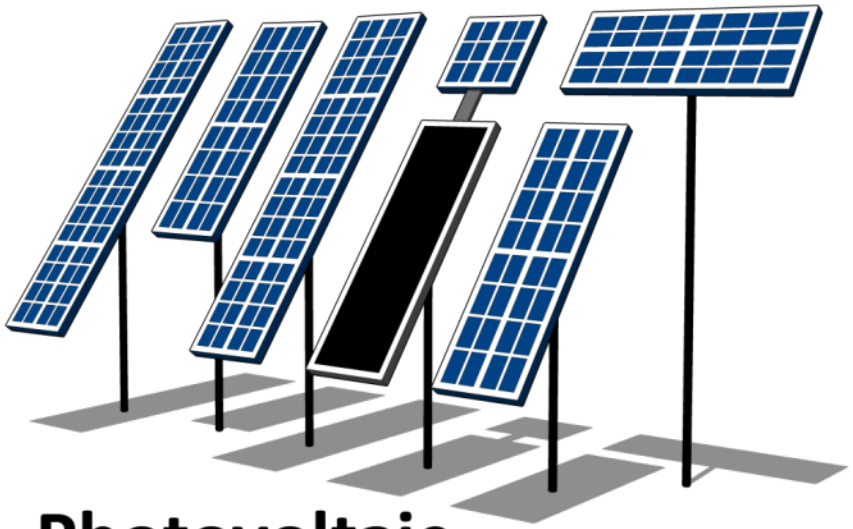
Diffraction Limited Storage Ring: Opportunities for Energy Materials Research

Rafael Jaramillo

Buonassisi Group

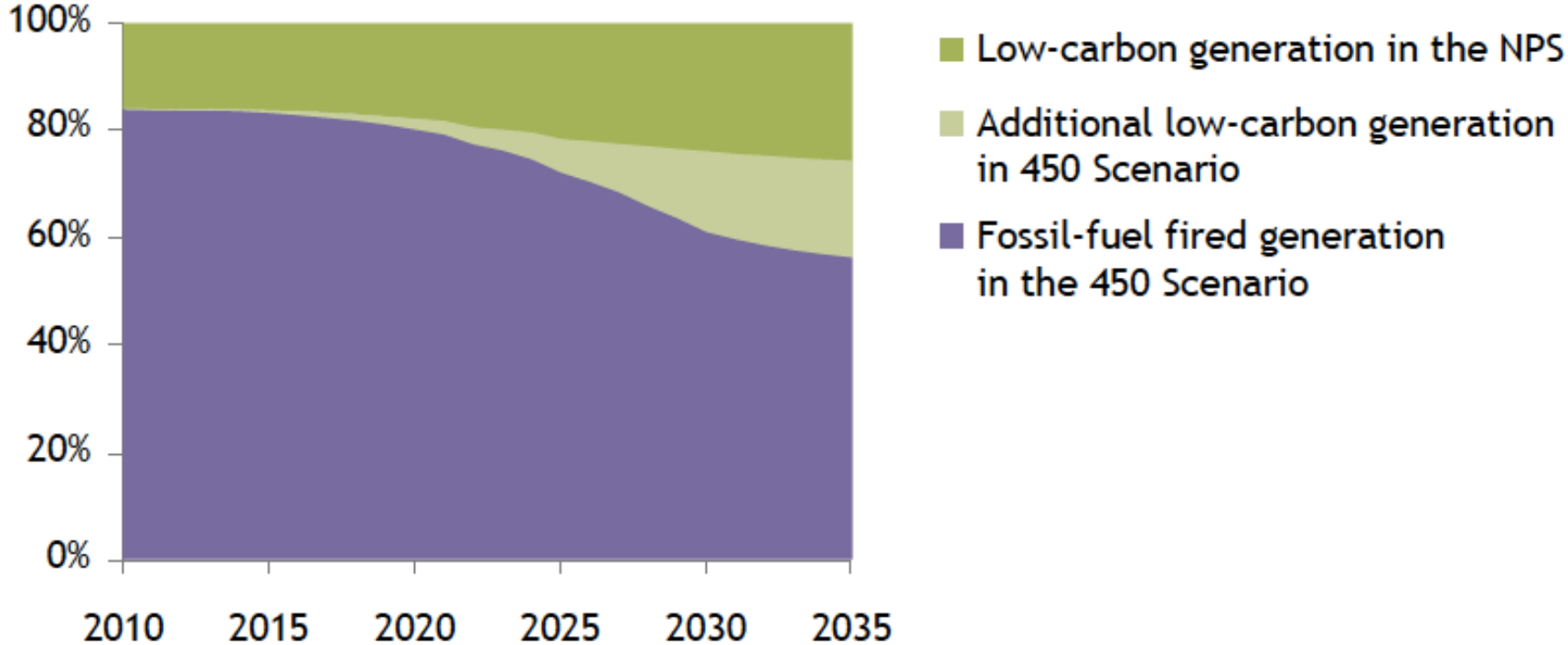
MIT



Photovoltaic Research Laboratory

Urgency & Opportunity

- **Globally, much more renewable energy is needed**
- *A quarter of fossil-fuel energy must be replaced by renewables by 2035, to stabilize atmospheric CO_2 at 450 ppm*



http://www.iea.org/media/workshops/2009/fromroadmapstoimplementation/tanaka.pdf

Urgency & Opportunity

- **In some localities, storage is already needed**
- *High local penetration of renewables affects market pricing, provokes back-lash from traditional utilities*

May 29, 2012

Germany Hits World Record for Solar: 50% of Electricity Last Weekend

SUSTAINABLEBusiness.com

January 16, 2013

German Power Tumbles to Record Low as Solar Damps Demand

Bloomberg

August 22, 2013

Vermont Solar Advocates Fuming Over Net Metering Limitation

RENEWABLE ENERGY WORLD.COM

July 24, 2012

Stat of the Day: California's Big Utilities at 20.6 Percent Renewables in 2011

greentechmedia:

October 12, 2013

The Economist

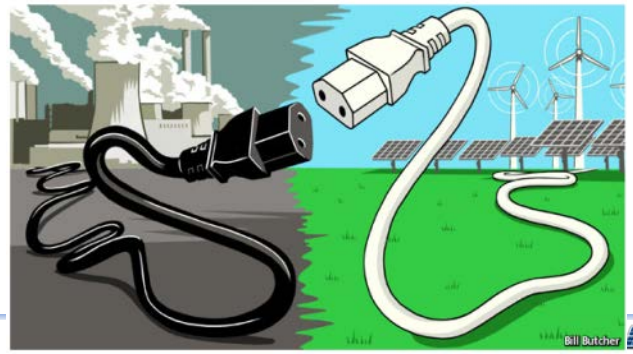
European utilities

How to lose half a trillion euros

Europe's electricity providers face an existential threat

Oct 12th 2013 | From the print edition

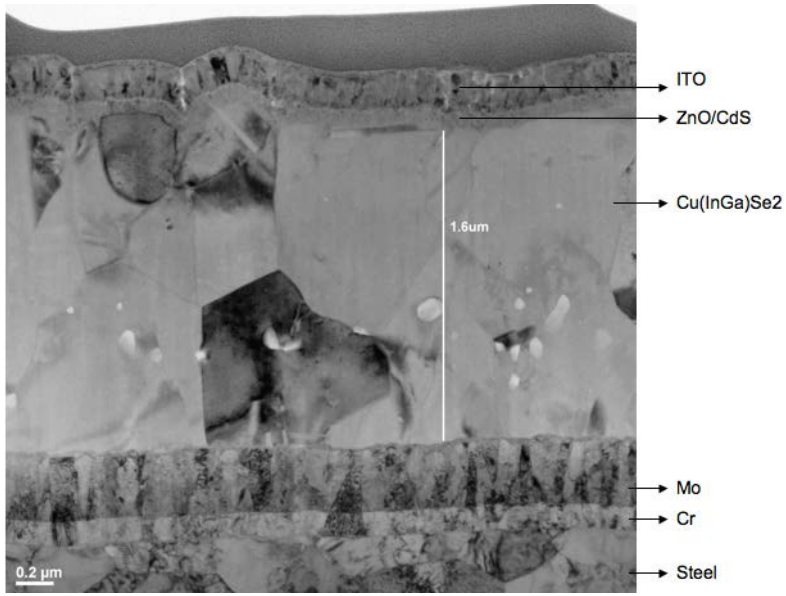
Like 5k Tweet 467



Urgency & Opportunity

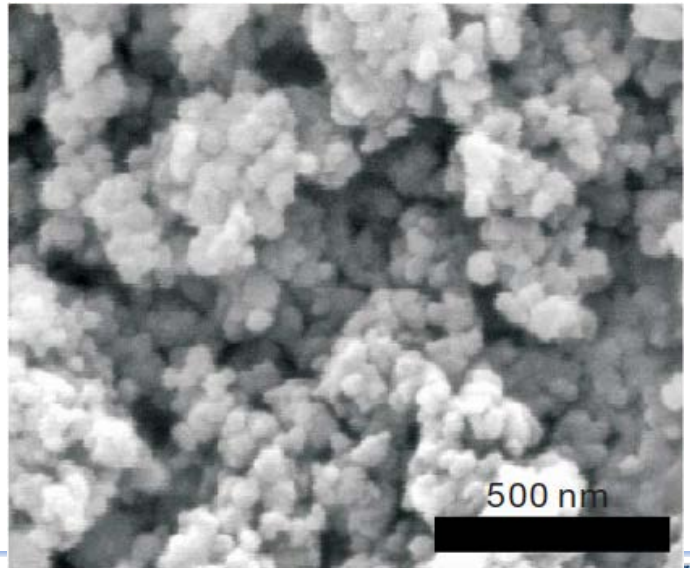
- **Problem**: Adoption of RE generation & storage inhibited by high cost, due to low efficiency and/or expensive materials
- **Grand challenge**: Achieve excellent performance using cost-effective, scalable materials
- **Approach**: Increasing performance requires solving the "structure → process → transport" relation for complex heterogeneous systems

$CuIn_xGa_{(1-x)}Se_2$ (for photovoltaics)



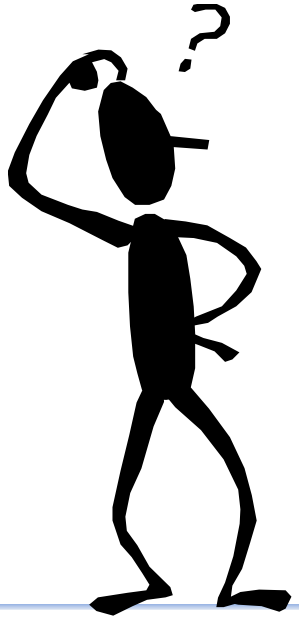
http://www.nanoscience.co.jp/application_notes/surface_analysis01.html

$LiFeO_4$ (for batteries)



B. Kang & G. Ceder, *Nature* **458**, 190 (2009)

A User's Perspective



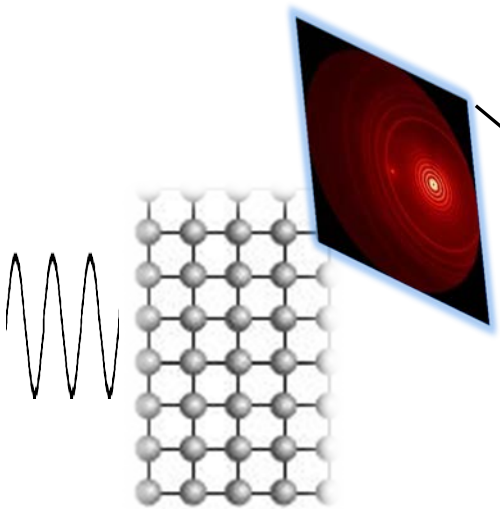
Multiscale visualization

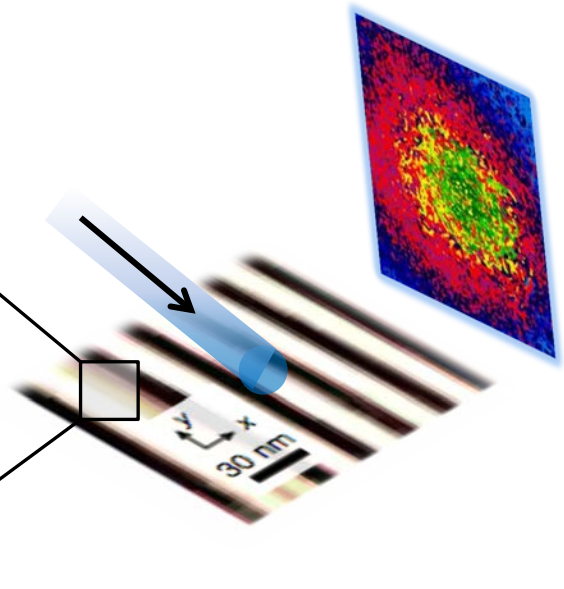
Enabled by enhanced brightness

Atomic Scale ↕ X-Ray Wavelength

Mesoscale ↕ Focused Beam

Macroscale ↕ Scanning Image





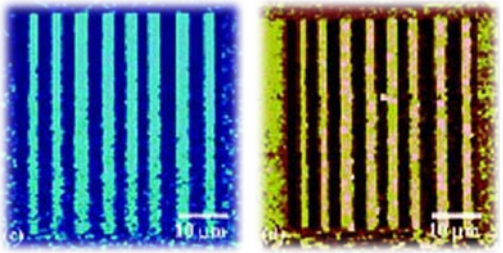
Polarization Domains in $PbTiO_3$
Hruszkewycz *et al.*, PRL (2013)

Memory cells in EPROM chip
Science Photo Library

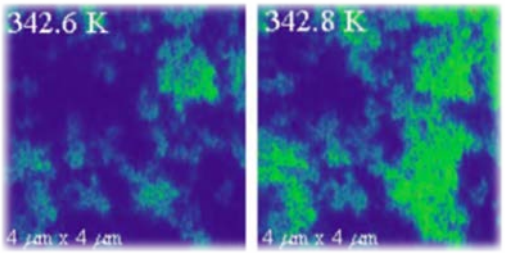
Multiscale visualization

Mesoscale phenomena, mesoscale beam

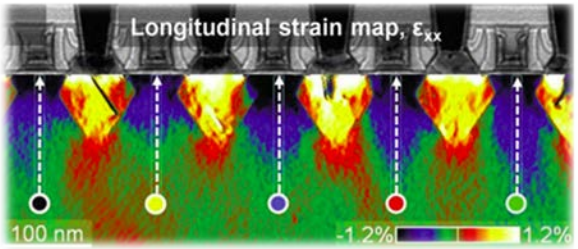
Inhomogeneity requires microscopy



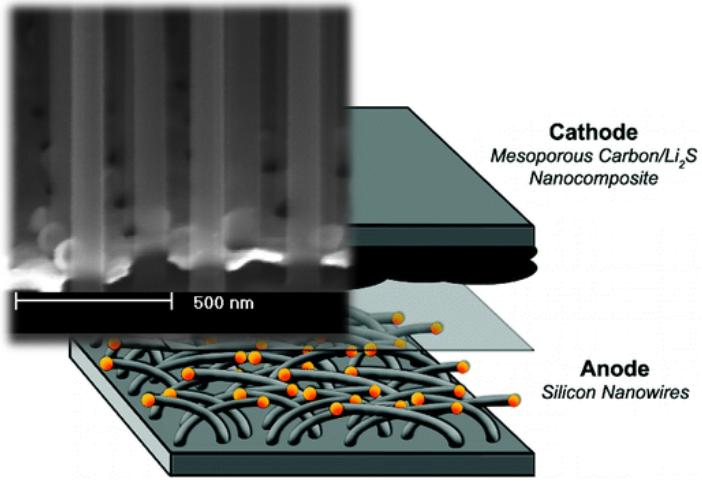
Polarization Domains in $BaTiO_3$
Dawn Bonnell



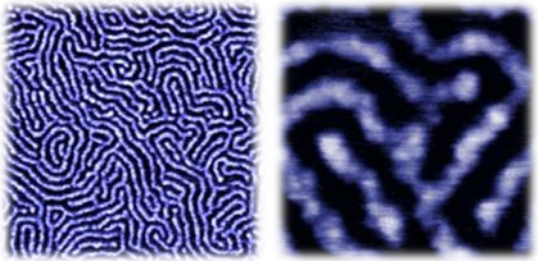
Metallic domains in VO_2
Dimitri Basov



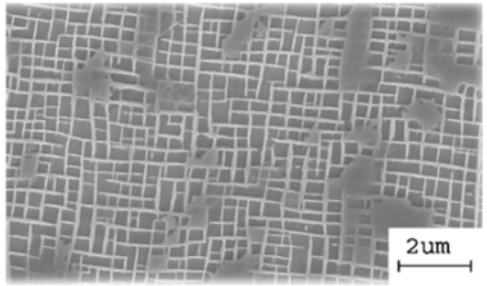
Strained MOSFET channels
Christoph Koch



Si nanowire battery anode
Yi Cui and Pulickel Ajayan



Block co-polymer solid
Christoph Koch



Microstructure of Ni superalloy
Sammy Tin

Multiscale visualization

Macroscale statistics and fast scanning

When did any microscopy get 10,000x faster??

Faster = Different

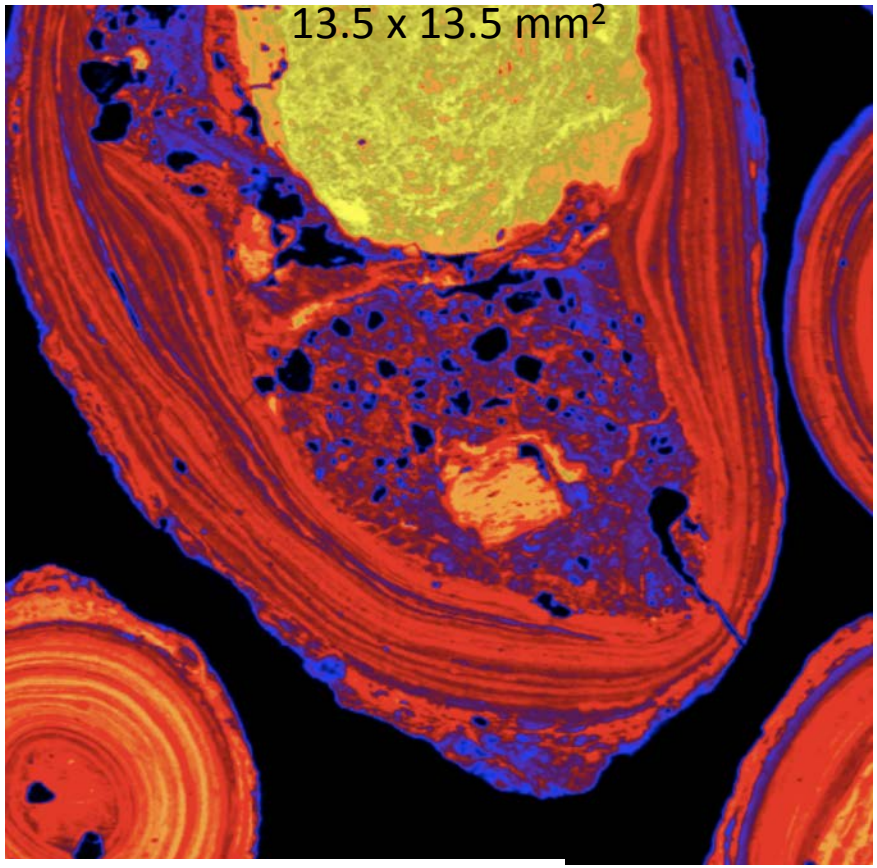
- Numerous contrast modes currently available but all are slow
- Without ability to scan square microns of material, impossible to capture data on "reasonable" area
- Speed can be improved by factor of 1,000 – 10,000
  - 100x gain in brightness = more focused photons on the sample
  - 10-100x gain due to endstation improvements (*c.f.* plans for in situ nanoprobe)
- Faster moves many experiments from realm of demonstration to realm of metrology
  - *e.g*. Nano-XANES to measure fraction of completed redox reactions in an operating electrochemical cell. Relevant timescale = seconds-to-minutes.

Multiscale visualization

Fast scanning for heterogeneous materials

Standard (1500ms/pt) step scan, 10 µm/pixel 0.8 x 0.8 mm^2

Multichannel detector (5ms/pt) slew scan, 10 µm/pixel 13.5 x 13.5 mm^2



Iron-oxide nodules, Rose Dam, WA

Data from studies and related presentations of:

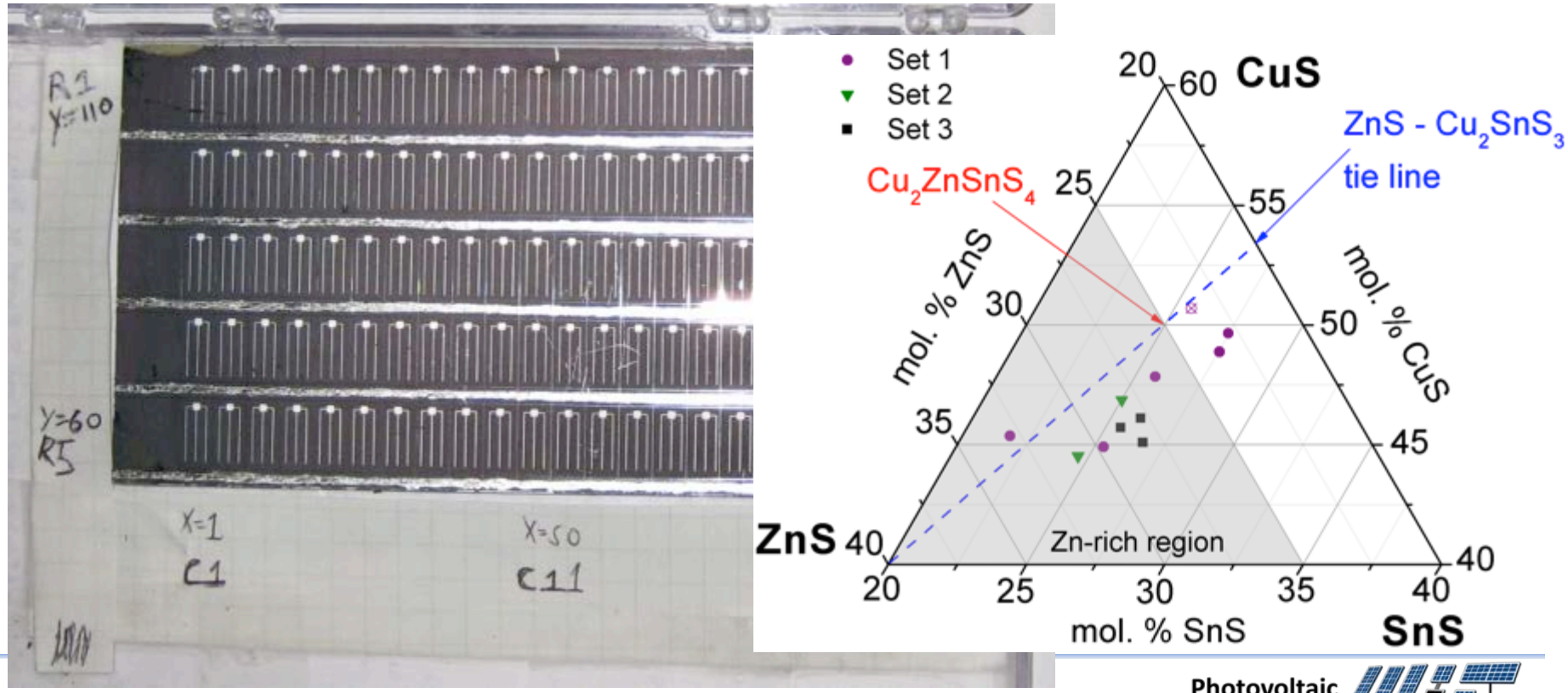
D.P. Siddons *et al*.
DOI: 10.1017/S1431927605510298

C.G. Ryan *et al*.
DOI: 10.1016/j.nima.2009.11.035

Multiscale visualization

Fast scanning for materials discovery

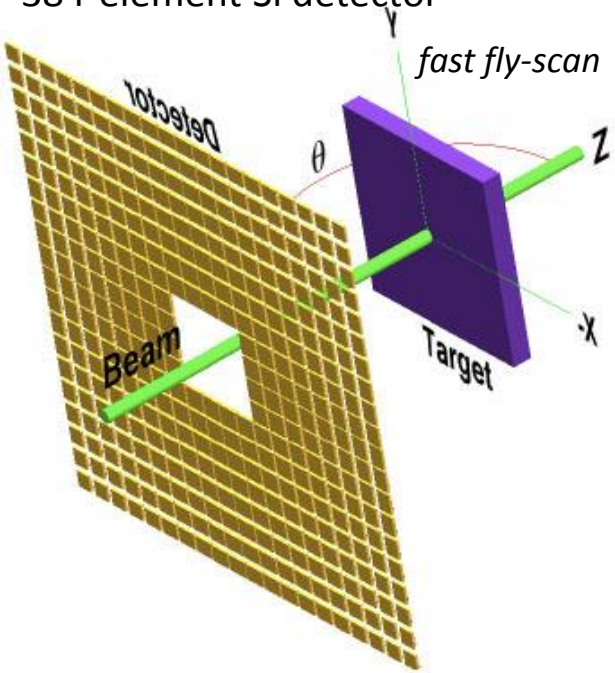
- Capability: Slewscan, fluorescence, quick-xafs probe large material volumes
- Discovery: Enables combinatorial materials discovery and characterization



Multiscale visualization

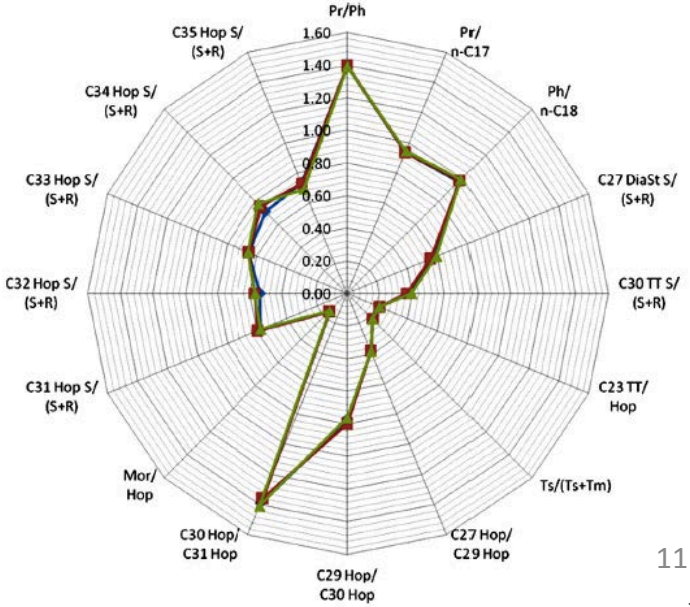
Fast scanning & user productivity

384-element Si detector



- Rapid data processing & visualization enables on-the-fly decision-making, improved data quality, statistics
- Zoom between multiple length scales enables ROI identification, correlation with ex-situ nanoscale techniques
- Point-click interface renders synchrotron accessible to new users
- Online data management enables collaborative research
- *Greatly enhance impact for a fraction of total beamline cost*

spider plot → data correlation



top: C.G. Ryan *et al*.
DOI: 10.1016/j.nima.2009.11.035

bottom: A.E. Pomerantzetal *et al*., *Org. Geochem.* **41**, 812 (2010)
http://www.lanl.gov/orgs/mst/mst6/eml/jeol_6300fxv.shtml

Process control

The *in situ* nanoprobe beamline

X-rays allow true *in situ* studies with unique contrast modes

Inhomogeneous Processes

- Heterogeneous Catalysis
- Device Failure
- Refining & Annealing
- Water Splitting
- Electromigration
- Crystallization
- Phase Transitions
- Thin Film Growth

in situ nanoprobe

X-Ray Contrast

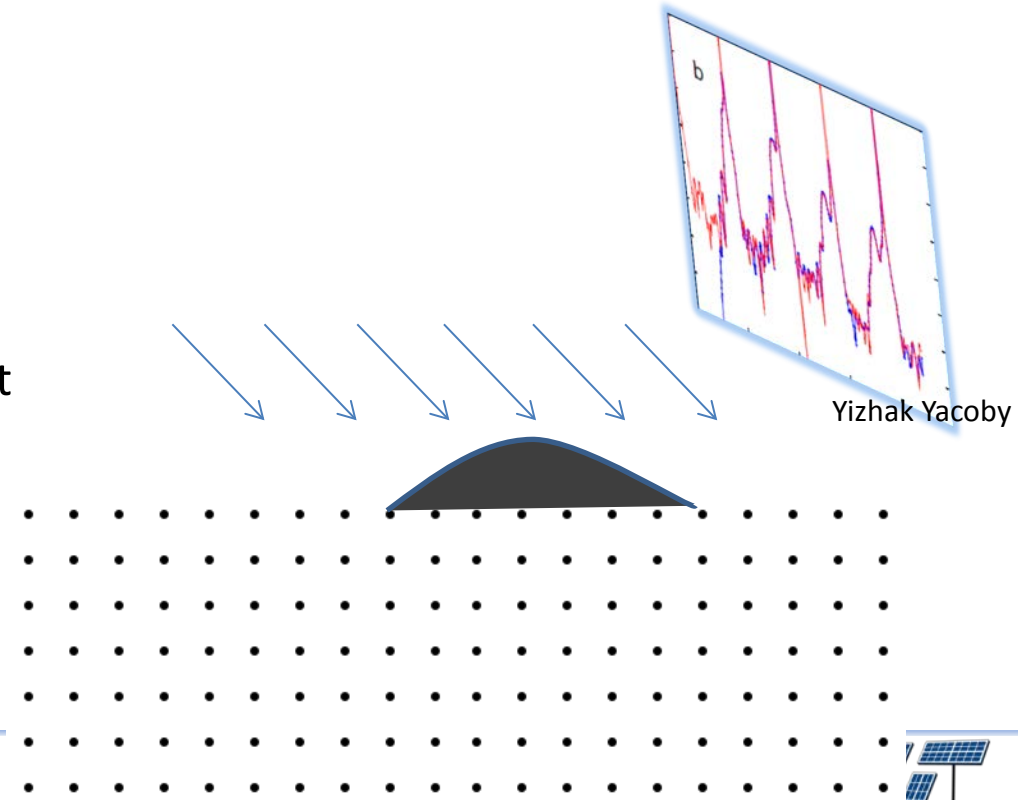
- Crystallography
- Bandstructure
- Chemical Environment
- Elemental Analysis
- Fast & Slow Dynamics
- Collective Excitations
- Packing Density

Process microscopy

Coherent Imaging of Grain Nucleation

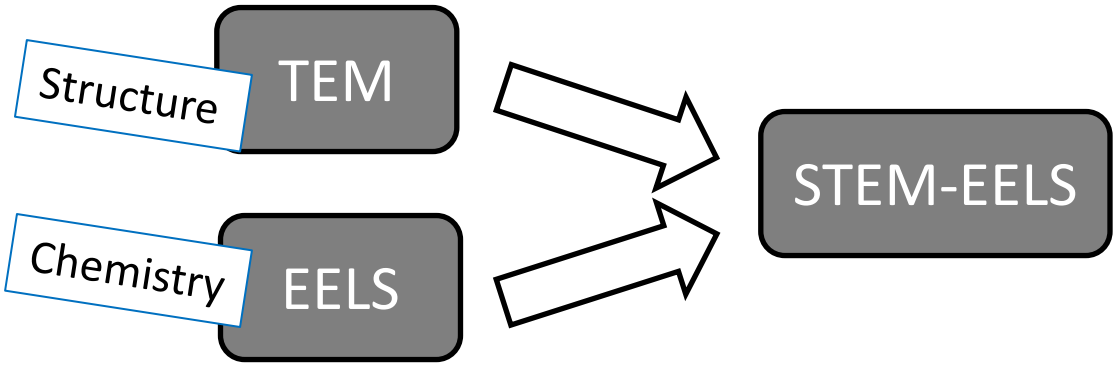
- Coherent reconstruction of thin films & periodic structures is established (COBRA) but it cannot capture the critical first stages of nucleation and coalescence
  - Inherently inhomogenous
- Small & coherent beam can connect
  - Non-equlibrium structures (most materials)
  - Thin film growth parameters
  - Interface structure (key for device performance)

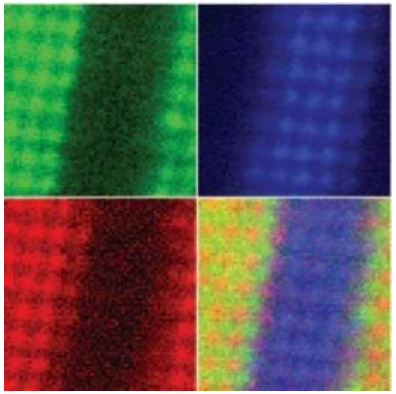
In situ microscopy of thin film grain nucleation and growth



Chemistry & structure, now in situ

Compliments & complements to electron microscopy





Robert Muller

- X-ray SPM is complementary to TEM
  - True *in situ* and *operando* studies impossible with TEM
  - Unique contrast mechanisms

Process microscopy

Need for *in situ* chemical state mapping

- In-situ, high-temperature, sub-micron chemical mapping will elucidate material kinetics and thermodynamics under realistic conditions, enabling:
  - √ Defect mitigation technologies
  - √ Predictive simulation (materials by design)
  - √ Faster cycles of learning
  - √ Realization of promising candidate materials for energy

	Solar Cell	Thermo-electrics	Catalysis	Batteries	Fuel Cell
Temperature (°C)	500-1500	500-1000	400-2000	~500	600-1000
Pressure	1 atm	1 atm	1 atm	1 atm	1-5 atm
Length Scale (Defect - Device)	nm - cm	nm - cm	nm - cm	nm - mm	nm - mm

Process microscopy

Battery failure analysis

- Li metal dendrites cause catastrophic failure
- No other technique can monitor damage on relevant length scales during operation
- Nano-XANES + Nano-XRF + Nano-tomography
  - Identify chemistry-structure-process relationships leading to failure

Process microscopy

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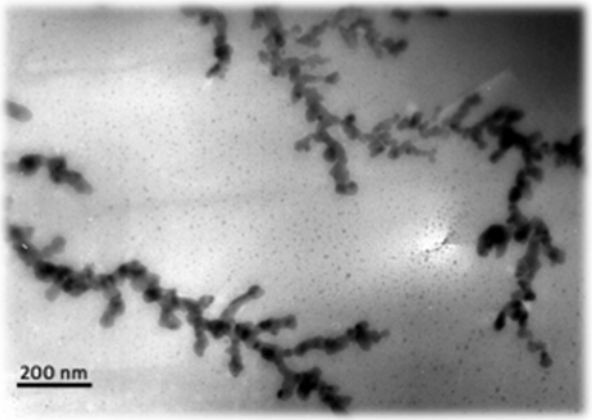

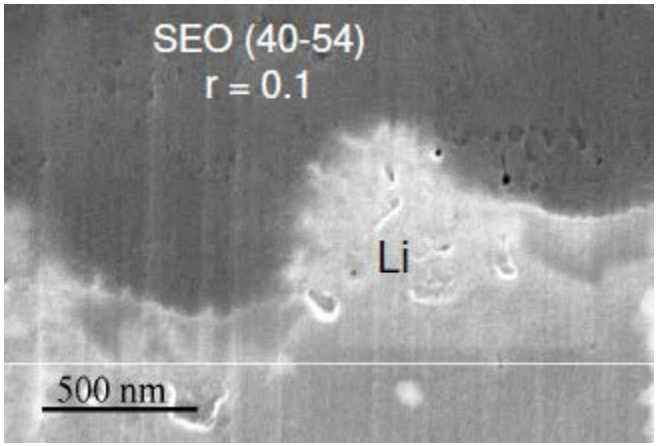

Nitash Balsara

Process microscopy

Battery failure analysis

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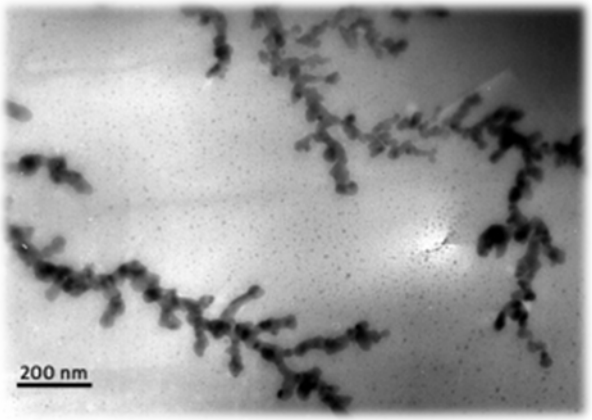
- Nano-XAN
  Nano-tom
  - Identify c
    process r
    failure



ARTICLES

PUBLISHED ONLINE: 16 MAY 2010 | DOI: 10.1038/NMAT2764

nature materials

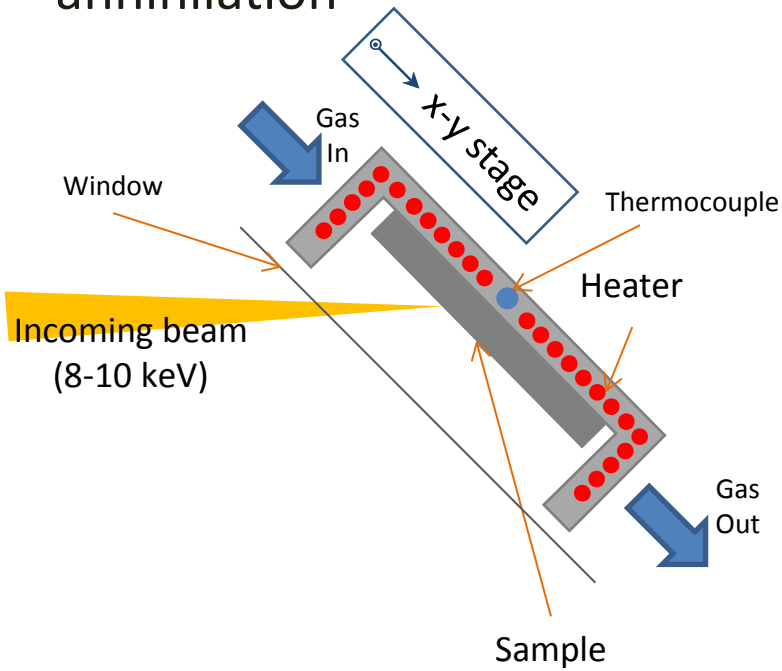
In situ NMR observation of the formation of metallic lithium microstructures in lithium batteries

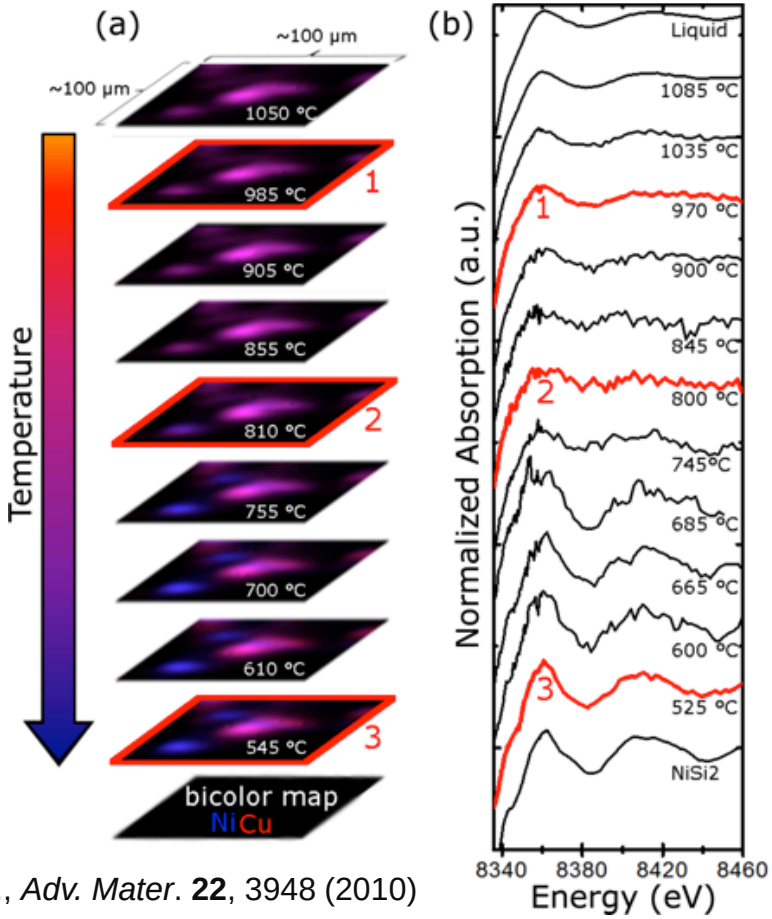
Rangeet Bhattacharyya[1], Baris Key[1], Hailong Chen[1], Adam S. Best[2], Anthony F. Hollenkamp[2] and Clare P. Grey[1,3]*

Process microscopy

In situ nano-fluorescence mapping

- Capability: Variable temperature stage from 90 K → >800 C with nanoprobe
- Discovery: Thermodynamics and kinetics of defect generation and annihilation





Hudelson *et al.*, *Adv. Mater.* **22**, 3948 (2010)

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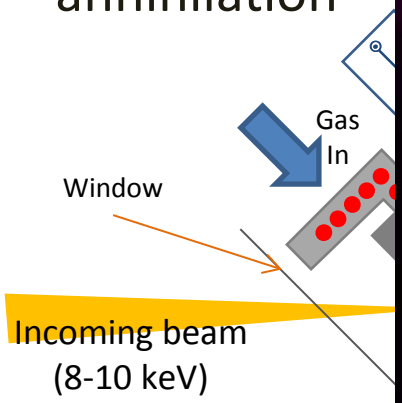

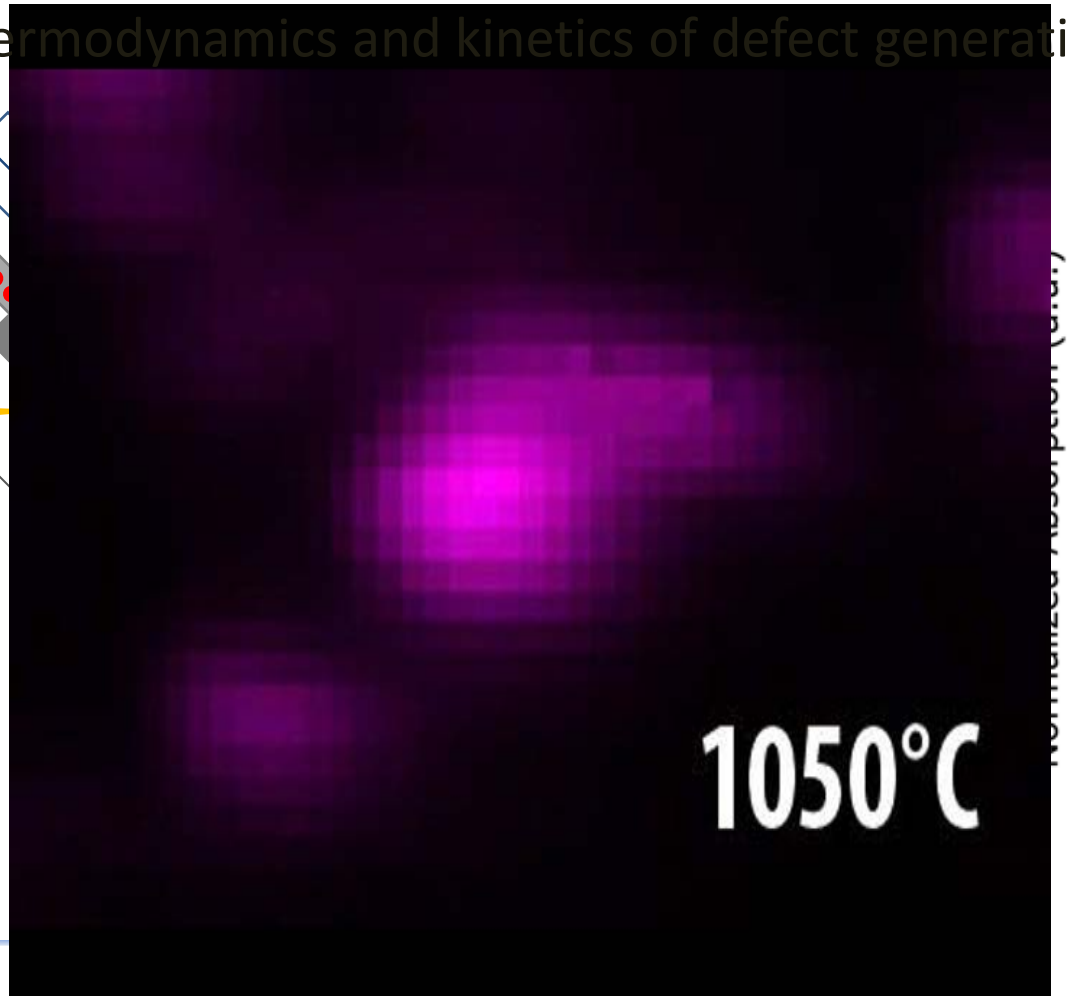

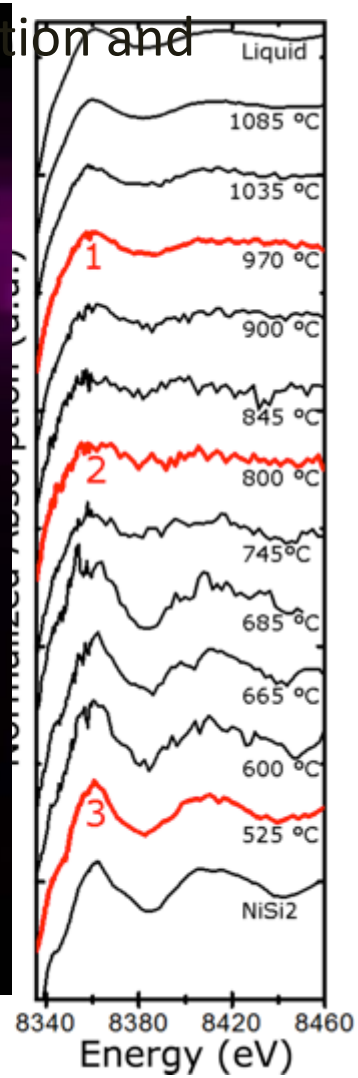

100x100 μm²

Hudelson *et al.*, *Adv. Mater.* **22**, 3948 (2010)

Process microscopy

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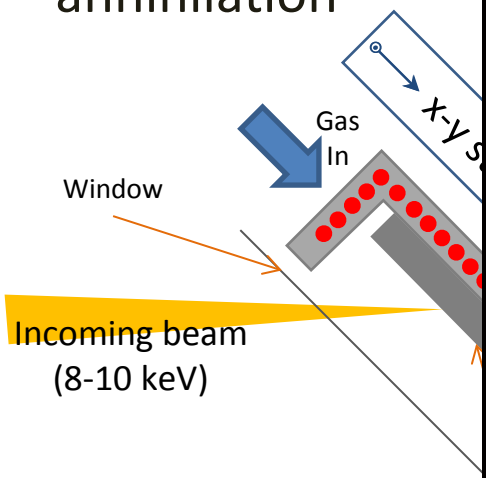
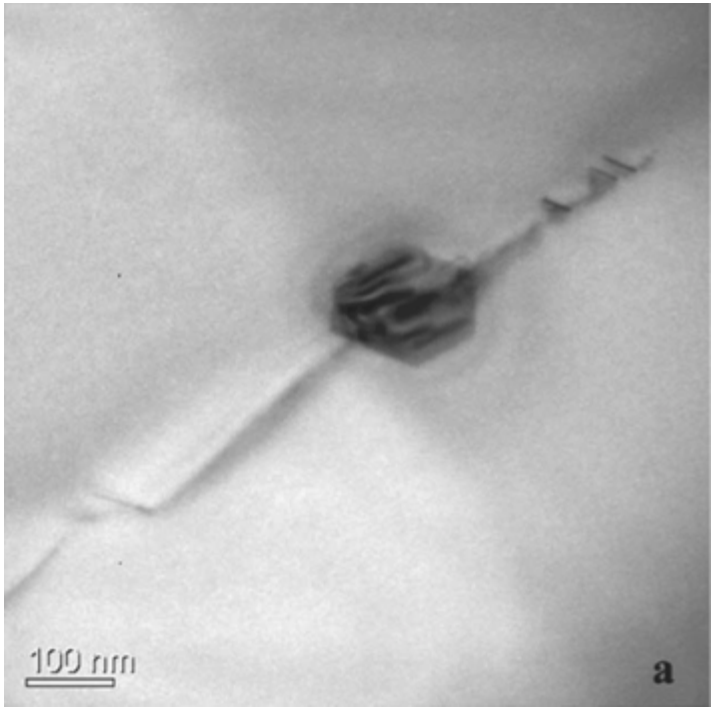
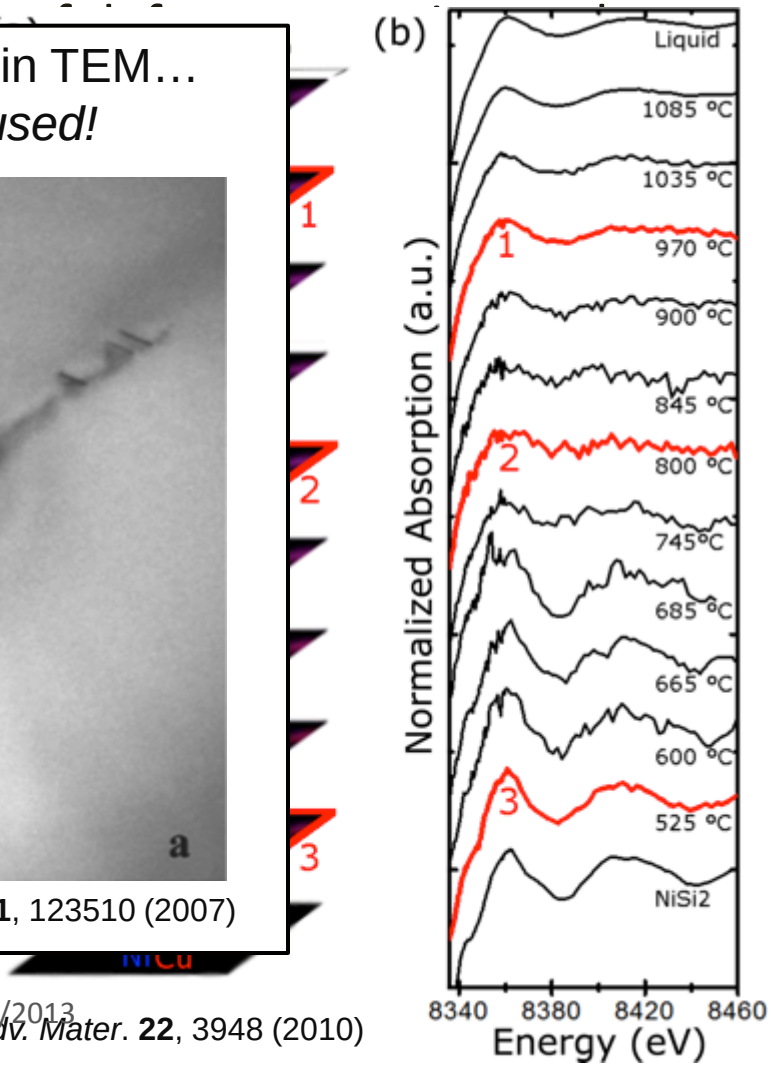


Previously attempted in TEM…
→ *but metals out-diffused!*



Heuer *et al*., *J. Appl. Phys*. **101**, 123510 (2007)



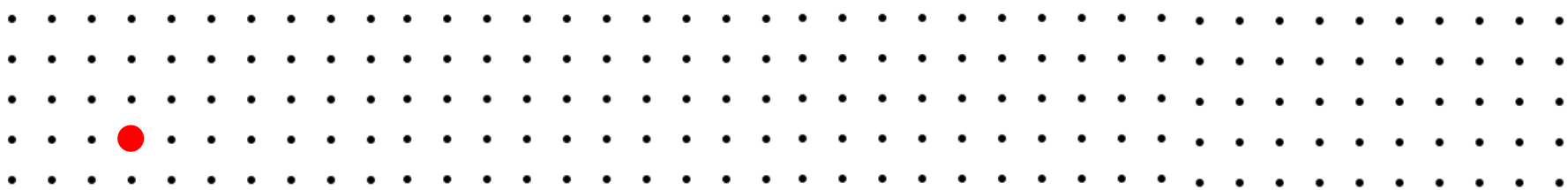
Hudelson *et al*., *Adv. Mater*. **22**, 3948 (2010)

Defects in "clean" materials

Anomalous Point Defect Metrology

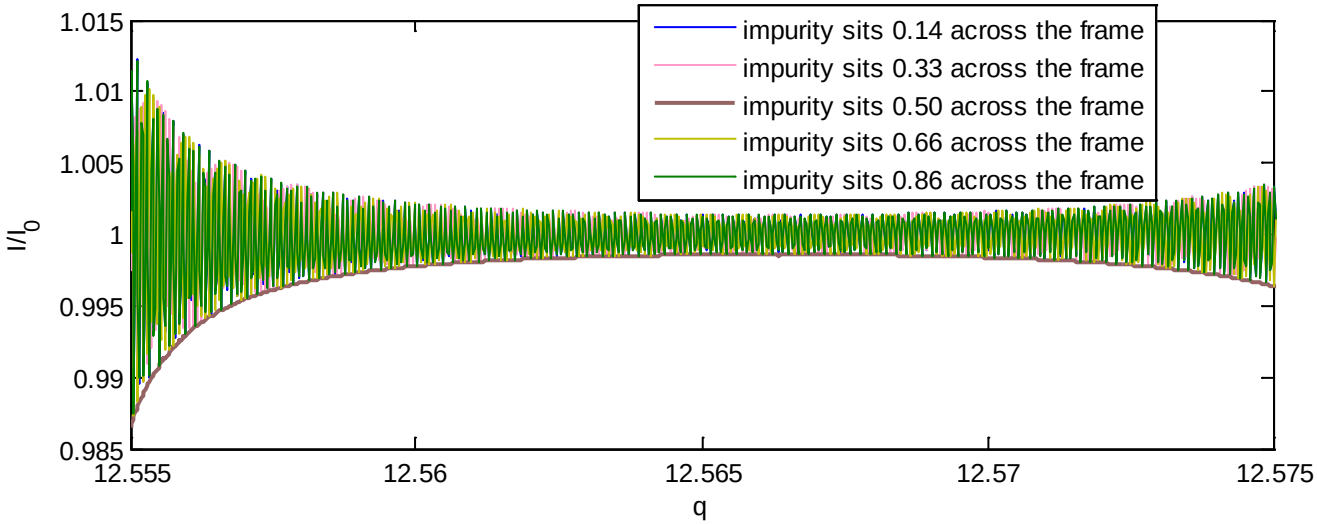
- Direct imaging of point defects in increasingly clean semiconductors
- *e.g.* 10^{12} cm^{-3} Fe interstitials in silicon
  - 0.1 part-per-trillion levels
  - 1 Fe atom every 5 frames (assuming 50 nm spot)
- Resonant speckle used to detect & identify point defects
- Experiments are most challenging for silicon, because it's cleanest
  - Easier for III-V, II-VI, *etc.*

We can find, identify, and study the needle in the haystack during in-situ materials processing and during operando conditions



Defects in clean materials

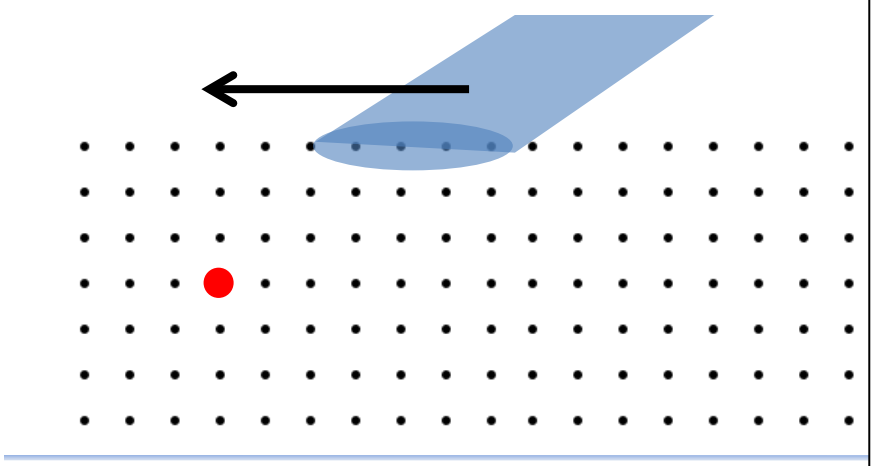
Anomalous Point Defect Metrology

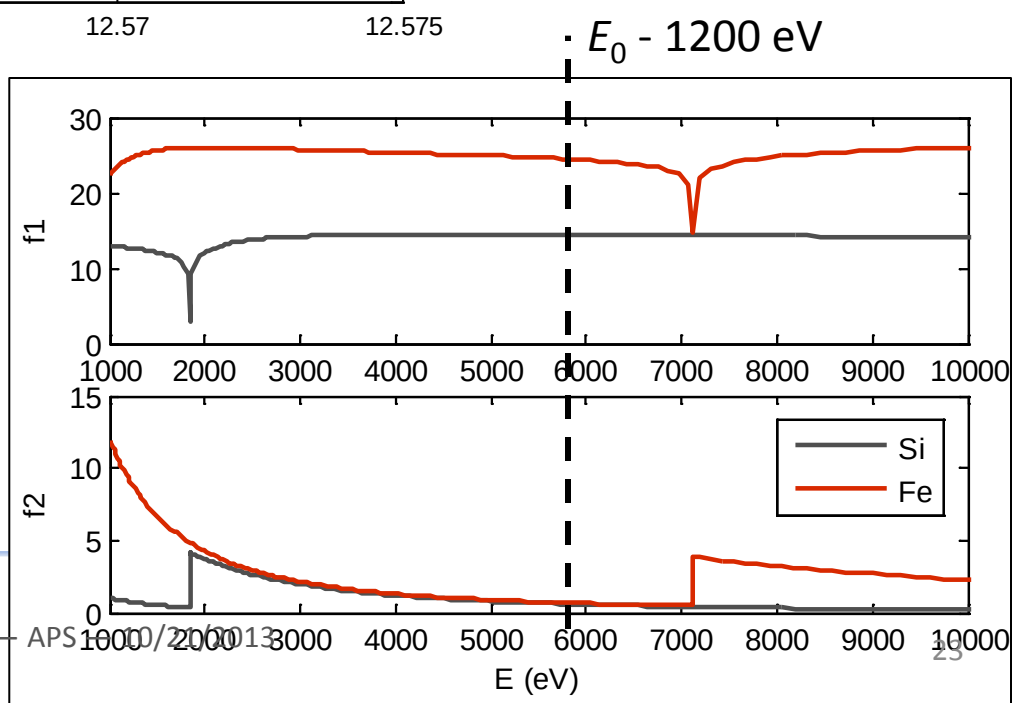


Beam size 20 < *w* < 50 nm

10^9 Si atoms

1 Fe atom

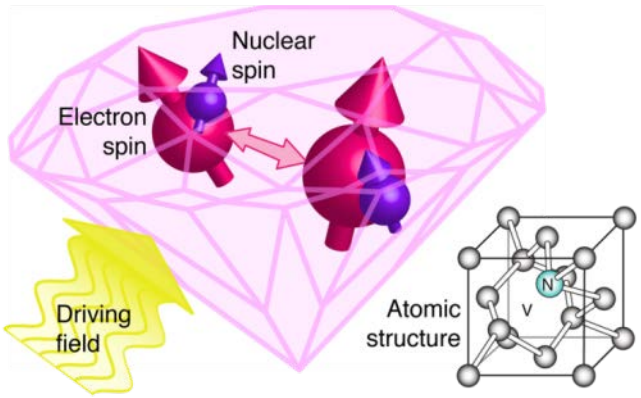




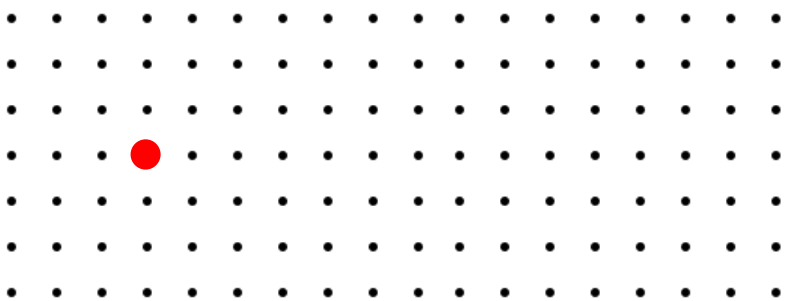
Defects in clean materials

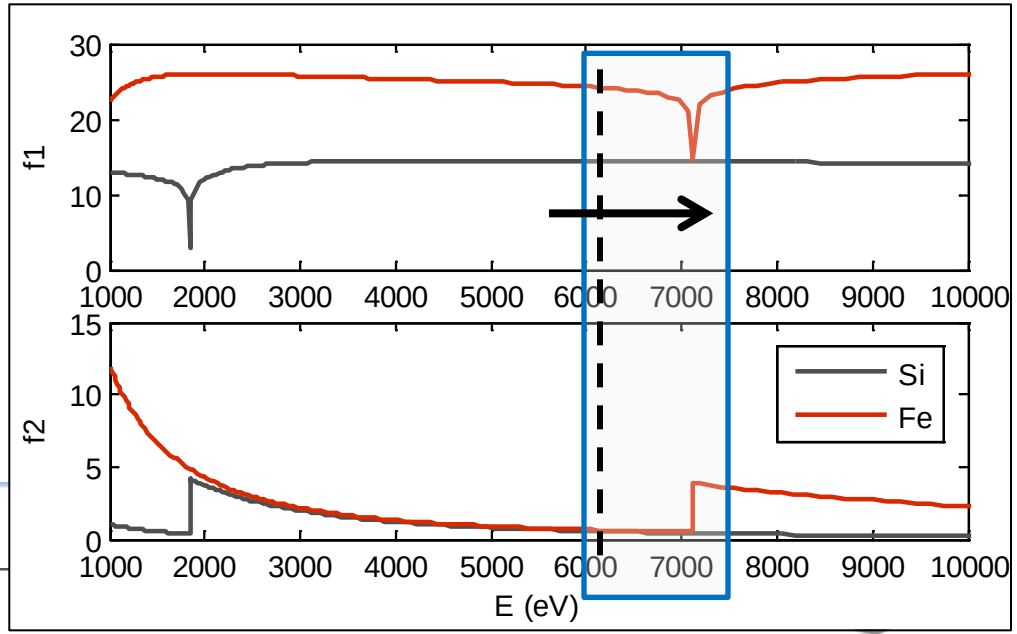
Anomalous Point Defect Spectroscopy?

- Speckle is acutely sensitive to scattering amplitude $f(E)$
- Could enable single-site point defect spectroscopy
  - Analogous to nitrogen-vacancy (NV) pairs in diamond



NV center in diamond
American Physical Society

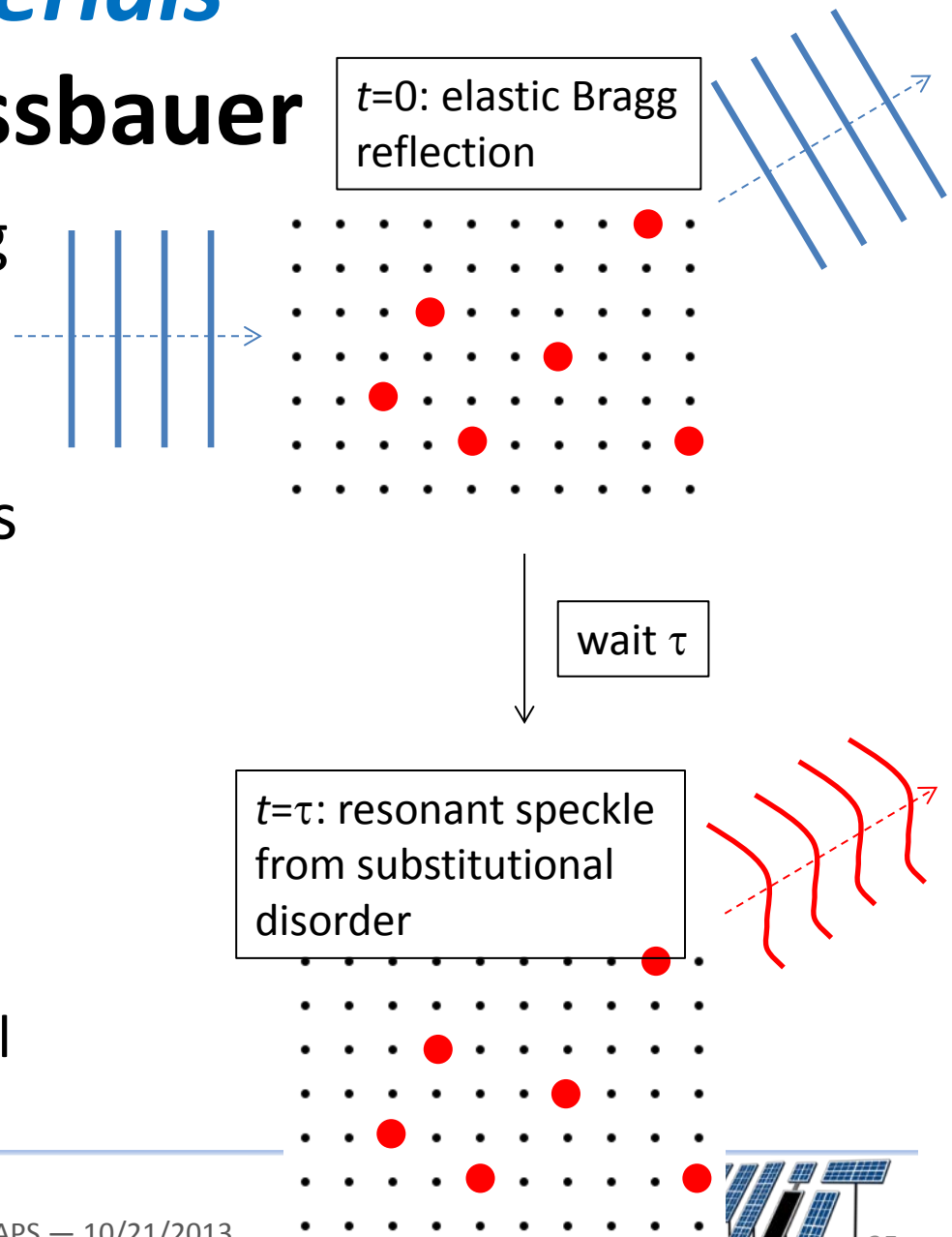




Defects in clean materials

High Resolution Mössbauer

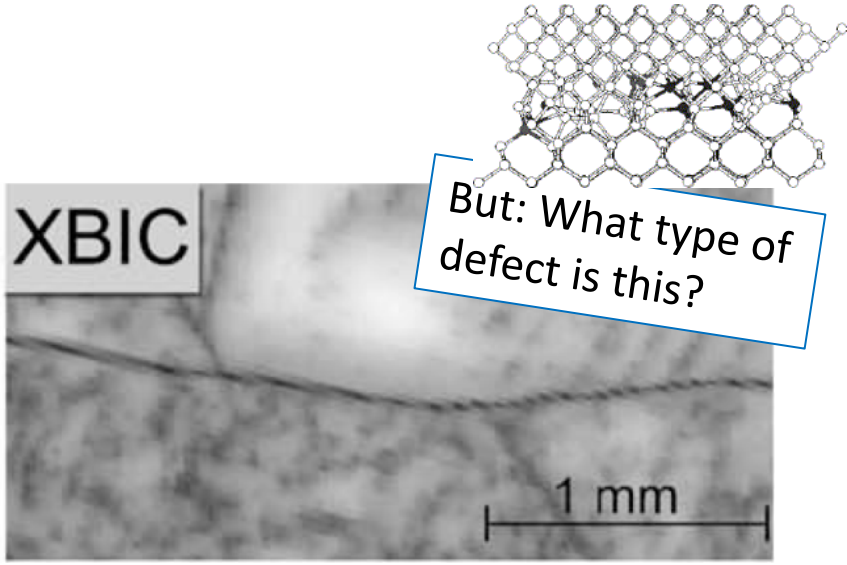
- Resonant nuclear scattering
  - Time discrimination
- $\Delta E/E \sim 10^{-7}$ available with high index monochromaters
- What happens when you add coherence to resonant emission scattering?
  - *e.g.* Would you get a speckle pattern in the delayed Bragg reflection from substitutional point defects?



Defects & performance

XBIC + Extended Defect Ptychography

- X-Ray beam induced current
  - Measure recombination activity of individual defects
- Extended defect ptychography
  - Atomic reconstruction of extended crystal defects



Recombination-active extended defect in Si solar cell
T. Buonassisi *et al.*, DOI: 10.1063/1.2048819

- Combined technique cuts out slow intermediate experiments (e.g. TEM)
- Faster learning cycles for photovoltaics and solid state lighting

Spectromicroscopy

Mesoscale electronic heterogeneity

- Correlate composition, spectra & function in inhomogeneous materials
- Quaternary semiconductors (*e.g.* CZTS for photovoltaics)

nano-XPS
nano-IPES

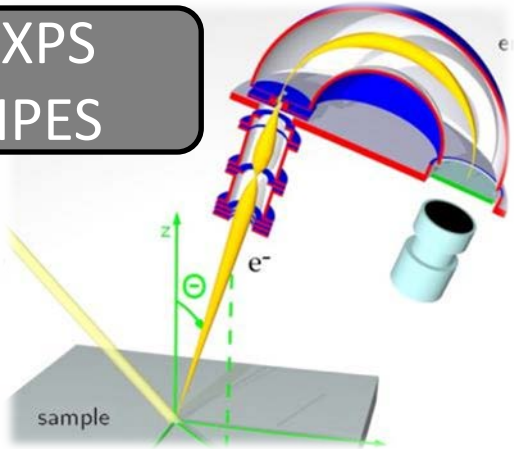


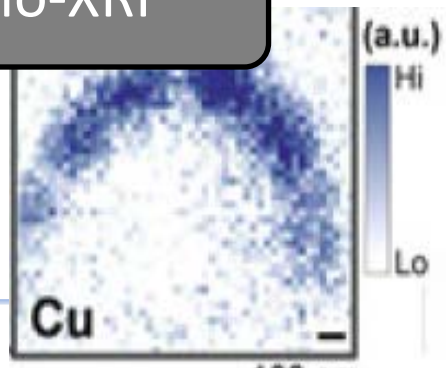
Photo- & inverse-photo-electron spectroscopy

CZTS solar cell

Todorov *et al.*, Adv. Mater. **22**, E156 (2010).

XRF

nano-XRF



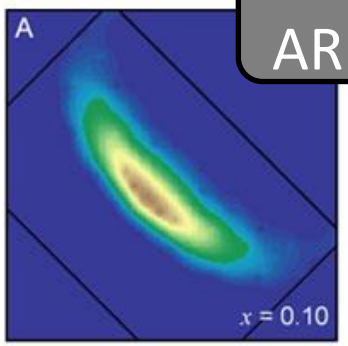
Spectromicroscopy

Mesoscale electronic heterogeneity

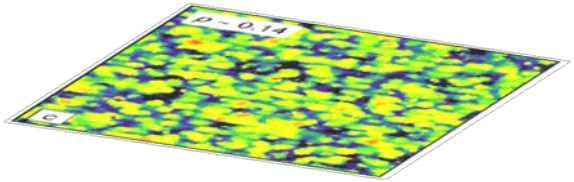
- Correlate composition, spectra & function in inhomogeneous materials
- Correlated oxides (*e.g.* high-T_c, manganites)

Quasiparticle spectroscopy

nano-ARPES



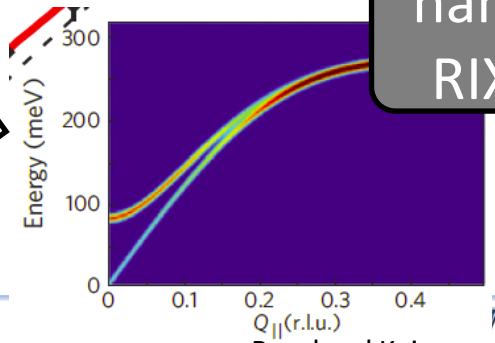
Zhi-Xun Chen



Inhomogeneous pseudogap in BSCCO
Seamus Davis

Magnon spectroscopy

nano-RIXS



Bernhard Keimer

+ analytical microscopy (XRF, X-ray Raman)

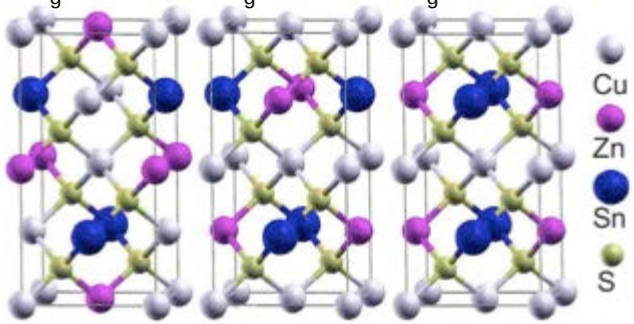
Spectromicroscopy

Spectral fingerprints for difficult-to-ID materials

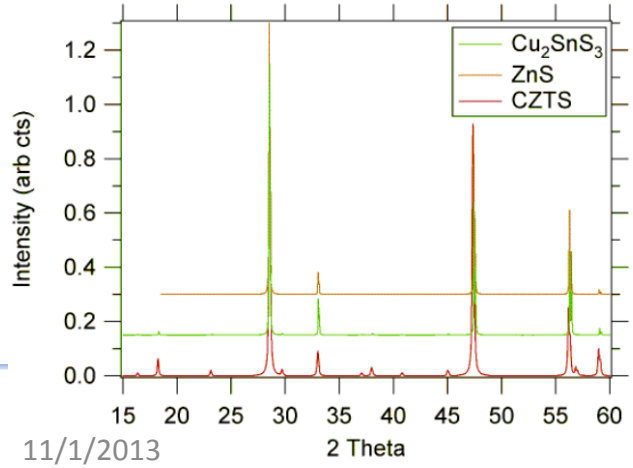
- Capability: Spectroscopy with 20+ nm spot
- Discovery: Oxidation state (local order)

CZTS Polymorphs

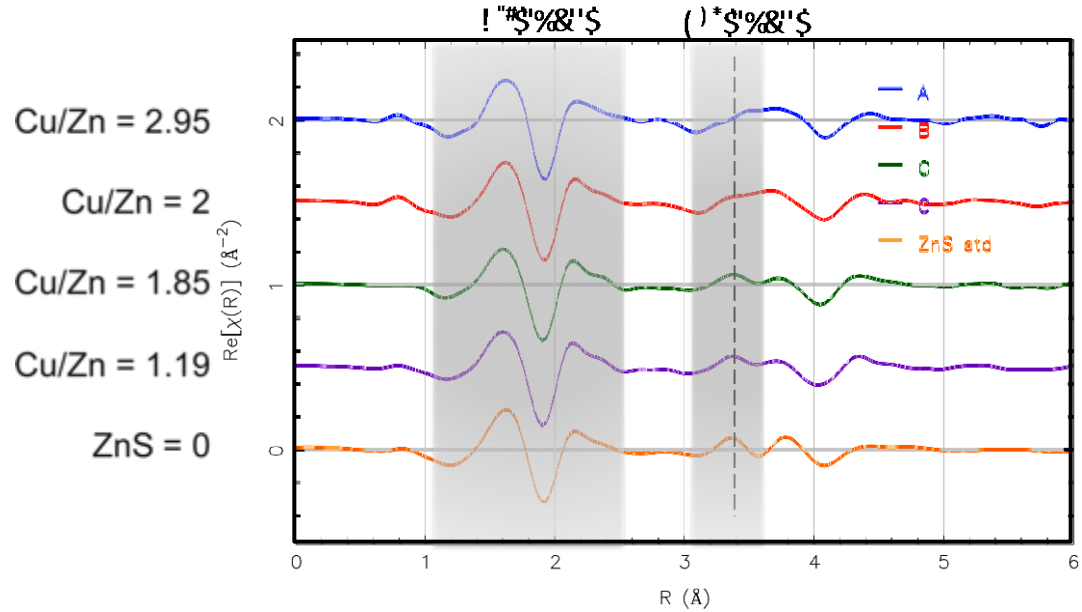
KS E_g=1.50eV | ST E_g=1.38eV | PMCA E_g=1.35eV



XRD → *Difficult to Distinguish*



CZTS EXAFS (Zn edge)

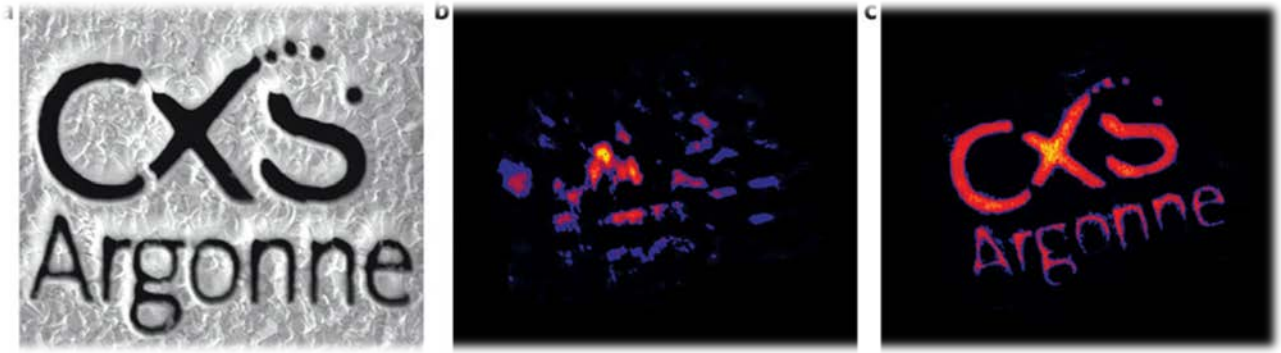


Hartman *et al.*, unpublished

Closing points

- Success will hinge on improving all aspects of the tool
  - Spot size is only 1 factor
  - Coherence & brightness are key
  - End-station usability
  - Superb sample environments
  - Accessible & specialized computing

Closing points



- Lens-less imaging (ptychography) must become standard
  - Move from demonstration to metrology
  - Beamlines need imaging tools that are customized & accessible
  - Analogy to Reitvelt refinement: everyone should be able to do it, given an honest effort

Closing points

- *In situ* is the killer app for energy technologies
  - X-rays offer unique contrast modes
  - Unmatched by "competing" microscopic techniques
  - *DLSR can take materials all the way from fundamental understanding to process control*