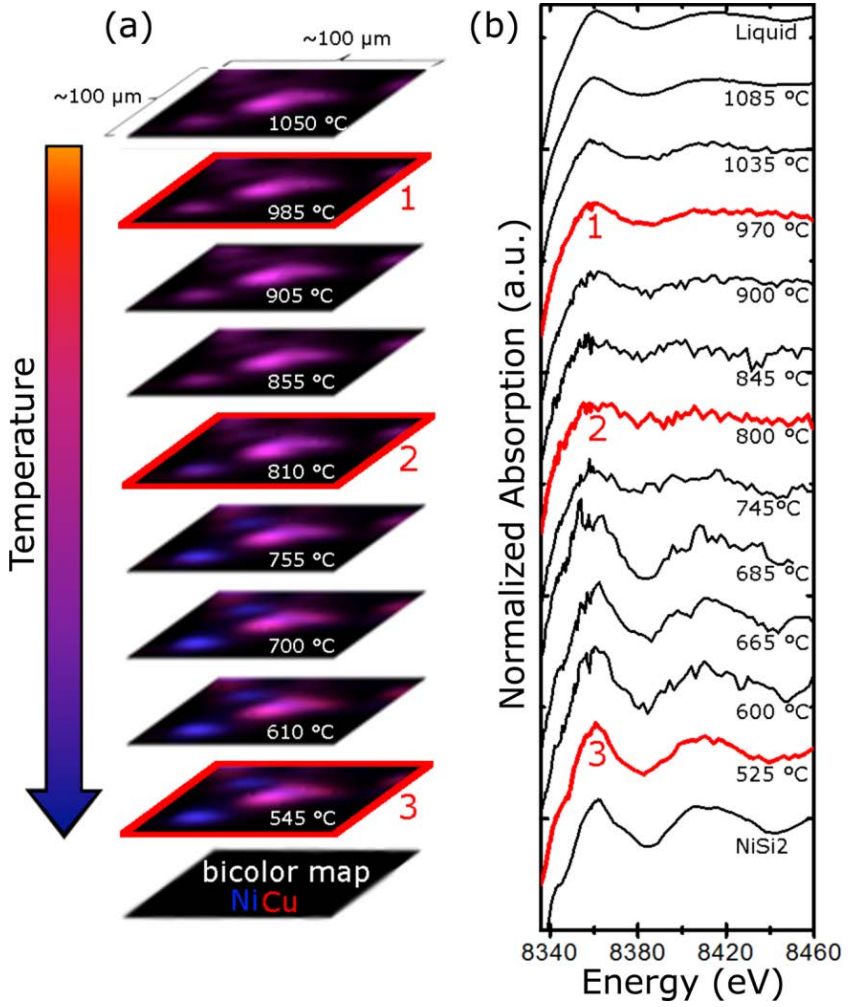
After R. Jaramillo

Photovoltaics:
Understand and Manipulate Defects in Inorganic Solar Cells

Opportunity:
Society: Gain in efficiency, reduction in cost
Science: Physics of defects

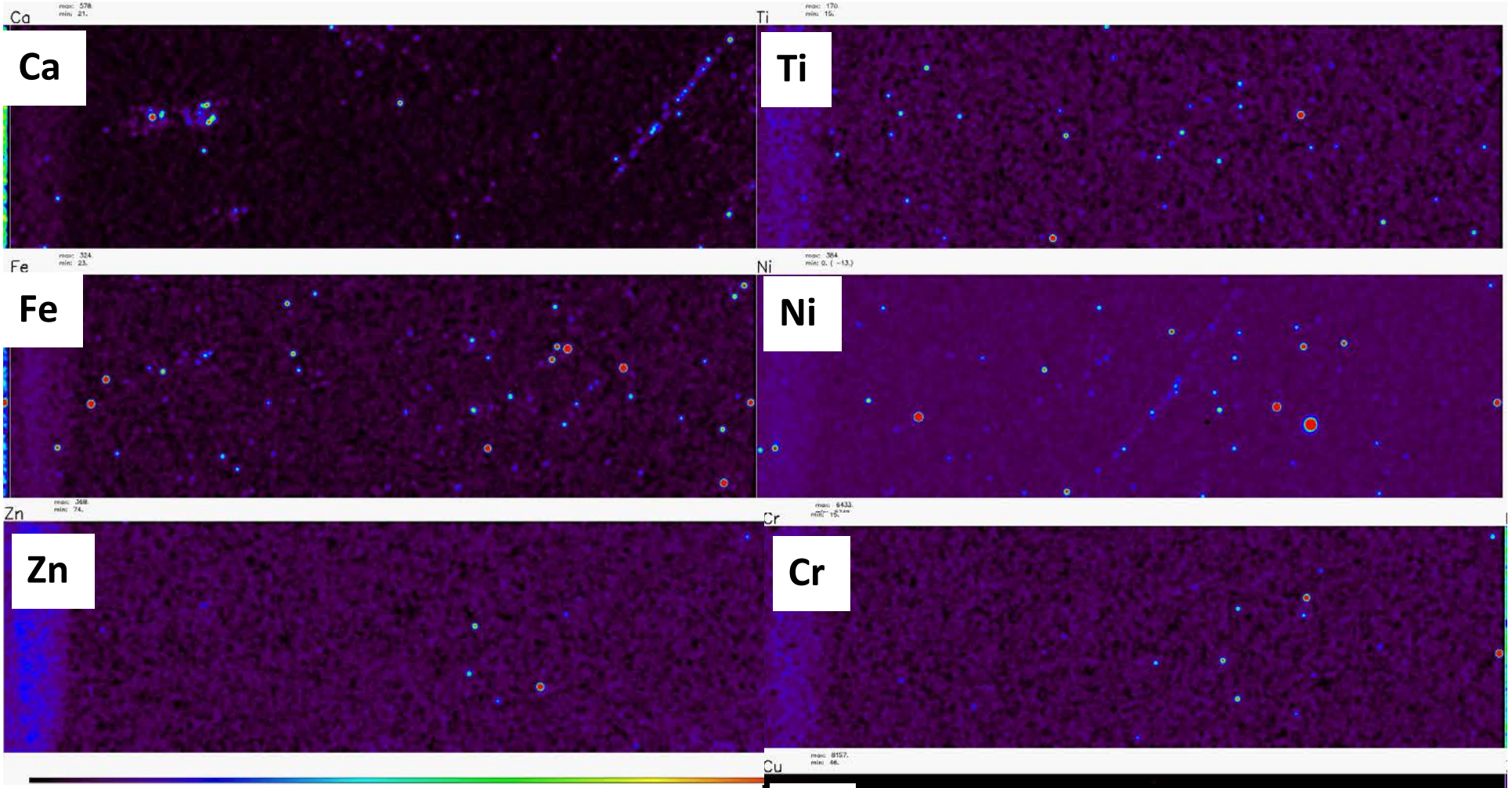


M. I. Bertoni, D. P. Fenning, M. Rinio, V. Rose, M. Holt, J. Maser, T. Buonassisi, *Energy Environ. Sci., 2011, 4, 4252-4257.*



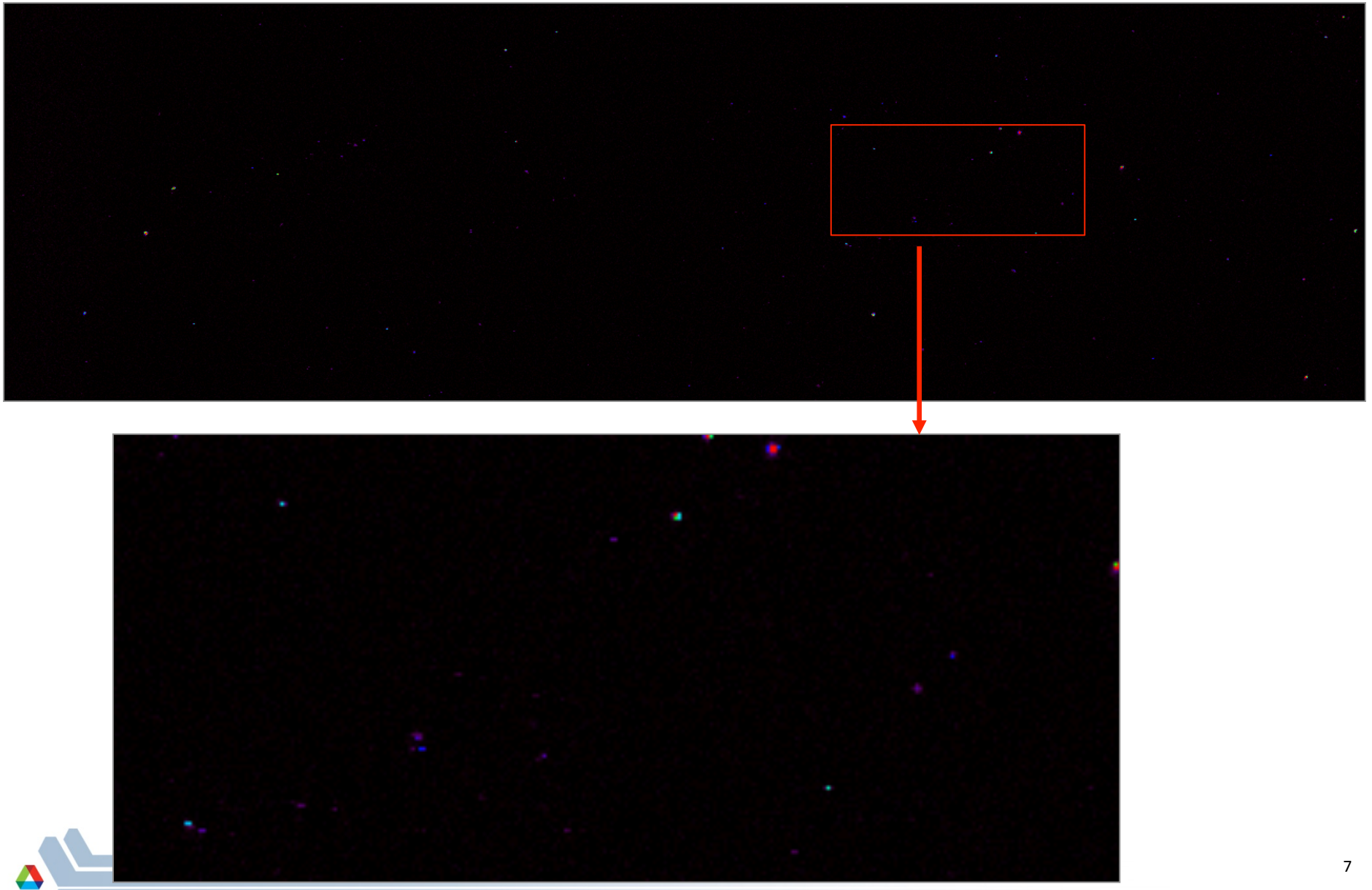
S. Hudelson, D. Newman, S. Bernardis, D. P. Fenning, M. I. Bertoni, M. A. Marcus, S. C. Fakra, B. Lai, T. Buonassisi* *Adv. Materials 2012, 22, 3948.*

But, need to survey ‘realistic’ sample



- Si based solar cell material
- Scan 1200x400 um,

But a lot of detail: example Fe signal

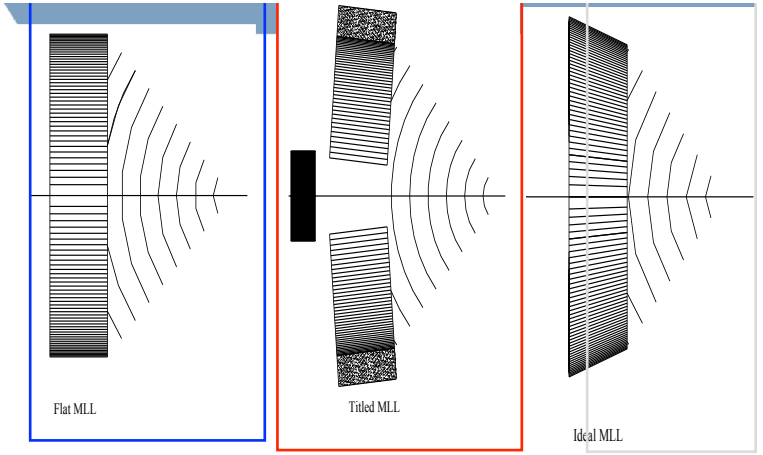


APS MBA upgrade for a nano-focusing beamline:

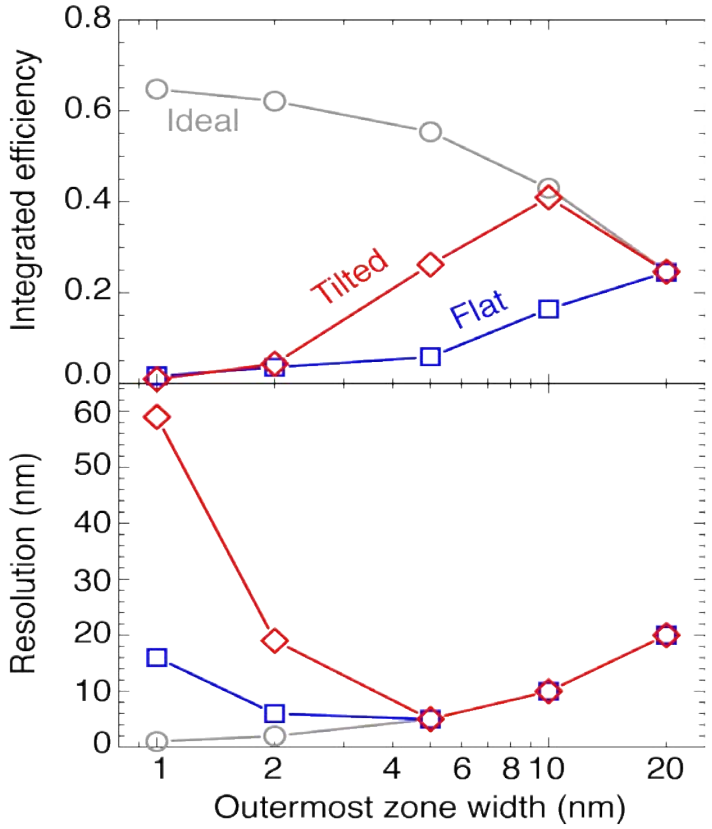
- Full APS flux into a ~250 nm spot
  - 'any' technique can now add microscopic resolution

Sacrifice some focused flux for further improvements in spatial resolution

- 50 nm for long working distance (10s of mm), e.g., using K-B mirrors
  - Enables in situ, complex sample environments
- 20 – 10 nm for high spatial resolution, but short working distance (eg, mm) , e.g. using zone plate optics
- 5 nm and below, for highest spatial resolution, using, eg, MLLs
- Can combine all of the above with CDI/ Ptychography for further improved structural resolution, and deconvolution
- Expect nearly direct translation of increased brightness into focused flux.



Flat MLL **Tilted MLL** **Ideal MLL**



Kang et. al, PRL, Apr., 2006

Dependent on optics and detectors, but linked to speed: sensitivity

Today at APS:

- (100 mA, 3.0 nm,UA, L=2.4 m)
- XRF detector collects 6% of 4πSR

	Spot size		
sample thickness [um]	200 [nm]	20 [nm]	5 [nm] (0.1s)
0.1 [um]	3500	35	15
10 [um]	26000	260	60

Future ?

- 100x more coherent flux
- plus assume XRF detector collects 30% of 4πSR

	Spot size		
sample thickness [um]	200 [nm]	20 [nm] (15ms)	5 [nm] (0.5ms)
0.1 [um]	180	6	4
10 [um]	1800	50	25

10 keV incident beam energy, biological sample in water (frozen hydrated)

minimum detectable Zn [#atoms], limited by rad damage:

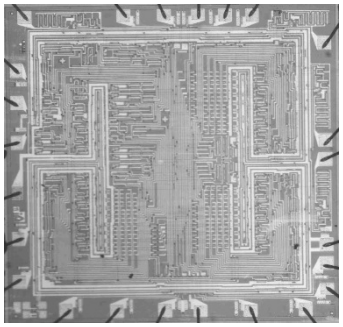
For materials sciences samples, radiation damage less of an issue

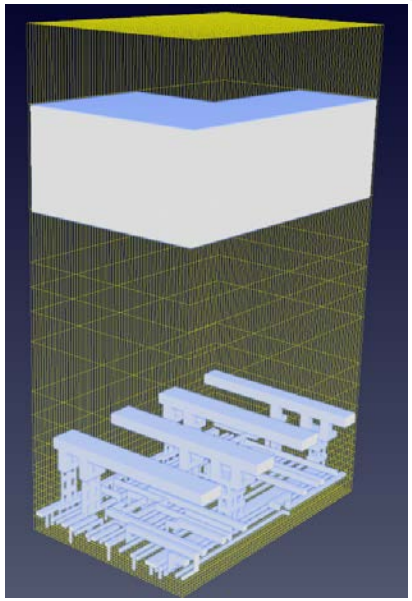
High resolution optics, and large area, minimum background detector modules required for highest sensitivity, need brightest source to make meaningful use

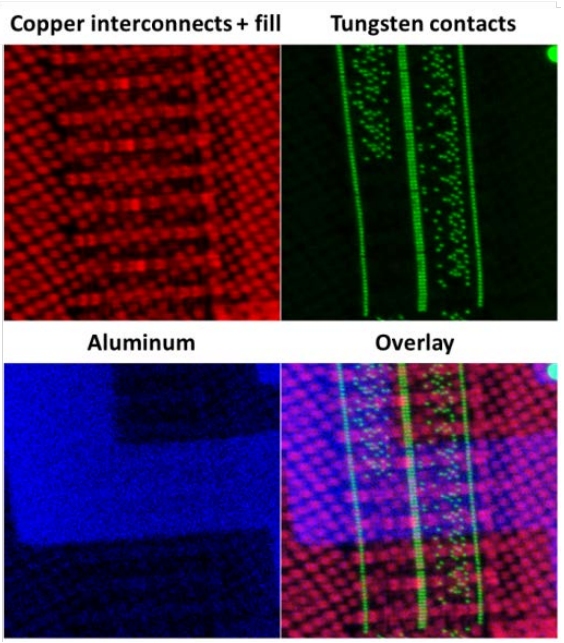
Enabler speed: spatial resolution in a large field of view

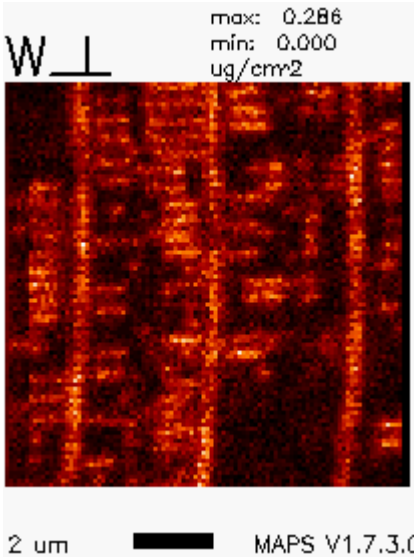
- Need high spatial resolution to resolve structures, achieve sensitivity: optics, detectors
- Need high flux to acquire data in reasonable time frame: **source**

APS Today			**APS-U:**		
Scan area	**Resolution**	**Dwell time**	**Scan time**	**Dwell time**	**Scan time**
10x10mm	100nm	5ms	1.5 years	**25 us**	3 days
100x100 um	20nm	0.1s	29 days	0.5ms	3.5h
10x10 um	5nm	0.1s	5 days	0.5ms	0.5h







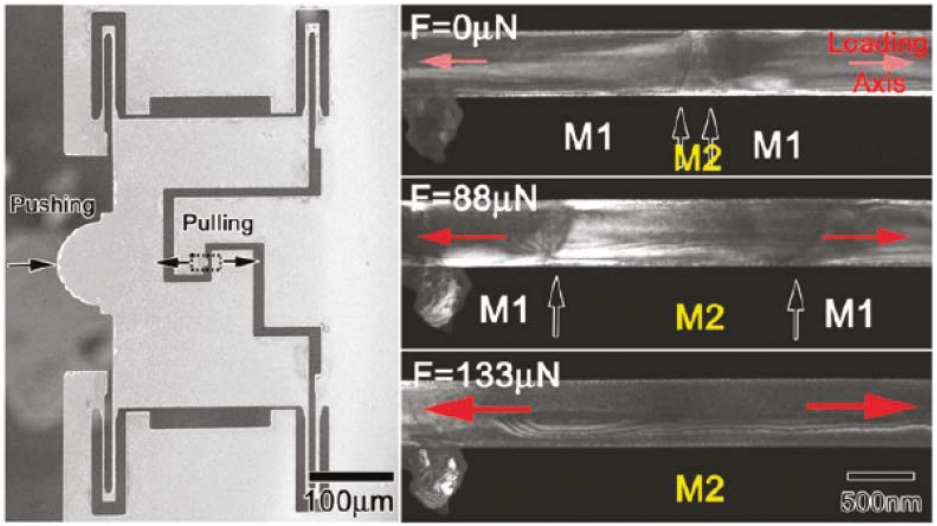


Part of a Microchip, scan 180x180 microns, 100nm steps, 6ms dwell

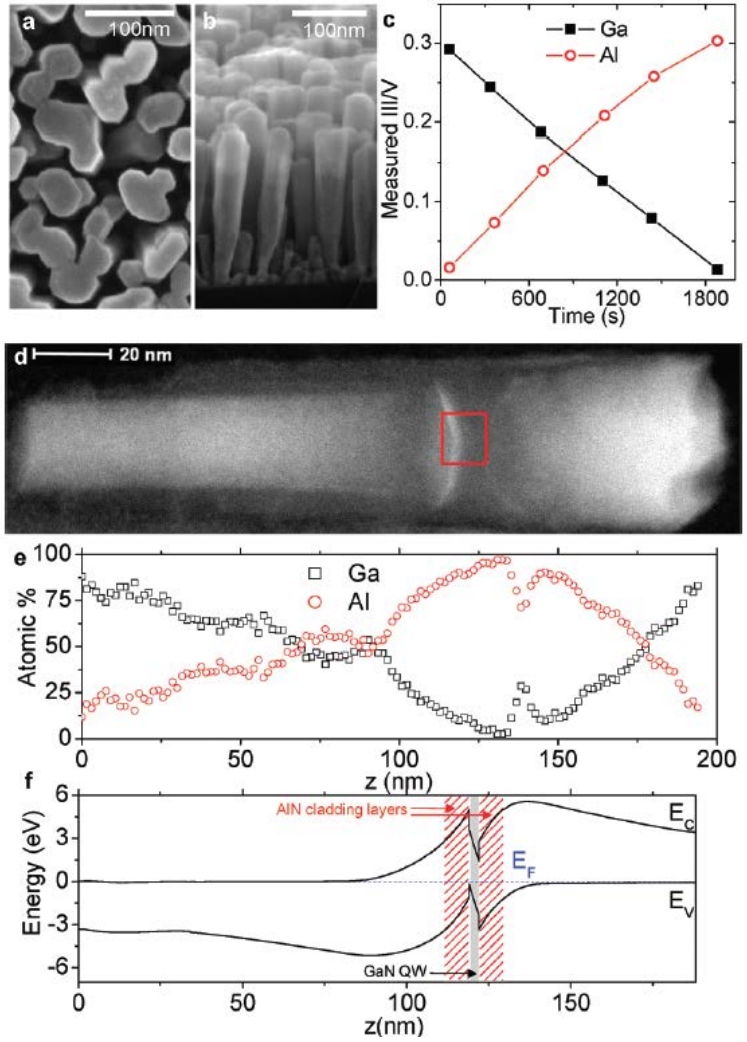
Integrated Circuits view by microprobe (E. Lavely et al), BAE

Speed enables dynamic microscopy

- **Observing response of real systems to real environments**
  - Beyond the pump-probe: continuous evolution at the nanoscale
  - Process induced structural evolution and trace metal spectroscopy of wide-bandgap semiconductors under growth conditions
  - Nanoscale statics and dynamics of phase transitions in correlated electron materials



Nanoscale pinning and de-pinning of M1-M2 structural phase transition in a stressed nanobeam of VO2



Growth of compositionally graded wide bandgap nanowires exhibiting virtual p/n junction behavior without impurity doping

H. Guo et al. *Nano. Lett.*, **11**, 3207-3213 (2011)

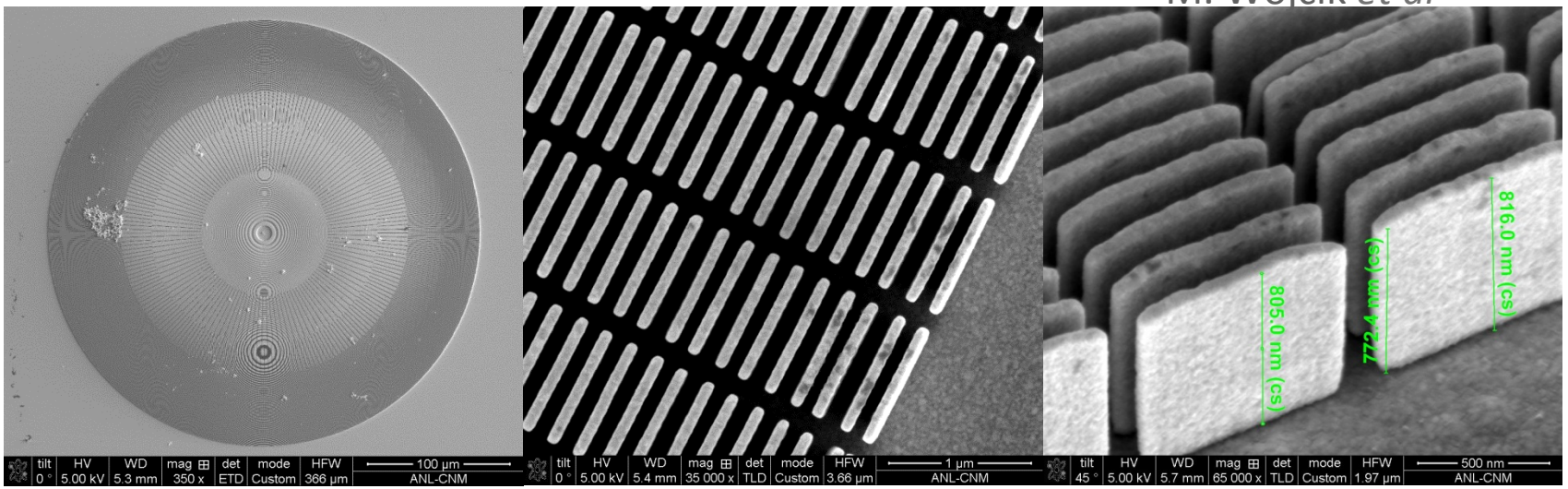
S. Carnevale et al. *Nano. Lett.*, **12**, 915-920 (2012)

Challenges

- Nano focusing Optics
  - Diffractive, reflective, refractive
  - Life time in beam
- Nanopositioning (in particular for *in situ*)
- Detectors
  - Speed
  - Resolution (spatial, energy)
  - Background
- Radiation damage (see tomorrow)
- **'Big data'**

Zone plate development:

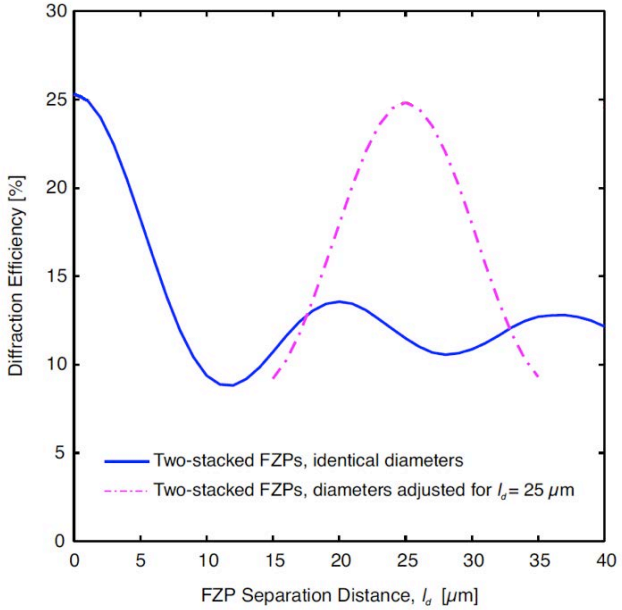
M. Wojcik *et al*



Zone plate with 100-nm-outermost zone width, 300-µm-diameter, 800-nm-thick Au zones; fabricated for stacking experiments (with matching twin zone plates).

Soft X-ray zoneplates lead the way re: spatial resolution
Increase aspect ration to achieve reasonable efficiency
Current plans: develop zone plate technology to go down to 10 - 20 nm spatial resolution, at high aspect ratios (=efficiencies), using multiple stacking / doubling approaches

Simulation: two stacked zone plates with dr_N=20 nm, optimized for different stacking distances
J. Vila Comamala *et al.*, J. Synch. Radiat. **20**, 3 (2013).

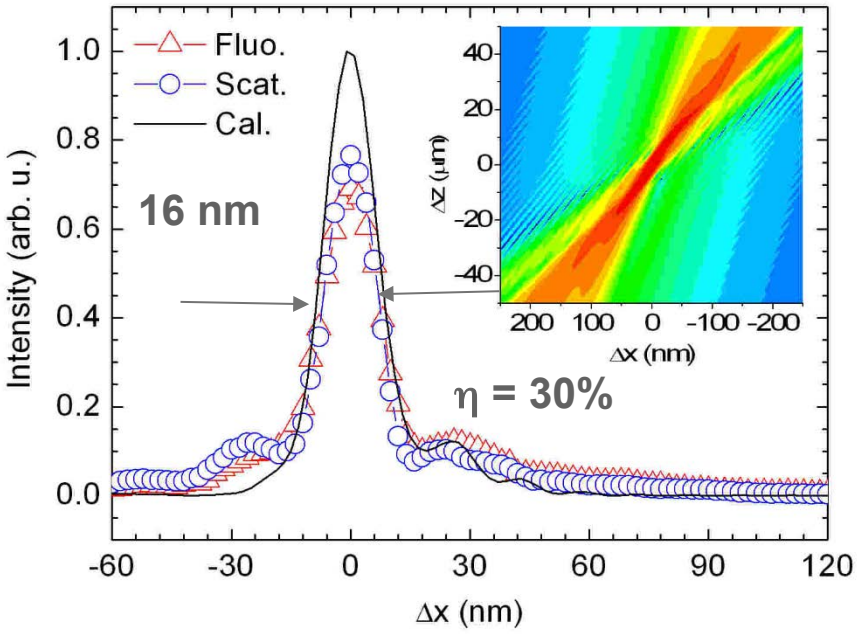


MLLs to go to 5 nm and below

- **Parameters:**
  - drN = 5 nm structure:
  - Deposited: 13.3 um of 30 μm

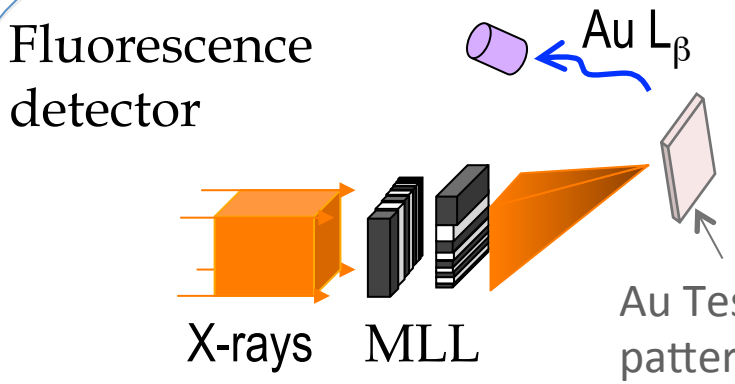
  → diffraction limit: 12.5 nm

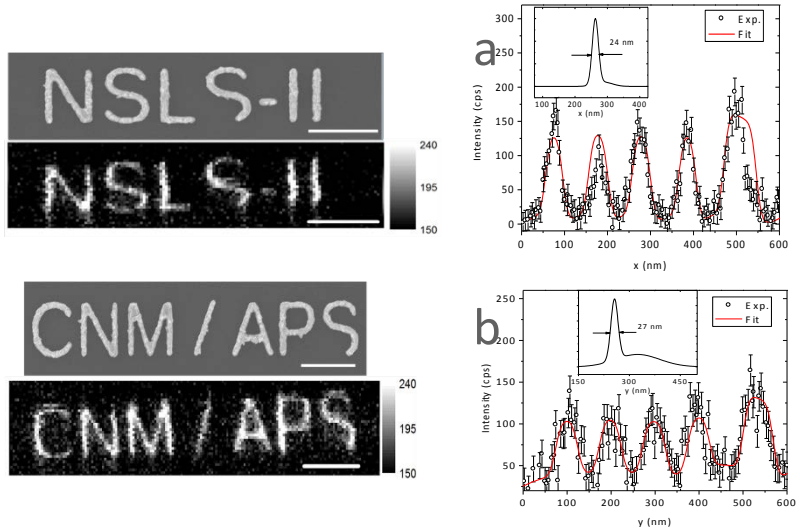
Photon Energy: 19.5 keV



1D Efficiency: 30% at 19.5 keV

Kang et al, APL 92, 221114 (2008)





Measured Spot size 25 x 27 nm, 12 keV

2D Efficiency: 17% at 19.5 keV

H. Yan et al., Opt. Express 19, 15069-15076 (2011).

Challenge: Nanopositioning

- Use of overfilled secondary source to 'stabilize' focused spot much less desirable
- For highest resolution, need to keep optics aligned with regards to specimen much better than 5 nm …
  - More challenging with *in situ*
- Greater speed enabled by DLSR actually helps ….

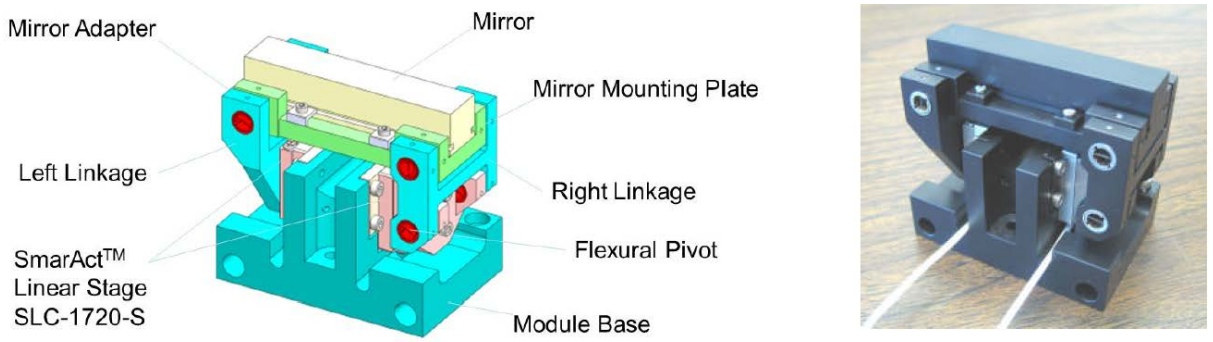
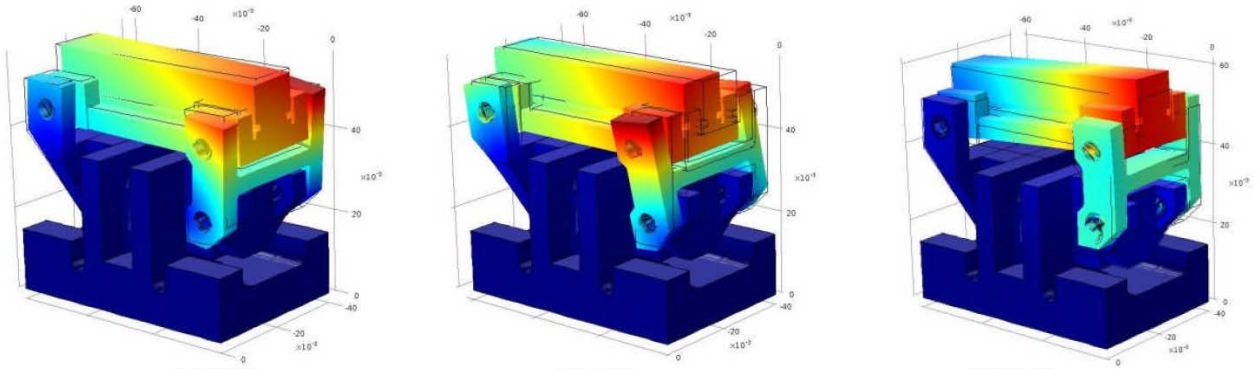
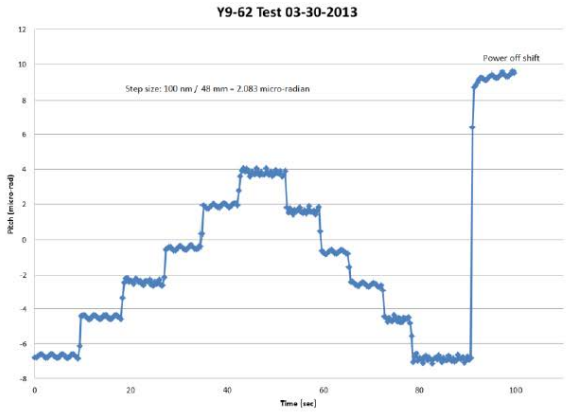


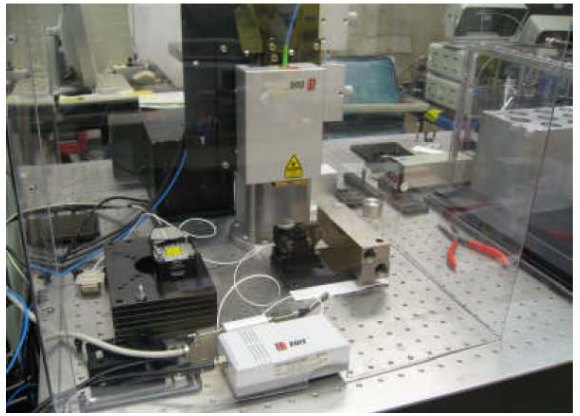
Figure 4. Left: A 3-D model of the mirror mount module for 40- to 80-mm long mirrors. Right: Photograph of the mirror mount module Y9-6201.



1471 Hz 1563 Hz 2624 Hz

Figure 5. Simulated 3-D models of the first three resonant frequencies using the finite element analysis method[10,11].





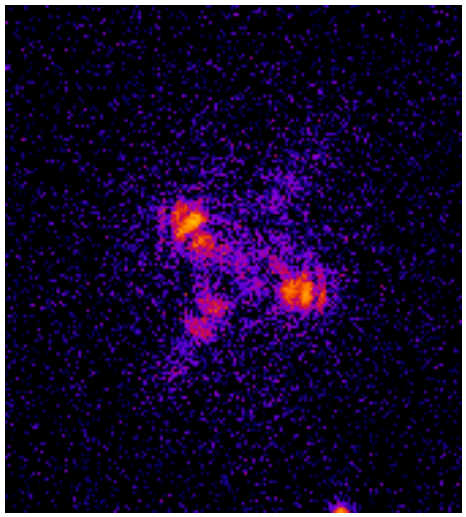
Detectors:

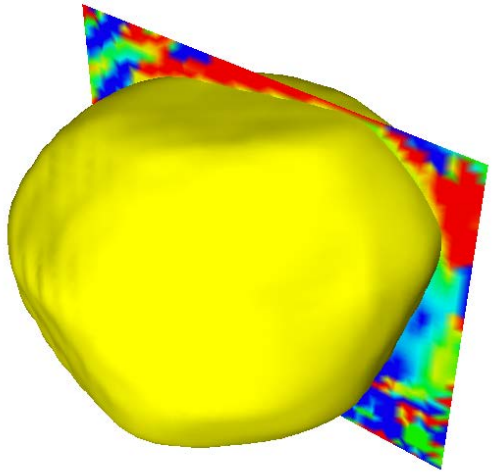
- Higher-speed, low-background, larger-dynamic range (2D) detectors required.
  - Combine ptychography with fast scanning for XRF
- XRF detectors need to be capable of processing **GHz** instead of **MHz** of signals

At APS 34-ID-C:
9.25 hours of scanning
0.64 hours of x-ray exposure

APS-MBA

10 sec?





~7nm data

- Developments are under way, eg., MAIA (XRF detection) can go to 10s of u-seconds, new electronics that can actually analyse pileup (OCR of 1Mcps using a conventional SDD)
- Additional future developments likely, eg, improved, modular, packing of multi element detector systems, etc. -> sensitivity
- Improve peak-to-background / Energy resolution for further improved sensitivity (detect single atoms)

Truly Exciting Opportunity: full chemical information in one shot

Challenge:

Determining chemical states at 30 to 100 nm scale is difficult. Energy scanning for XANES is time-consuming, requires high spatial stability as the energy moves, and puts a large radiation dose on the sample.

For spatial resolution below 20 nm on dilute sample, conventional XANES may be impossible (radiation damage).

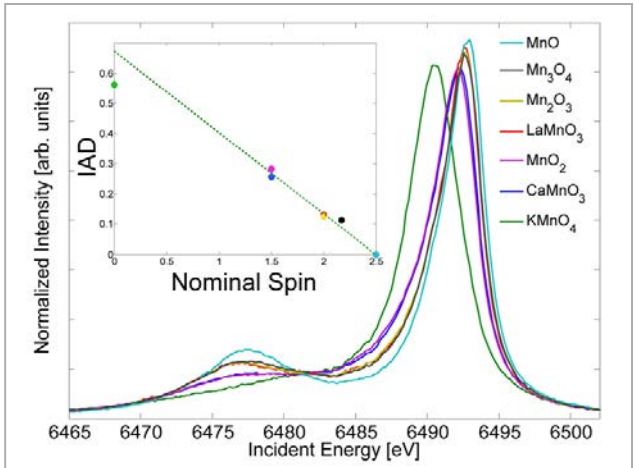


Fig. 6. Kβ main X-ray emission spectra normalized to the spectral area of manganese oxides, $K^{VII}MnO_4$ and perovskites $CaMn^{IV}O_3$ and $LaMn^{III}O_3$; (inset) IAD values with MnO as reference as a function of formal spin state with linear fit that considered MnO, MnO_2 and perovskites. The statistical error is smaller than the symbols.

Opportunity:

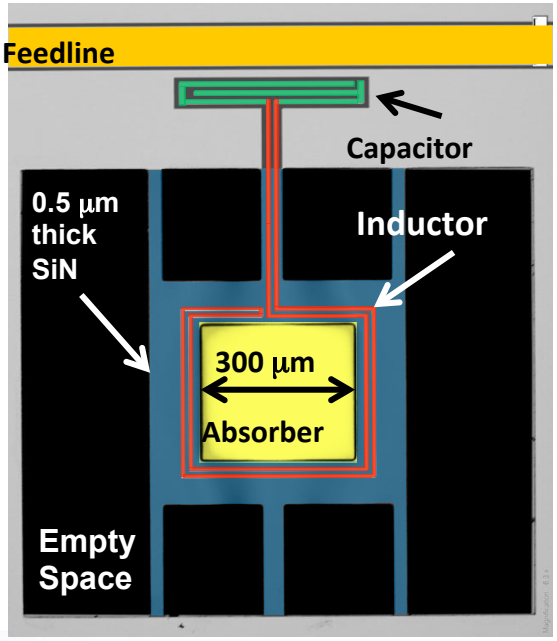
High energy resolution XRF (~1 eV at 6 keV) allows chemical/spin state determination without scanning incident energy.

Could get full chemical state information for ~all elements in illuminated spot simultaneously

Currently, need crystal analyzers with low efficiency, -> measurements photon flux limited and slow, can only measure one element at a time.

Recent developments at APS and NIST with superconducting XRF detectors promise ~1 eV resolution at 10^5 Hz. Coupled with a high flux nano-probe beam, this will allow chemical state determination for **multiple elements** simultaneously, without moving anything, and much less susceptible for radiation damage.

This will allow currently impossible nano-scale mapping of chemical states, and revolutionize scientific areas in biology, energy sciences, materials chemistry, and geo-sciences.



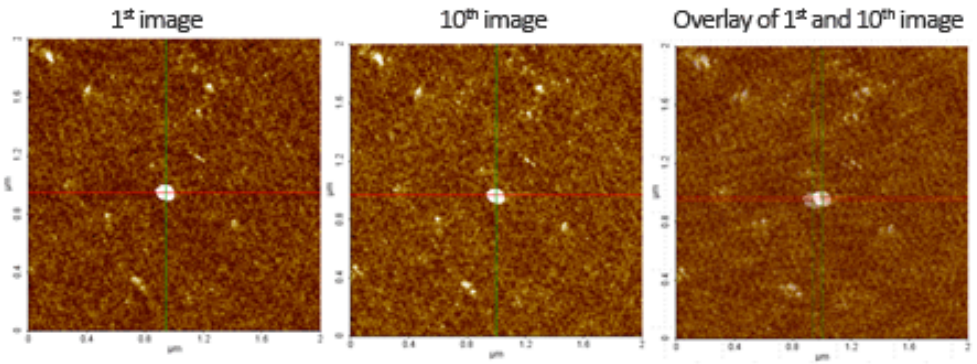
ANL test device: Miceli, Cecil *et al.*

Most interesting (complex ?) challenge: the software side

- Already today, data volumes are becoming challenging
- DLSR bring another factor 100x
- Datasets themselves become more challenging: combination of numerous contrast mechanisms (XRF, ptychography) within the same instrument, as well as in fusion with others (TXM, EM, visible light microscope,..).

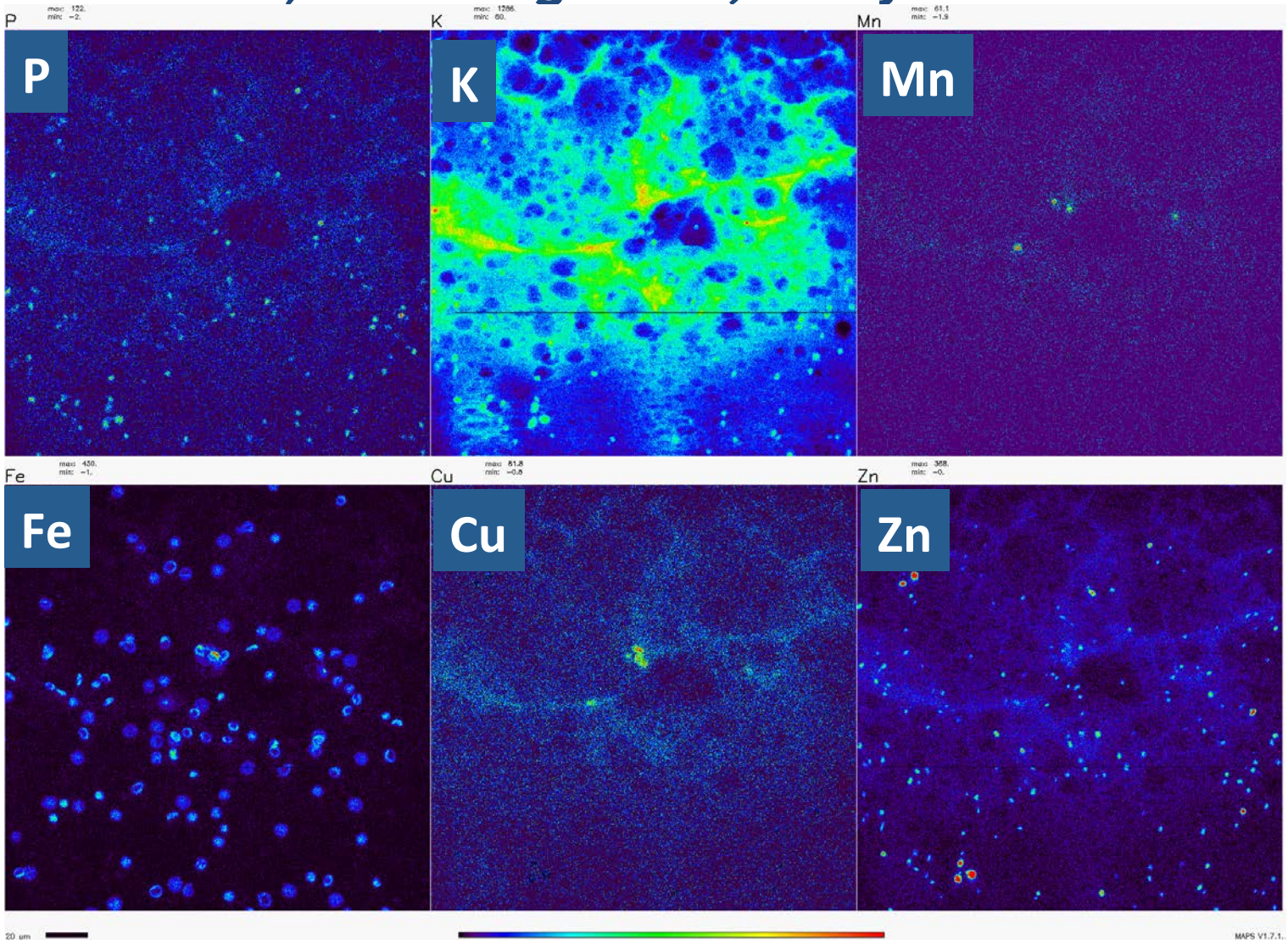
=> Interpretation without significant reduction from software becomes impossible (handling of volume not sufficient)

- *In situ / operando* in combination with tomography and spectroscopy
  - Sample drifts harder to measure
  - the sample is changing while being measured
  - Software to reduce complex data sets to few relevant numbers



X drift rate	0.738 nm/min
Y drift rate	0.523 nm/min

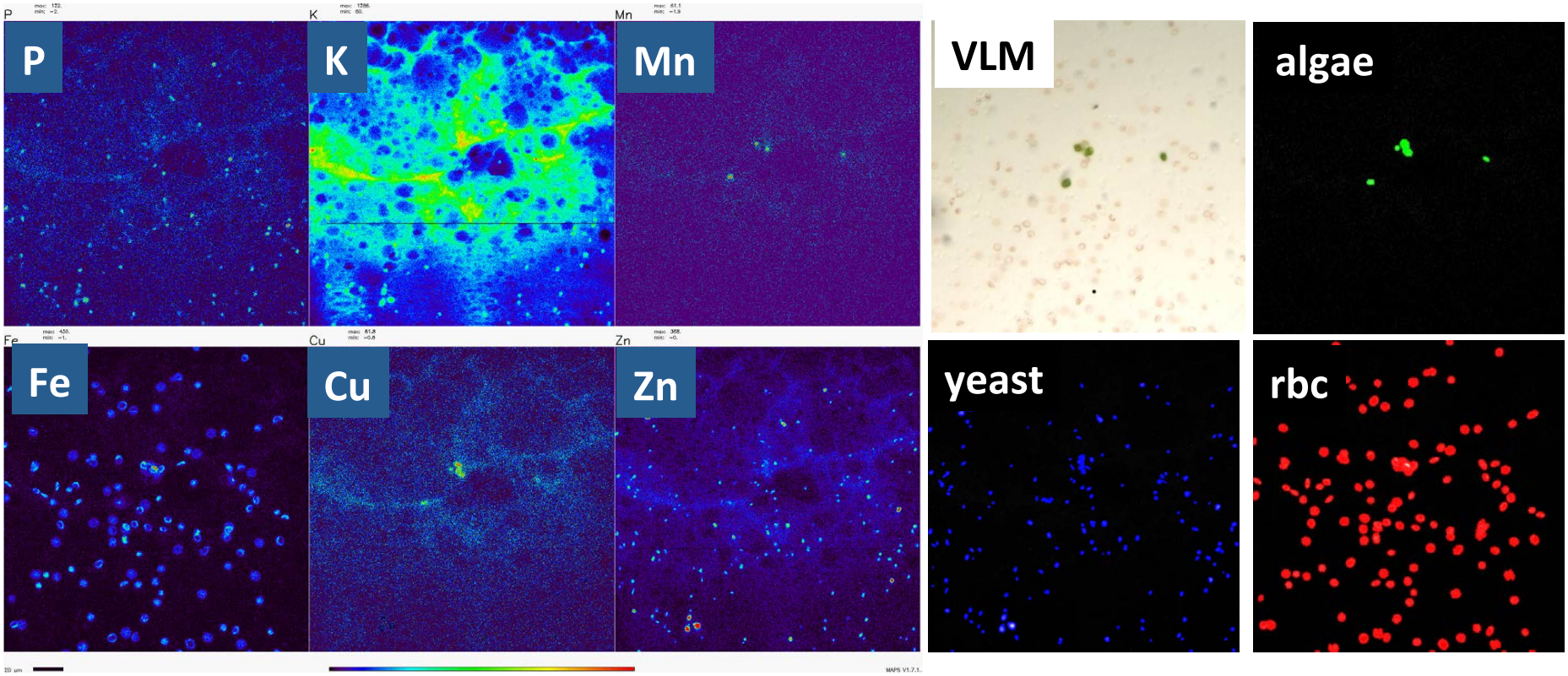
Example dataset: 3 different cell types(yeast, algae, red blood cells) on background, noisy data



Yeast: P+Zn, red blood cells: Fe, Algae: Fe+Mn

Dataset: 0.3x0.3um step size, 200x200um fov, 10 ms dwell time

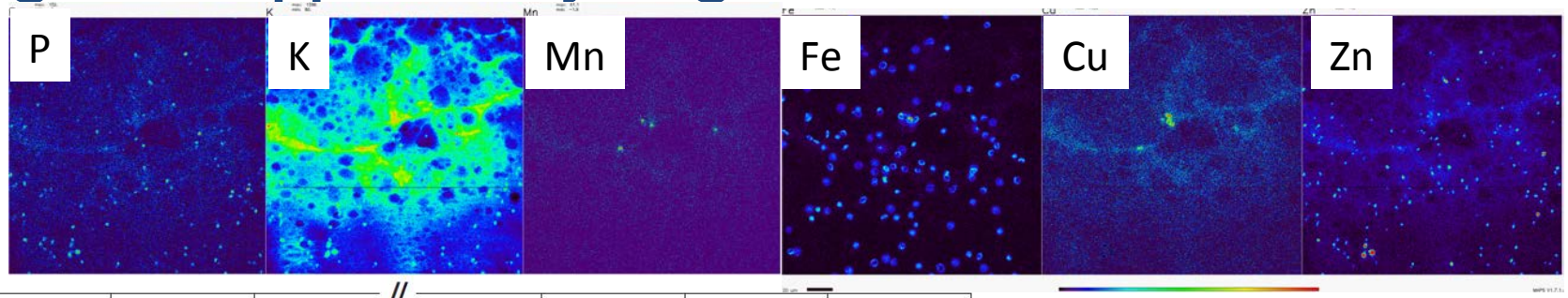
Example dataset: 3 different cell types(yeast, algae, red blood cells) on background, noisy data

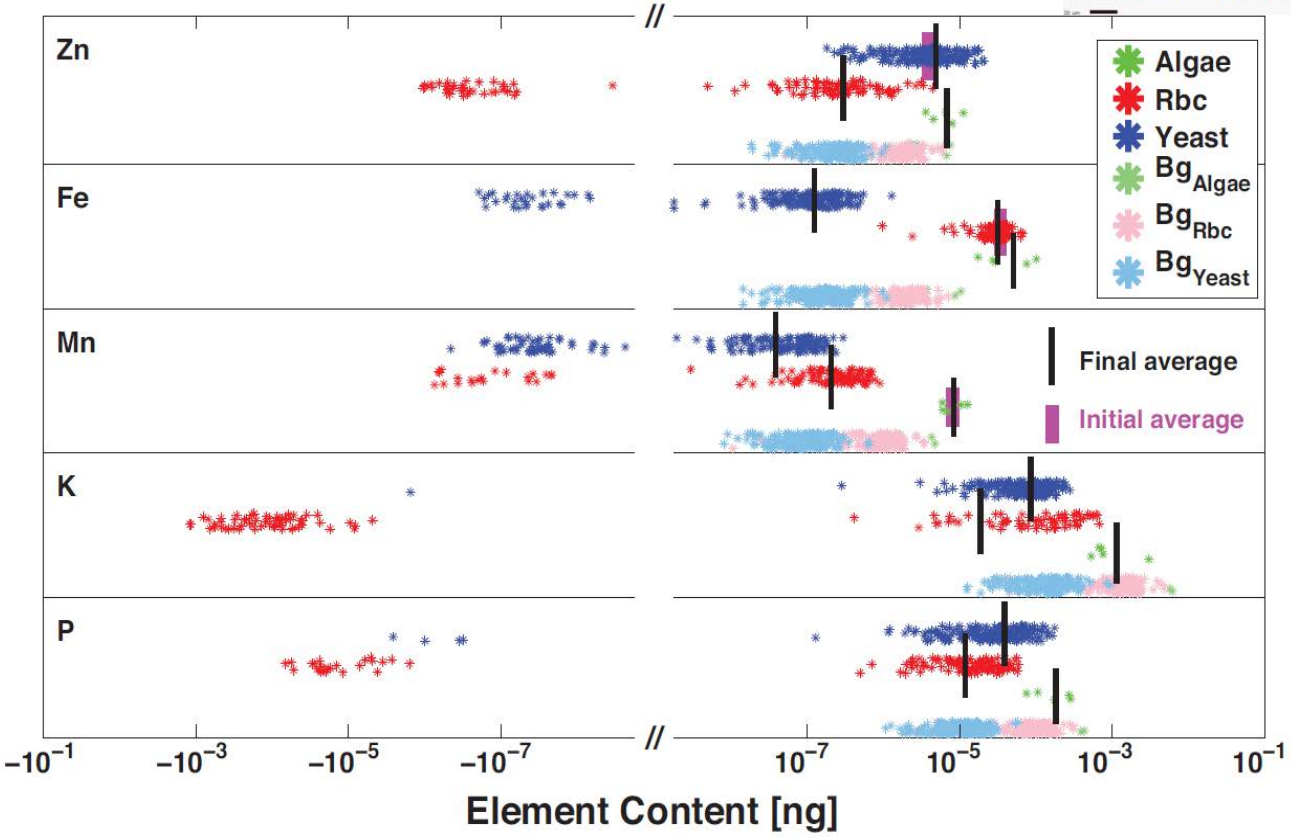


Algorithm is able to detect presence of cells and correctly classify cells into different categories.

Yeast: P+Zn, red blood cells: Fe, Algae: Fe+Mn
Dataset: 0.3x0.3um step size, 200x200um fov, 10 ms dwell time

Challenge and opportunity: Big Data





- Scalable (regions)
- Takes care of background
- Deals with **overlapping objects**
- unsupervised

Efforts under way include a finished LDRD, a director's LDRD, collaborations with Math and Computer Science, ASCAR, …

Siwei Wang et al, submitted

DLSR revolutionizes scanning probe microscopy

- Hierarchical visualization: From nanometers to full samples
- Directly improves spatial resolution in x-ray microscopy
- Enables XRF/XRD tomography at full fidelity, ie, with a 3D resolution matching the lateral spatial resolution of the instrument
- Permits high spatial resolution at the same time as a large field of view (we can actually find the proverbial needle in the haystack)
- Opens up the realm of studying dynamic processes for weakly interacting samples or samples requiring trace sensitivity
- Enables *in-situ* in real time (combinations with tomography, spectroscopy, etc)
- Could lead to full chemical analysis down to 5 nm, in real time. With KB mirrors, can achieve *in situ*, in real time down to 50 nm.
- Challenges:
  - Nano focusing Optics, Nanopositioning (in particular for *in situ*)
  - Detectors, Radiation damage (see tomorrow)
  - 'Big data'

Thank you for your a attention!