Transmission electron microscopy in liquids and gases

Workshop: Theory & Computation for Interface Sciences & Catalysis

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11/6/2014

Center for Functional Nanomaterials
Brookhaven National Laboratory

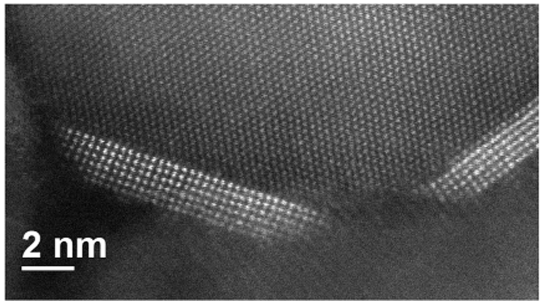
U.S. DEPARTMENT OF ENERGY | Office of Science

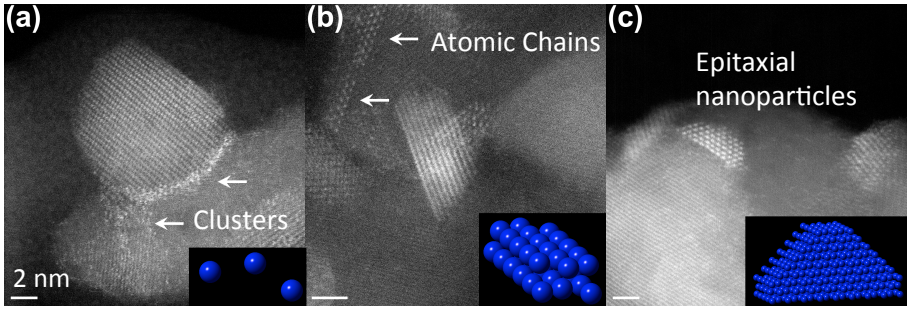
BROOKHAVEN NATIONAL LABORATORY

Transmission Electron Microscopy

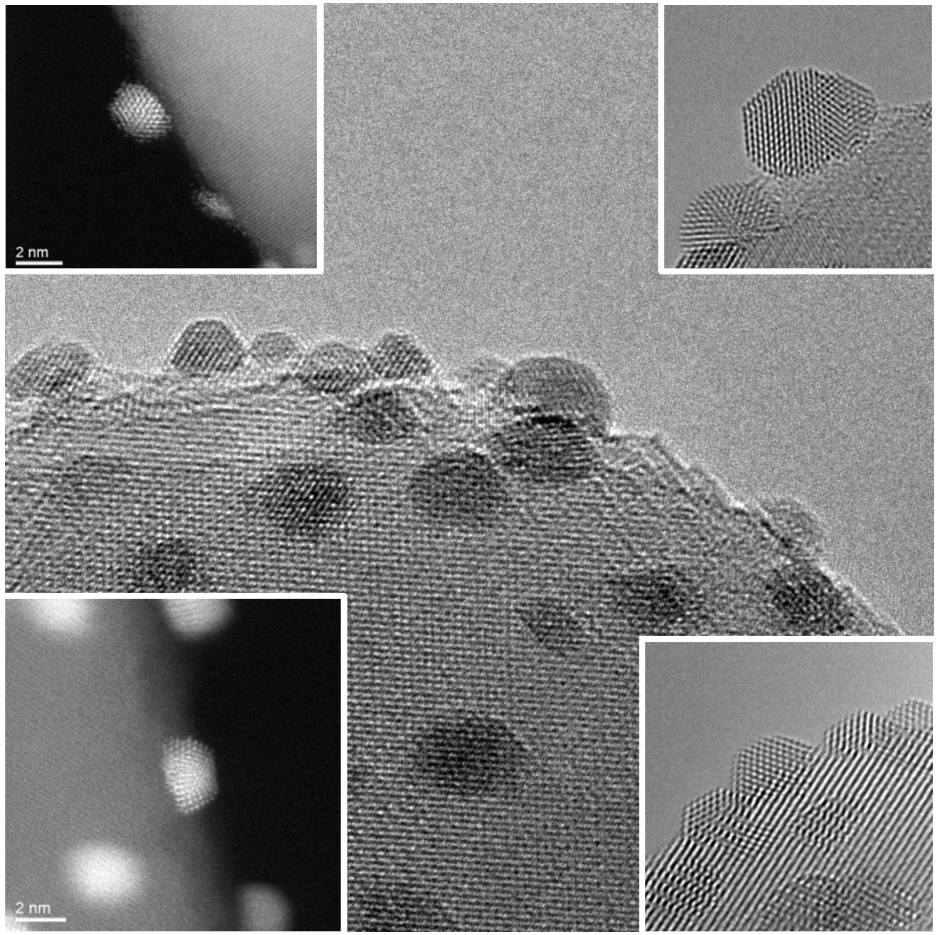
TEM is the primary tool for characterizing interfaces in materials

- **Atomic resolution imaging**
  - **Resolutions < 1.0Å**





A. Johnston-Peck, et al., JPCC, 117, 14463, 2013.

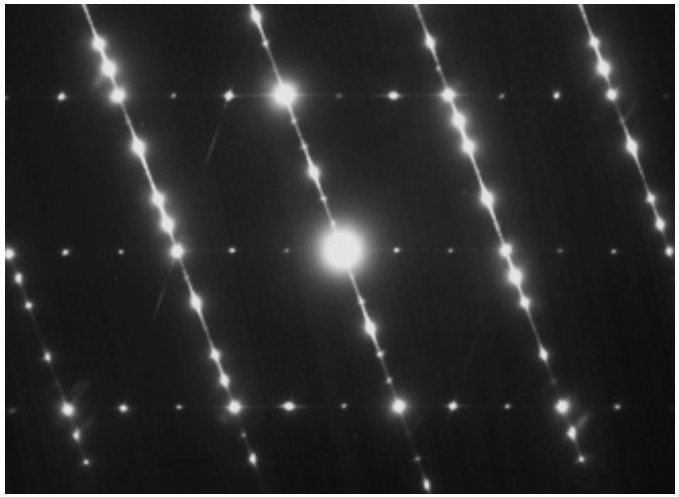


Setthapun, et al. J. Phys. Chem. C., **114**, 9758-9771, 2010;
Christensen, et al., Nano Lett., **10**, 3047, 2010.

Transmission Electron Microscopy

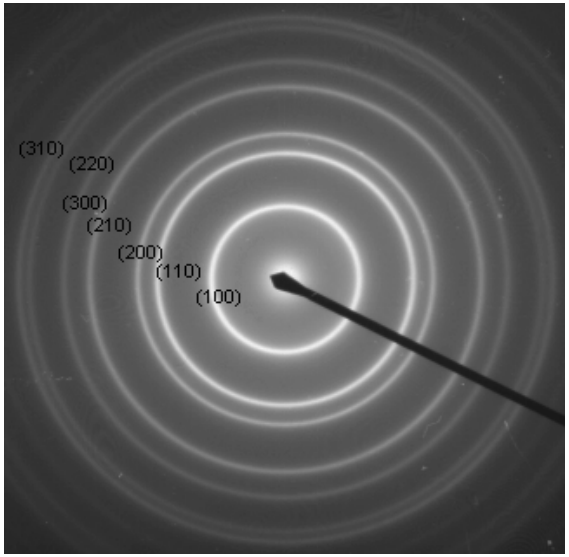
TEM is the primary tool for characterizing interfaces in materials

- **Atomic resolution imaging**
  - Resolutions < 1.0Å
- **Local electron diffraction**
  - Atomic and nanoscale
    - Atomic through FFT of HREM images
    - Nanoscale through focused probe
  - Full crystal structure determination (space groups) through convergent beam electron diffraction



Zone-axis electron diffraction pattern from a cubic/ hexagonal GaN interface

Electron diffraction "ring pattern" from a random polycrystal (equivalent to a XRD powder pattern)



Transmission Electron Microscopy

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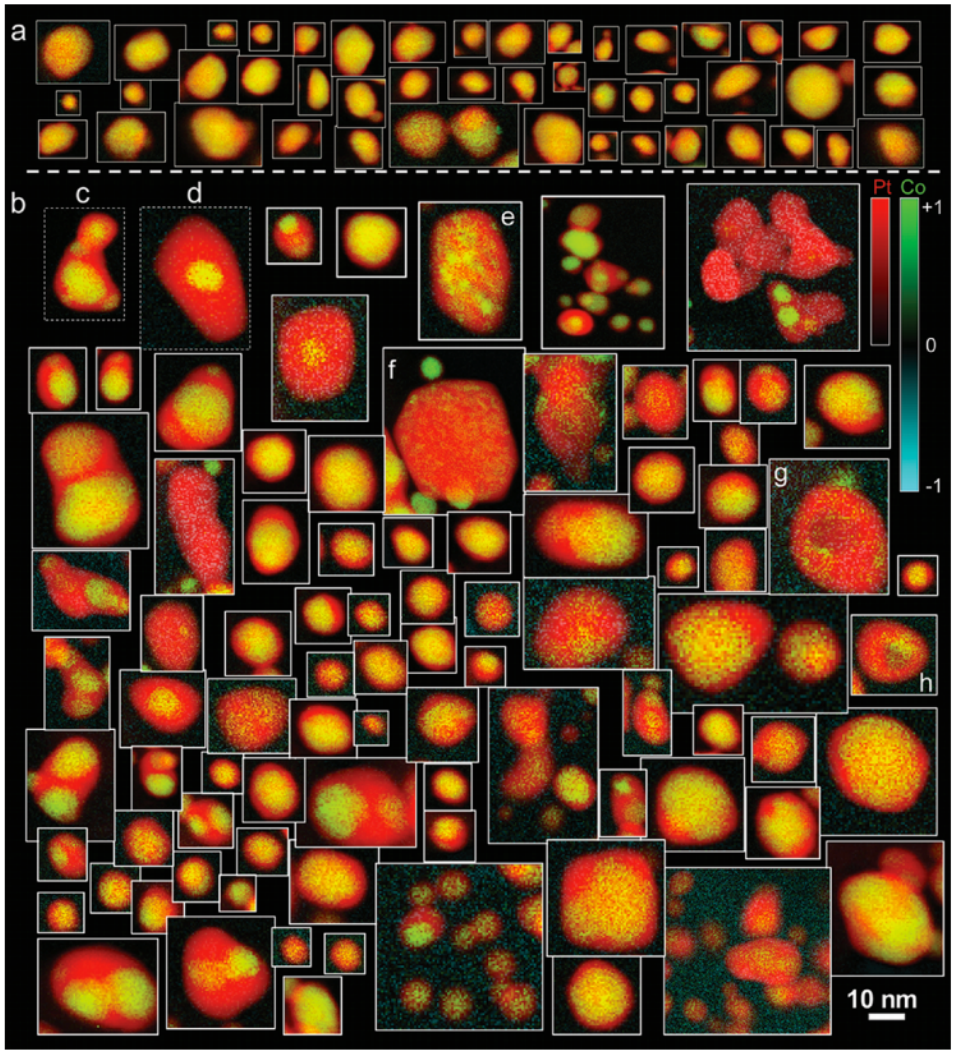
- **Local electron diffraction**
  - Atomic and nanoscale
- **Chemical characterization**
  - Energy dispersive x-ray spectroscopy
  - Electron energy loss spectroscopy



H.L. Xin, et al. Nano Lett., 12, 490, 2012.

Transmission Electron Microscopy

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  - Atomic and nanoscale
- **Chemical characterization**
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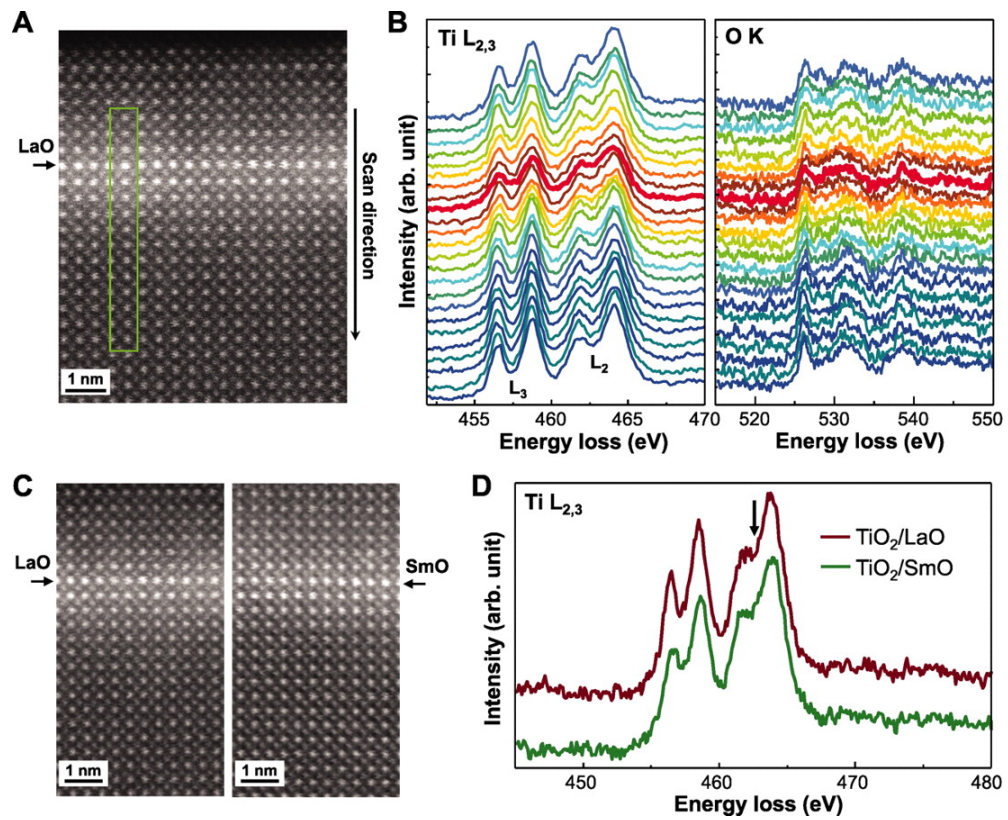
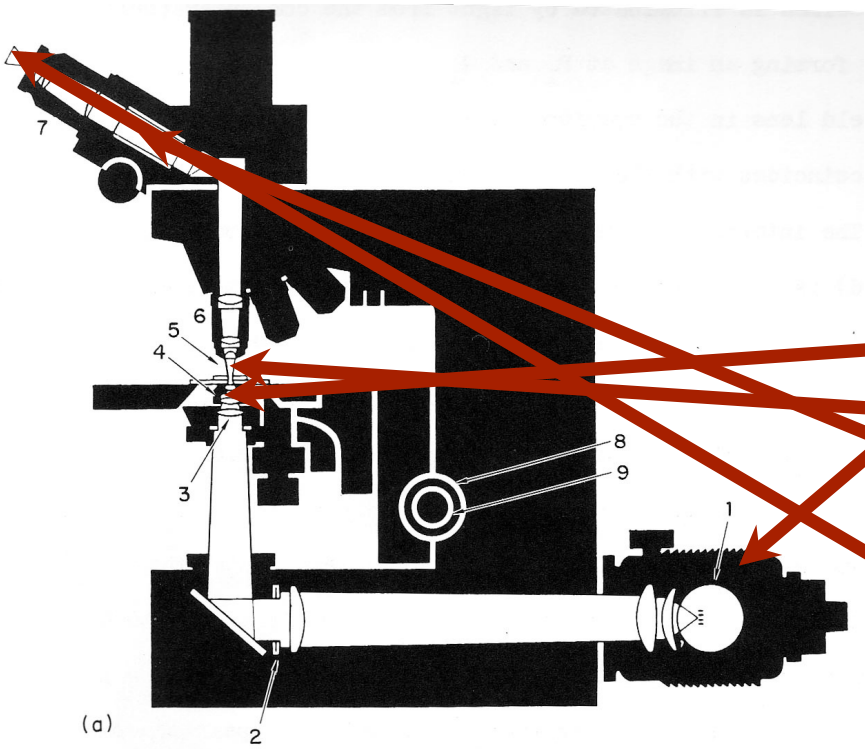
  - Electron energy loss spectroscopy
- **Chemical bonding**
  - Electron energy loss spectroscopy

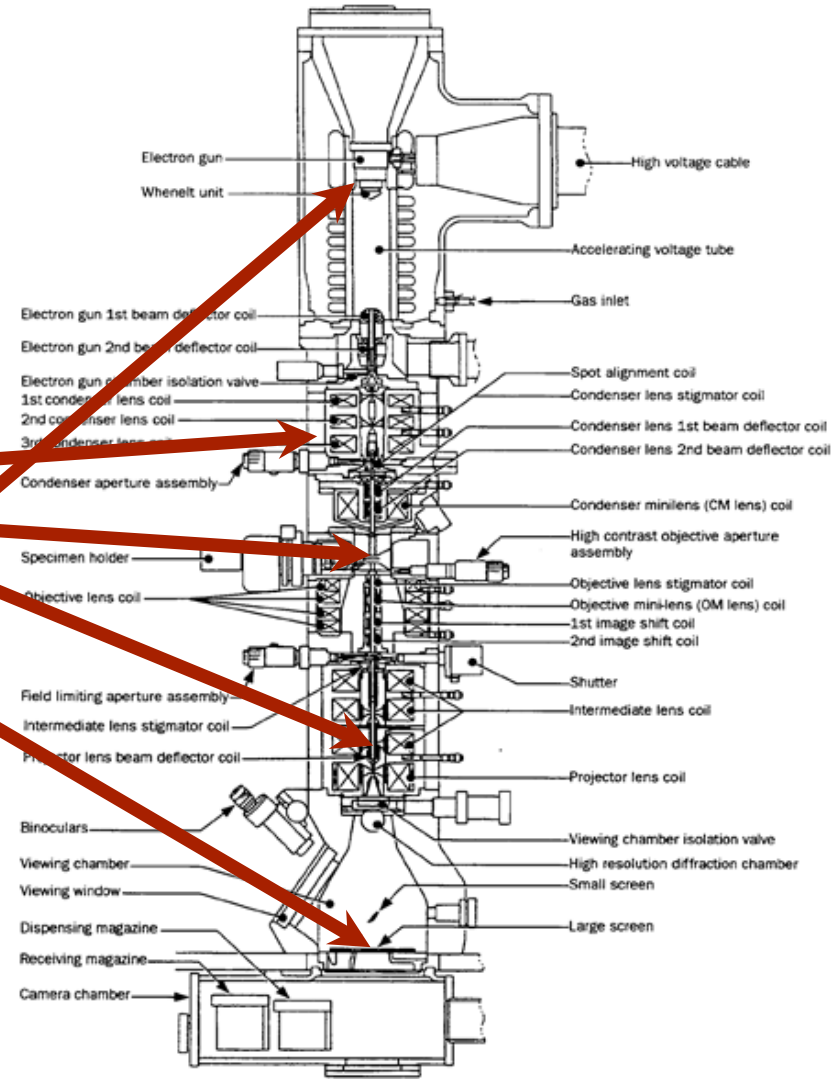


Jang, et al., Science, **331**, 886–889, 2011.

How does a TEM work?

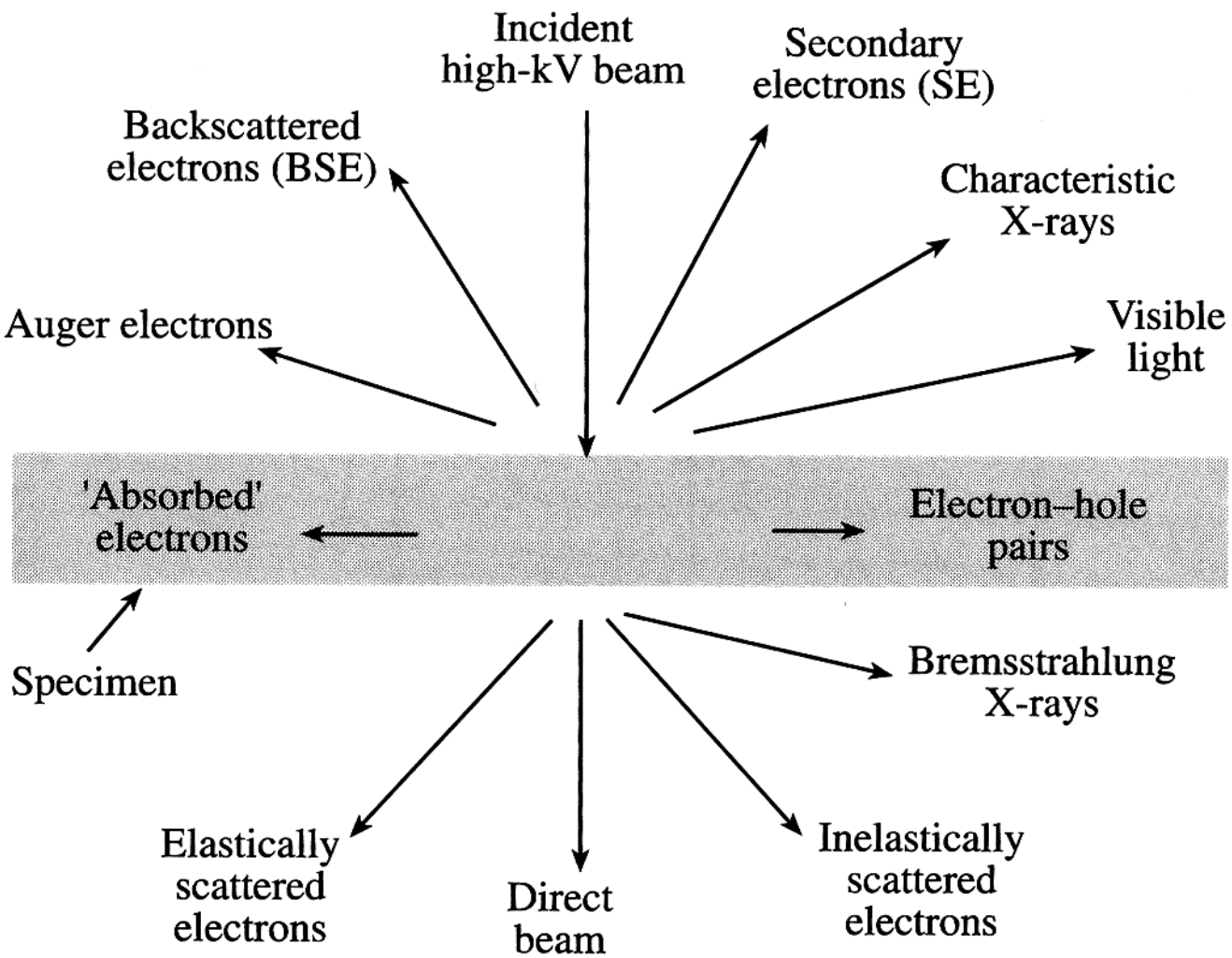


Optical microscope in transmission mode



Electron Scattering

Sample:
(10 nm to max 500 nm thick)



From Williams and Carter

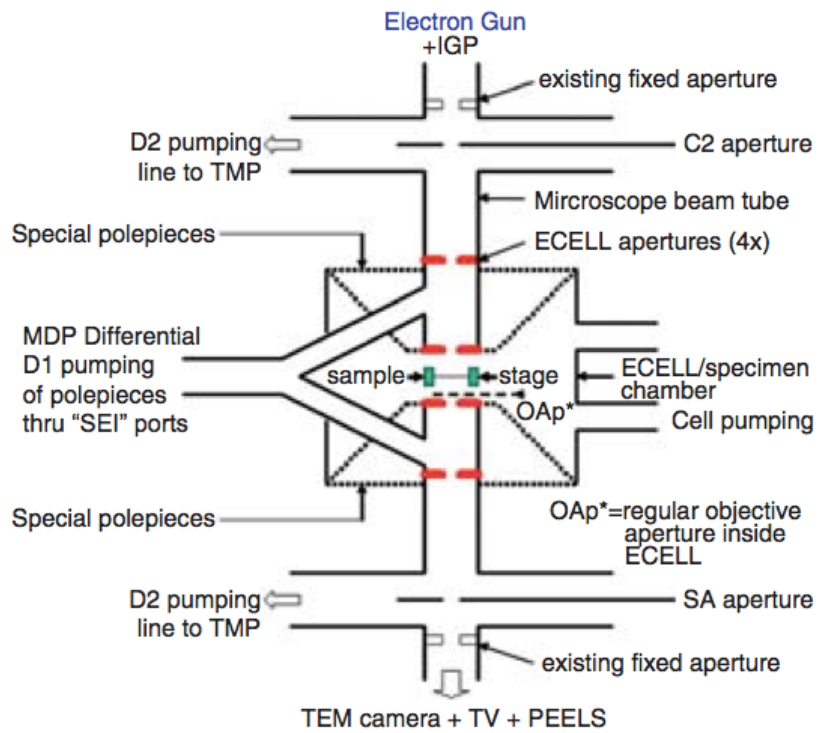
Environmental TEM

Uses a set of differential pumping apertures to keep gases confined to specimen area

- **If gases reach the electron source, it kills it …**

Environmental TEM allows a maximum pressure of 10 or so Torr of N_2.

- **Less for e.g. H_2 or He**
- **These pressures are similar to "ambient-pressure" XPS**
- **They are 7-9 orders of magnitude above surface science studies**



Schematic of differentially pumped objective lens

Environmental TEM

Differentially pumped ETEM

- Maximum pressure of 20 Torr
- Base pressure of 5 x 10^7 Torr
- Maximum temperature of 850°C

Highly capable STEM/TEM

- 1Å resolution @ 300kV / <1.4Å @ 80kV
- 1.35Å in STEM
- Full analytical capabilities
  - EELS, EFTEM, EDS

High frame rate imaging

- 400 frames/sec
- 4TB data in 15 minutes!

CFN's Titan ETEM

Fundamental studies of Cu oxidation

User project:

Guangwen Zhou – SUNY Binghamton

Judith Yang – University of Pittsburgh

Step-edge-induced oxide growth during the oxidation of Cu surfaces. **G. Zhou, L. Luo, L. Li, J. Ciston, E.A. Stach, and J. Yang, Phys. Rev. Lett., 109, 235502, 2012.**

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In-situ reduction and oxidation of <100> Cu films

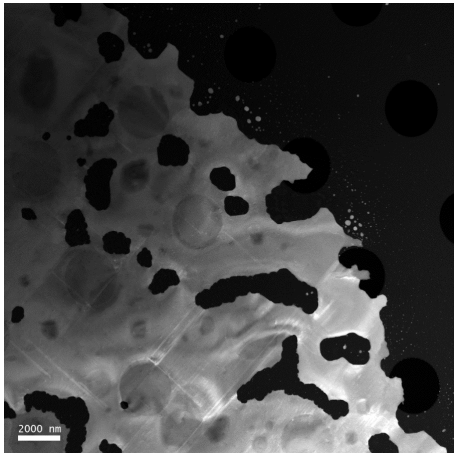
Many prior surface science studies of Cu oxidation

- **However, all conducted at low O_2 partial pressures**

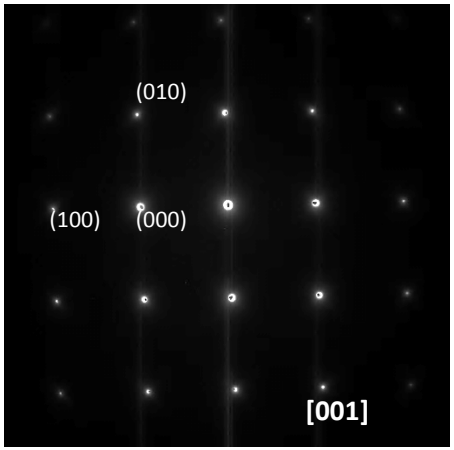
Prior understanding

- **Oxygen chemisorption and sub-surface incorporation**
- **Conversion of metal lattice to oxide phase**
- **Significant bulk diffusion to interface through oxide, then a solid-solid phase transformation**

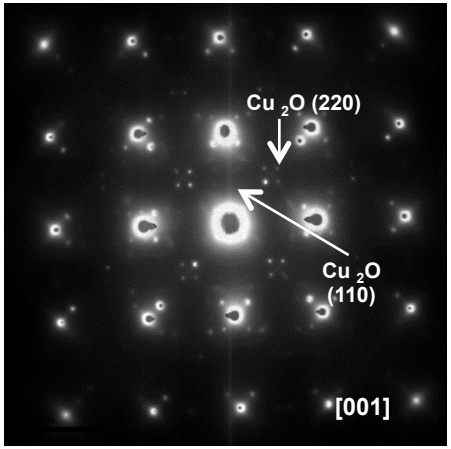
STEM image of reduced, single crystal <001> Cu film



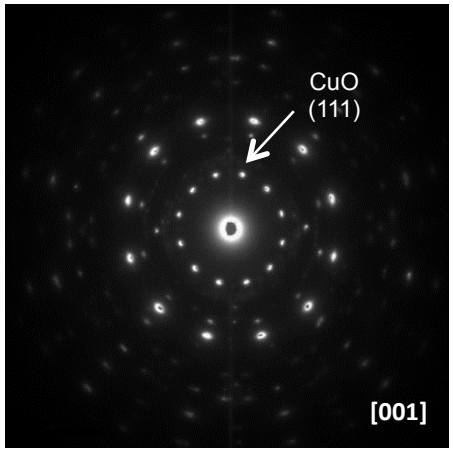
Film reduced to eliminate native oxides 1Torr of H_2 at 300C for 60'



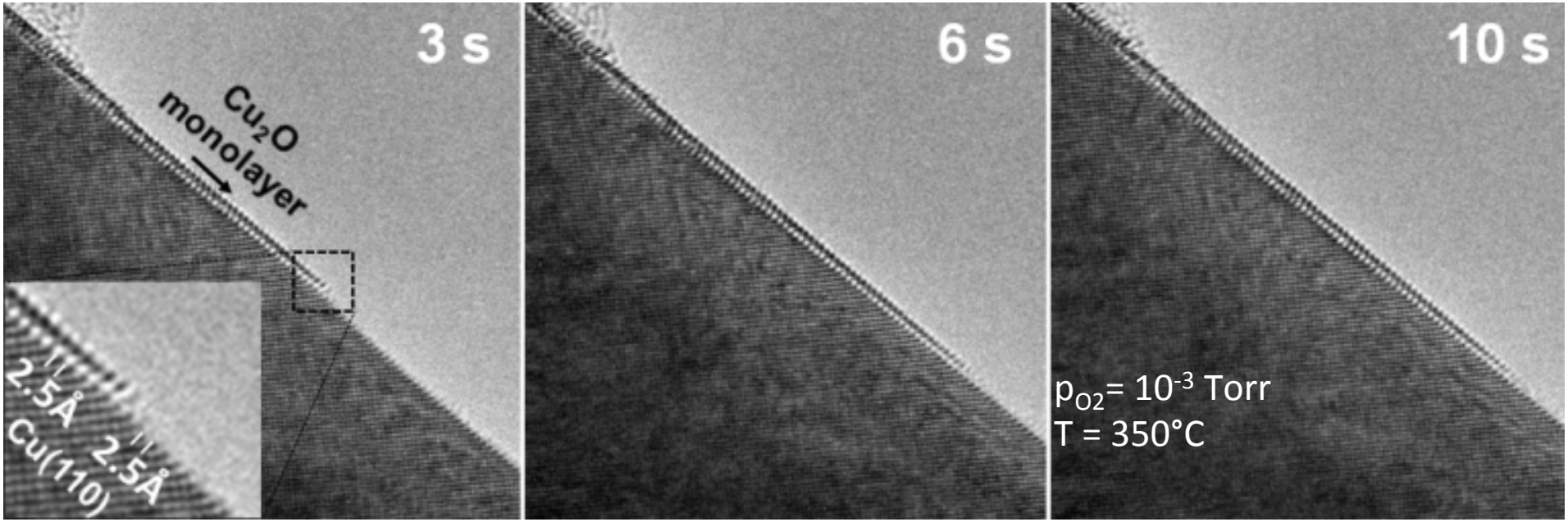
Cu_2O
After introducing 40mTorrr O_2 at 300C for 3'



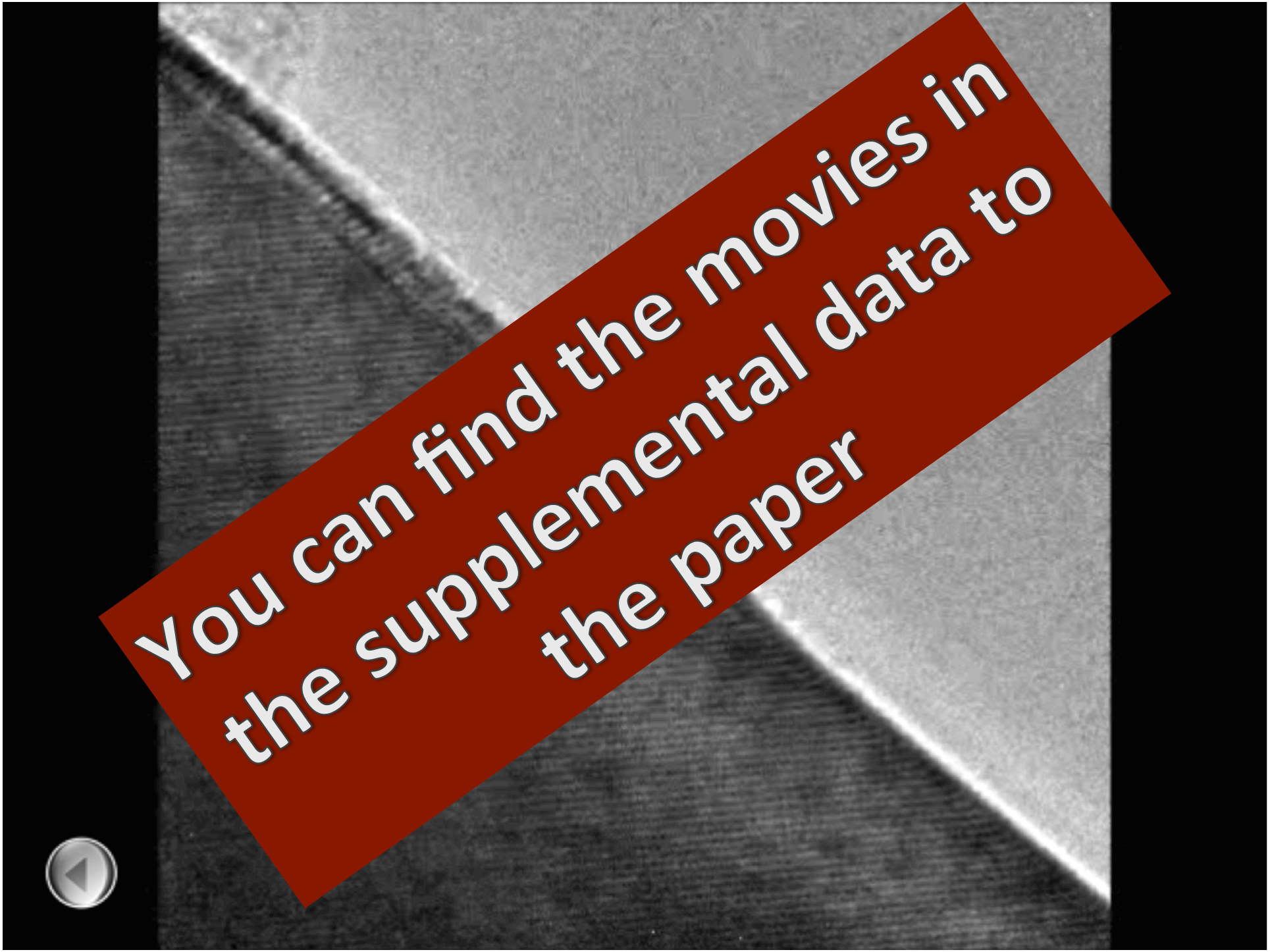
CuO
After introducing 70mTorrr O_2 at 300C for 10'



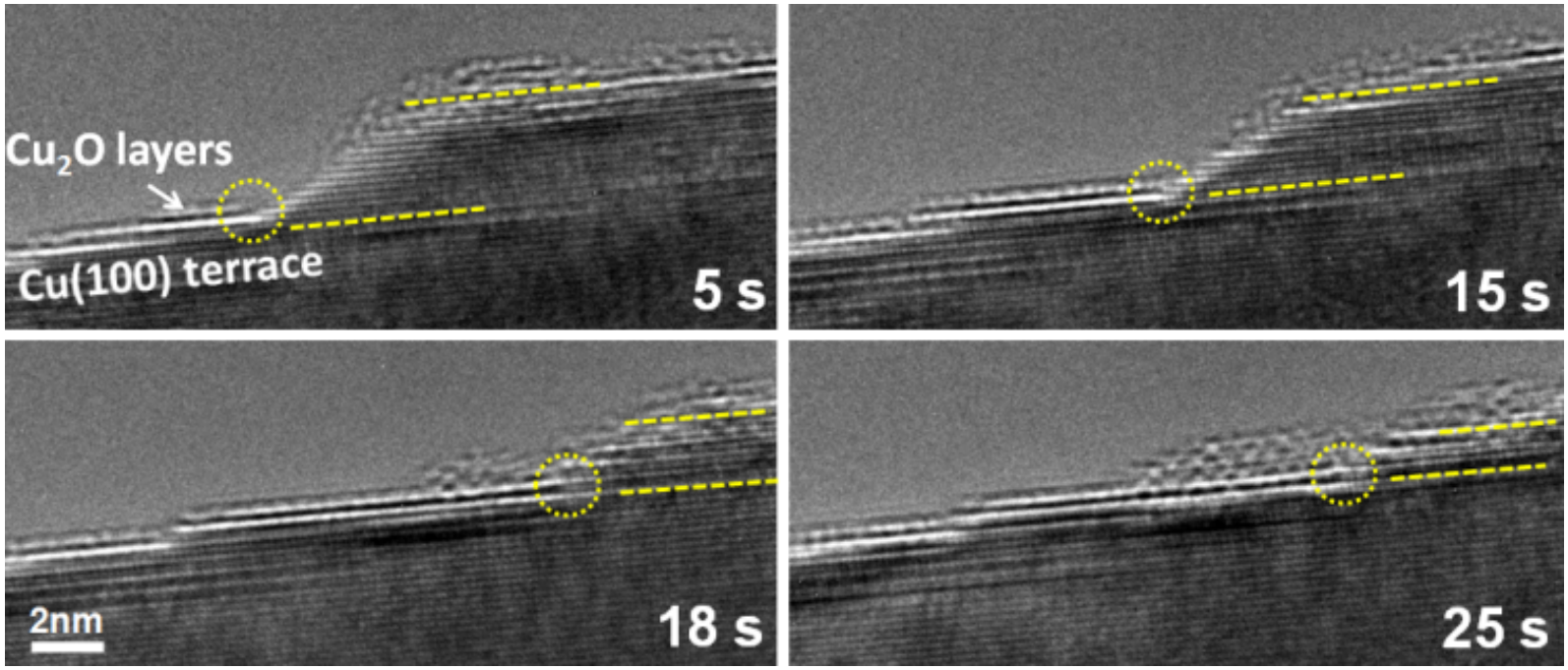
Growth of Cu_2O by adatom attachment



- Growth of Cu_2O via direct adatom attachment
- Measured lattice parameter of 2.8Å indicates it is compressed
- Movie (next) shows oscillatory step motion with adatoms


You can find the movies in
the supplemental data to
the paper

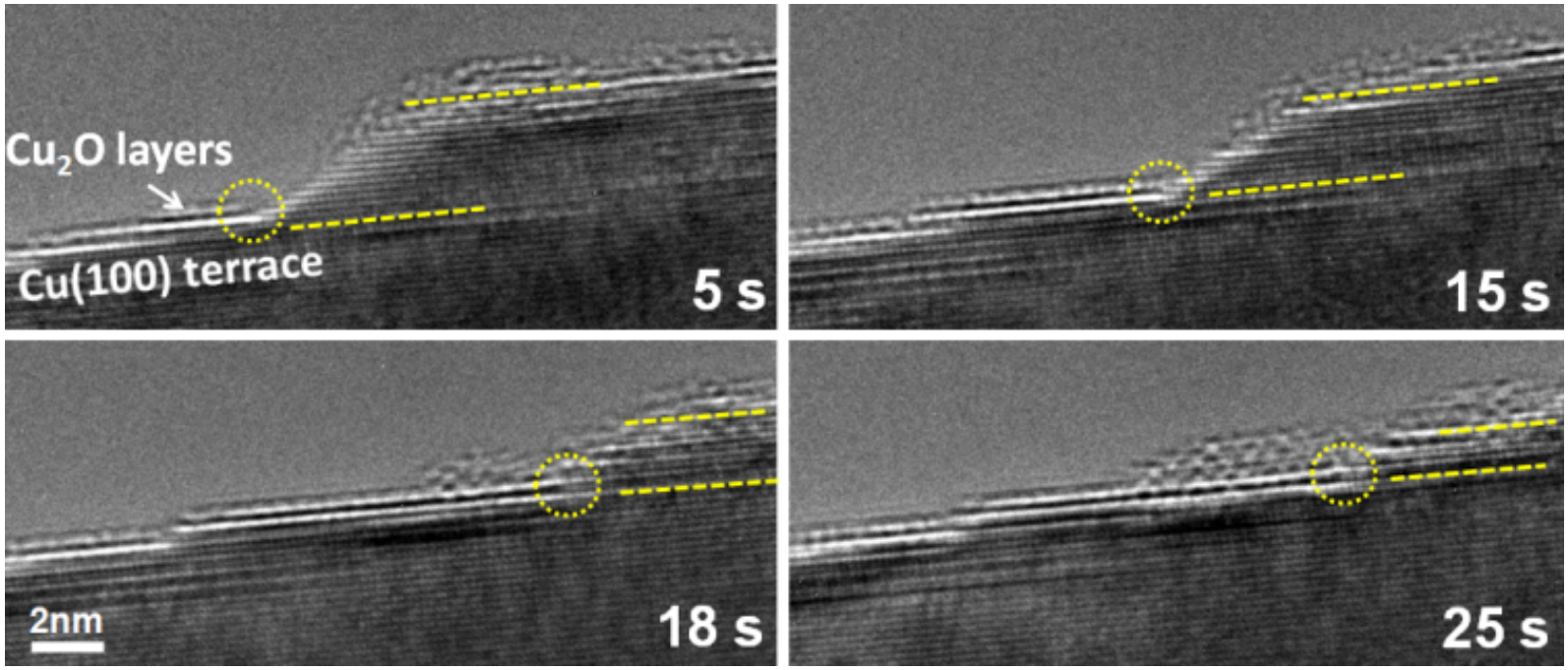
No evidence for bulk diffusion

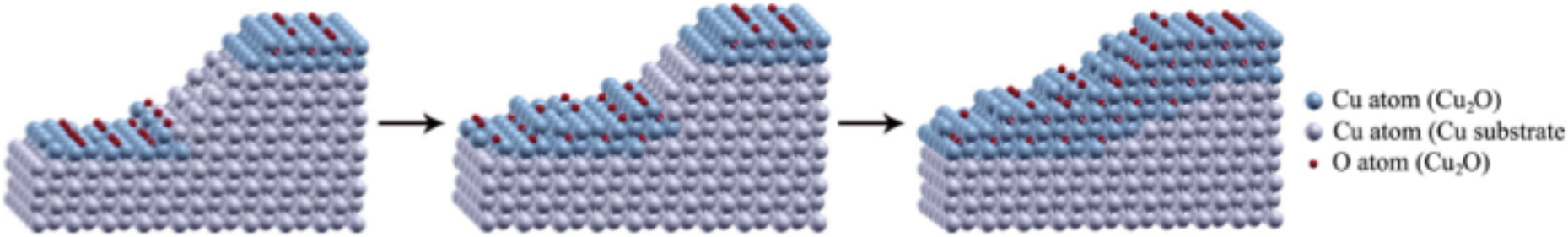


- **Oxide thickens via nucleation and growth of new layers at the surface**
- **Interface does not move inwards**
- **Atoms supplied from the step-edges**

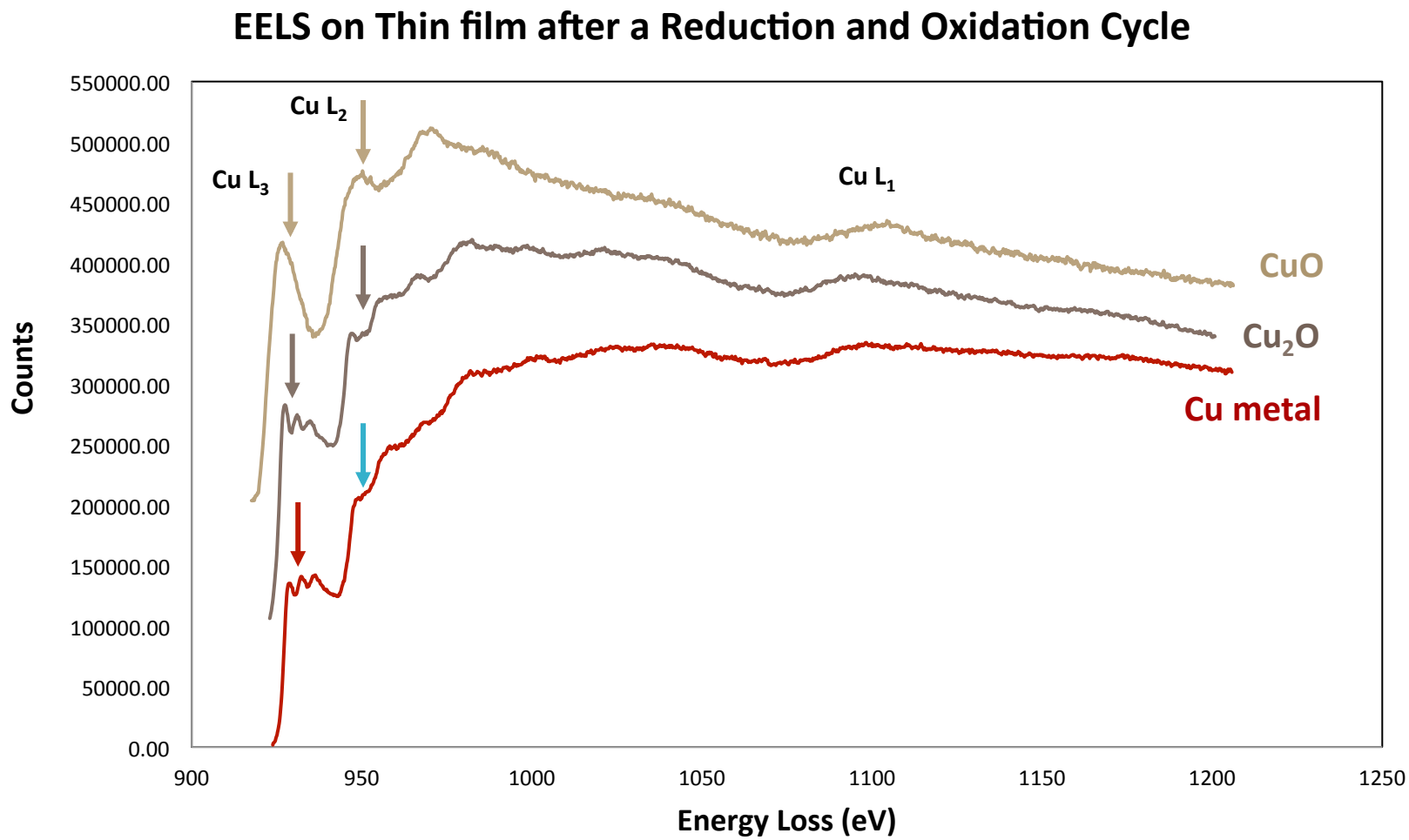
You can find the movies in
the supplemental data to
the paper

No evidence for bulk diffusion



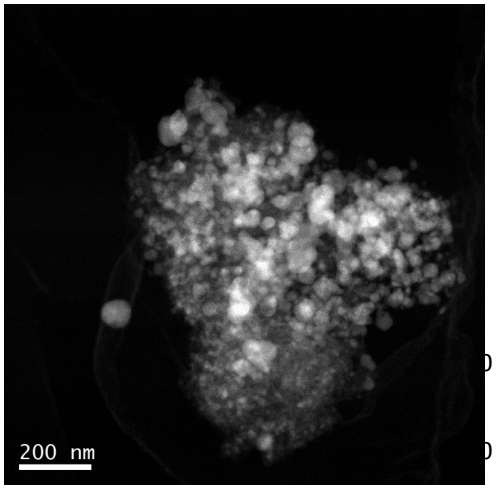


In-situ EELS of Cu thin film

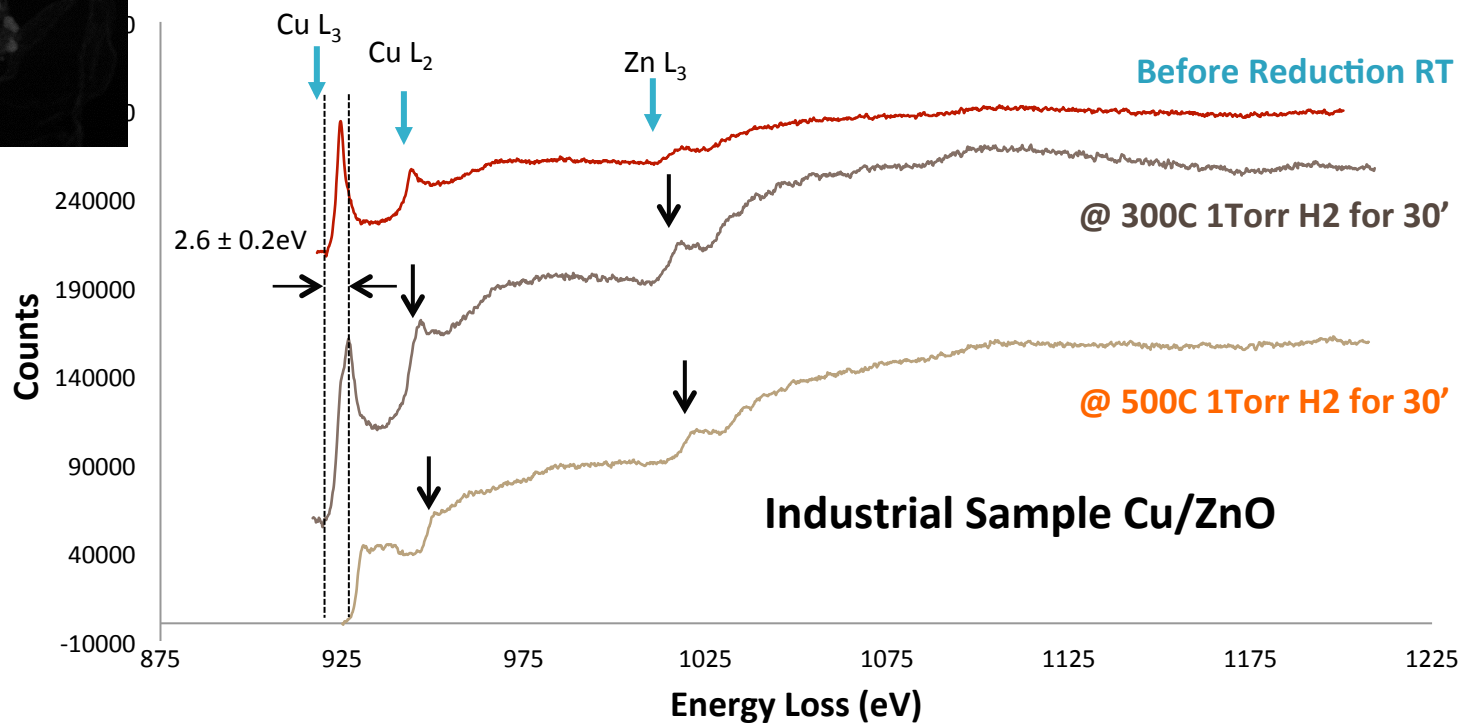


Use of Ne gas in ETEM to define spectral locations, edge shifts

In-situ EELS of Cu nanoparticles

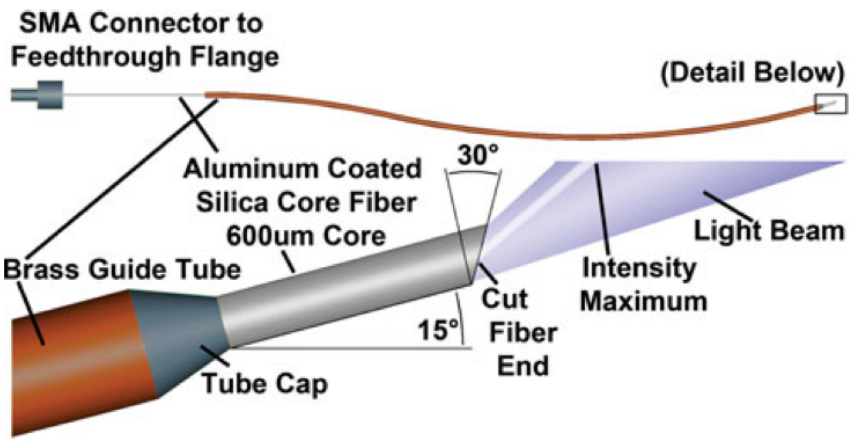


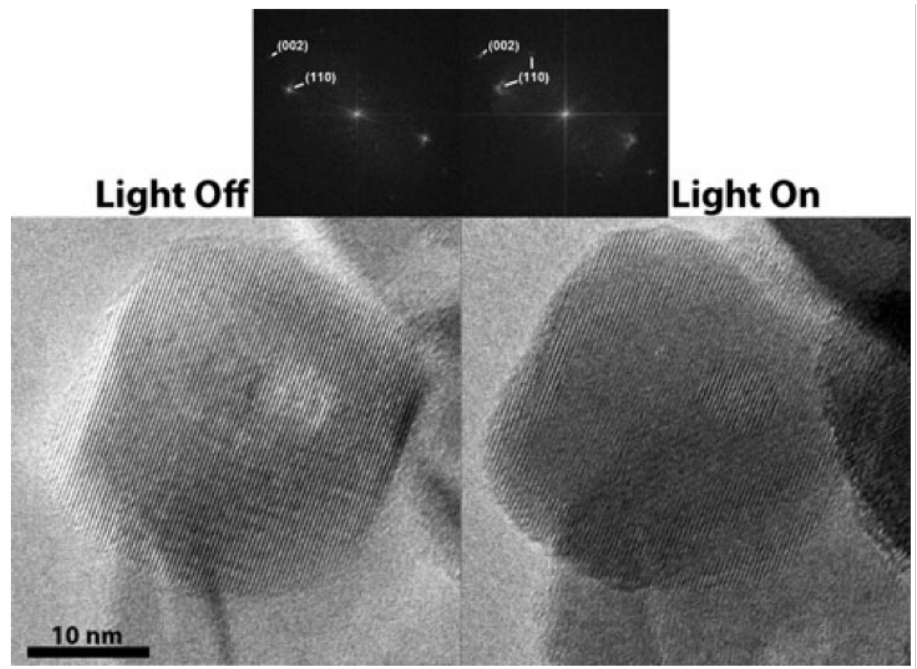
- Allows us to track oxidation and reduction of individual nanoparticles & subtleties of electronic structure.
- Probe size of 1nm required to obtain reasonable signal
- Correlation with XANES & EXAFS to understand 'complexity' due to heterogeneity



Photocatalysis

Direct provision of full spectrum light to a heated sample





B.K. Miller and P. Crozier, Microsc. Microanaly., 19, 461–469, 2013

Concept of 'closed cell' TEM

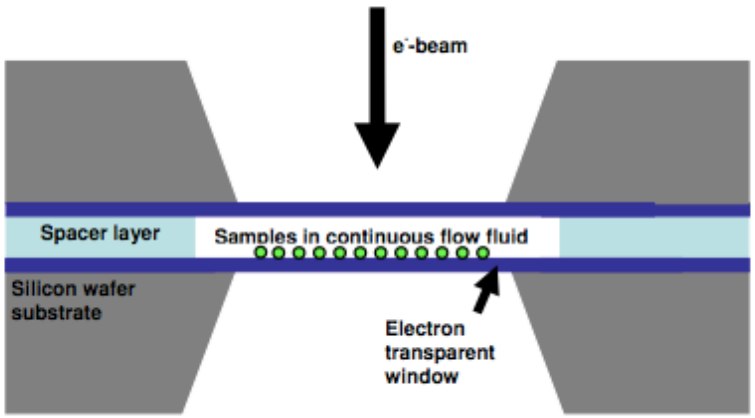
Confine sample of interest in between two microfabricated 'windows'

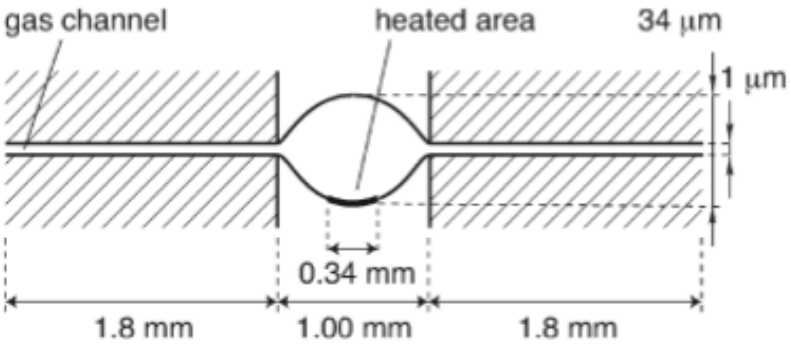
Protects microscope vacuum from either liquid or high gas at high pressures

Conventionally, the windows are made of 'stress-free' silicon nitride

- Standard back-side chemical etch is used to open up the windows

Windows bulge due to differential in pressure

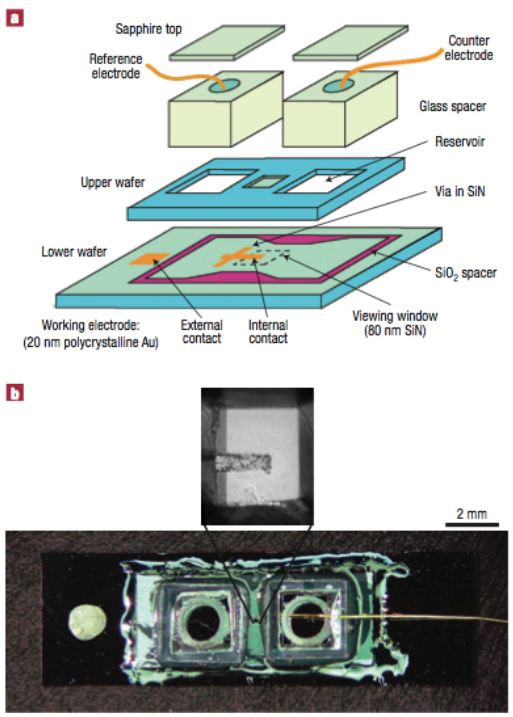




Some history

First examples now over a decade old

- Pratihba Gai @ Dupont
- Frances Ross @ IBM Watson



M.J. Williamson, R.M Tromp, P.M. Vereecken, R. Hull, F.M. Ross, *Nat. Mat* **2**, 532 (2003).

P.L. Gai, *Microsc. Microan*. **8**, 21 (2002).

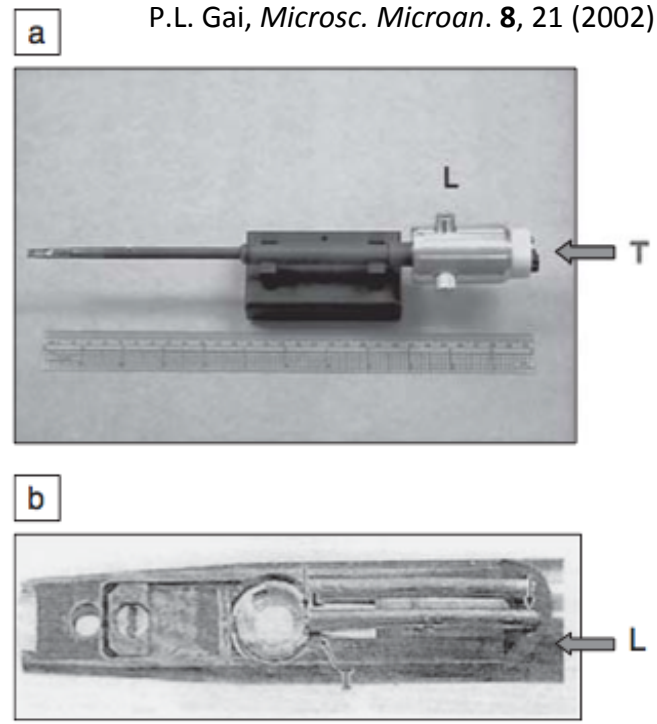


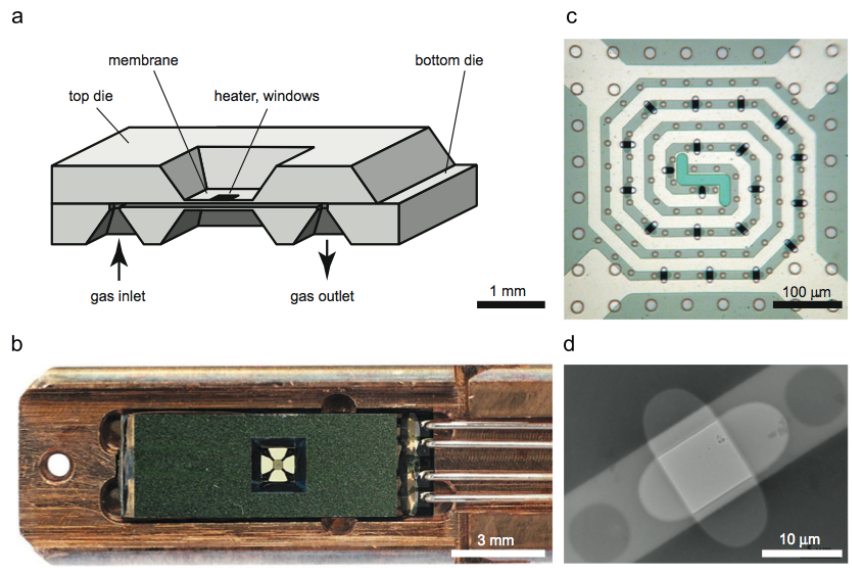
Figure 2. Sample holder for ETEM studies in wet environments: (a) holder with liquid injection tube (L) and heating (T); (b) Enlarged tip of the holder. L and T denote liquid injection tube to the sample in the furnace and the thermocouple, respectively.[31]

Some history

Large "ESTEEM" project in Europe led to development of first systems for gases

Incorporates a heater through microfabrication

Temperature measurement correlated with changes in electrical resistance



J. F. Creemer, S. Helveg, G. H. Hoveling, S. Ullmann, A. M. Molenbroek, P. M. Sarro, and H. W. Zandbergen, "Atomic-scale electron microscopy at ambient pressure," *Ultramicroscopy*, vol. 108, no. 9, pp. 993–998, 2008.

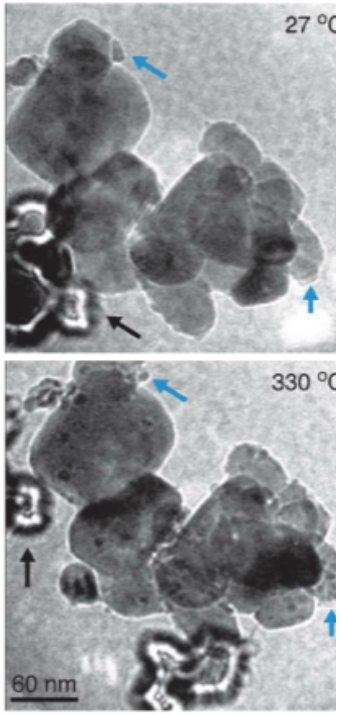
J. F. Creemer, S. Helveg, P. J. Kooyman, A. M. Molenbroek, H. W. Zandbergen, and P. M. Sarro, "A MEMS Reactor for Atomic-Scale Microscopy of Nanomaterials Under Industrially Relevant Conditions," *Journal of Microelectromechanical Systems*, vol. 19, no. 2, pp. 254–264, Apr. 2010.

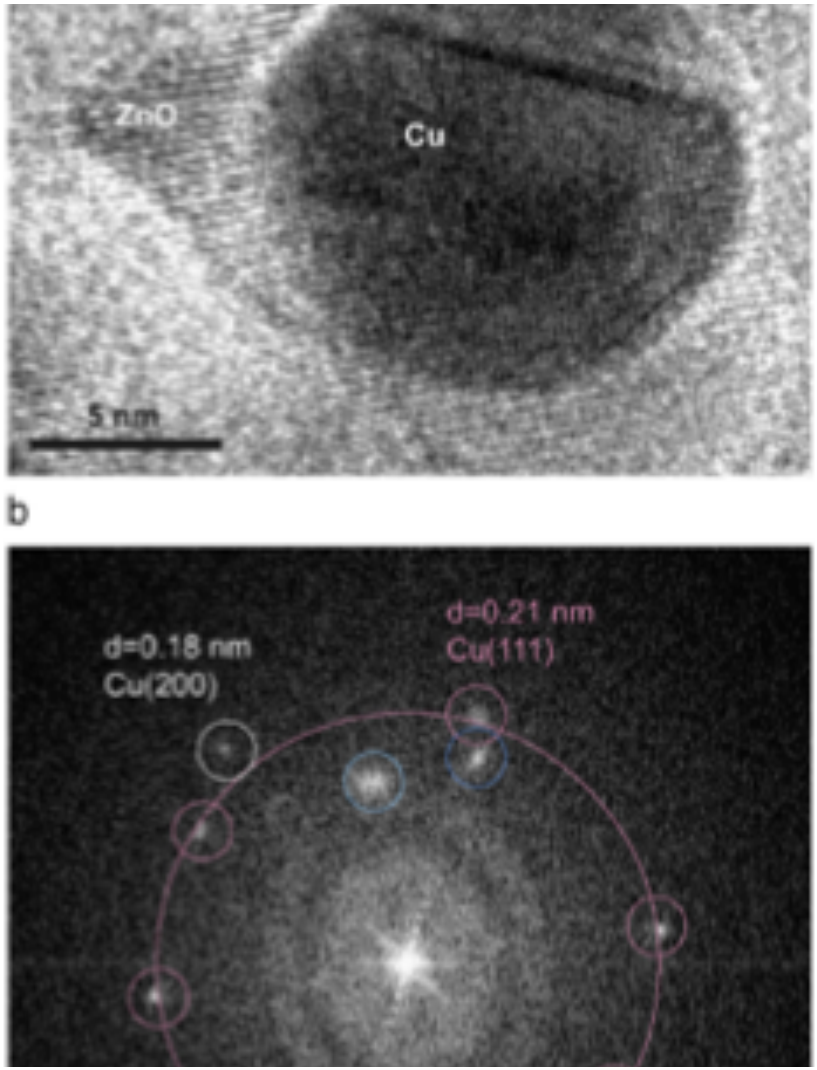
Some history

Nice results!

Better than 2Å resolution at 1 atm / 500°C

So: why has this not become ubiquitous?

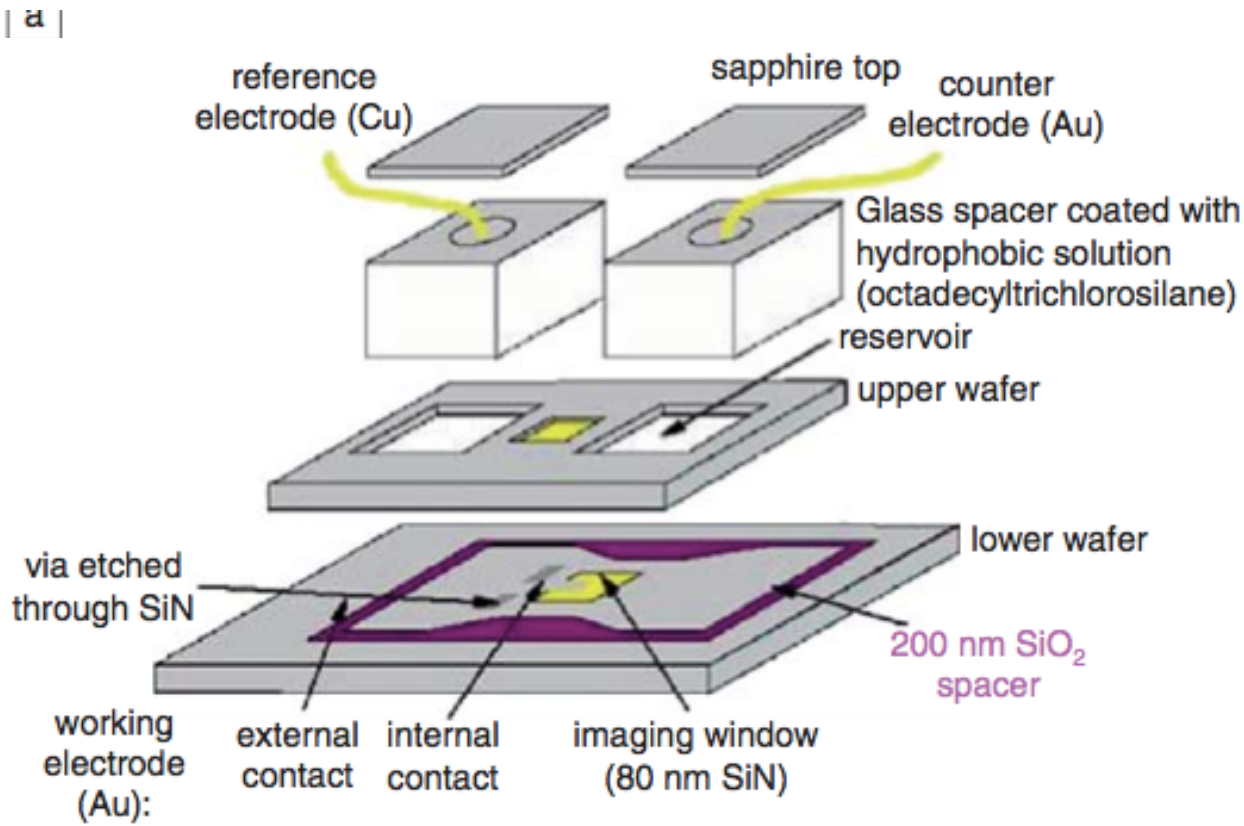




Difficulties in fabrication & use

Original cell used in Ross work was 'one in 10'*

- **System was glued together with a UV cured glue**

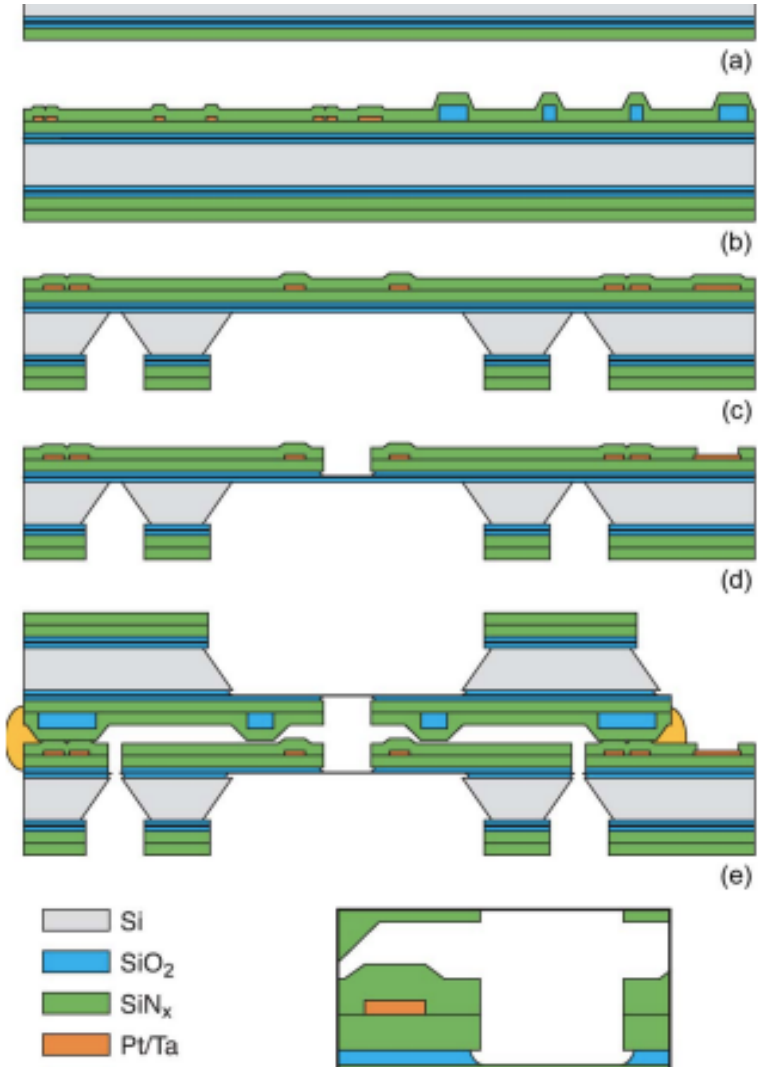


* A quote from lead author Mark Williamson

Difficulties in fabrication & use

ESTEEM design is the same

Final product must be glued together to make it work



Work of NCEM group

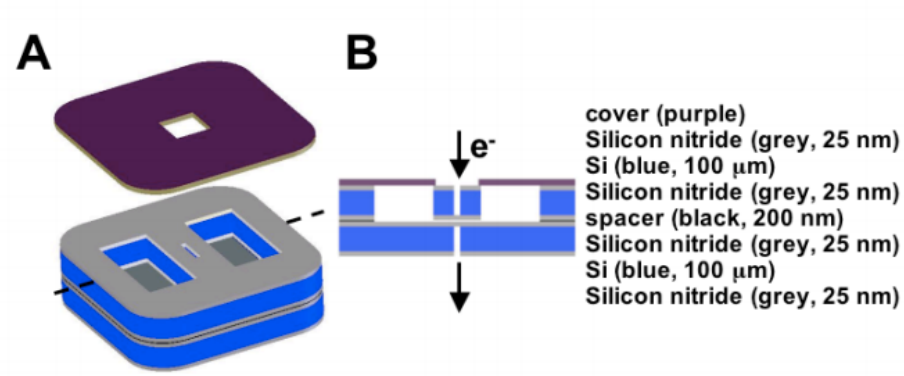
An obvious, but smart step

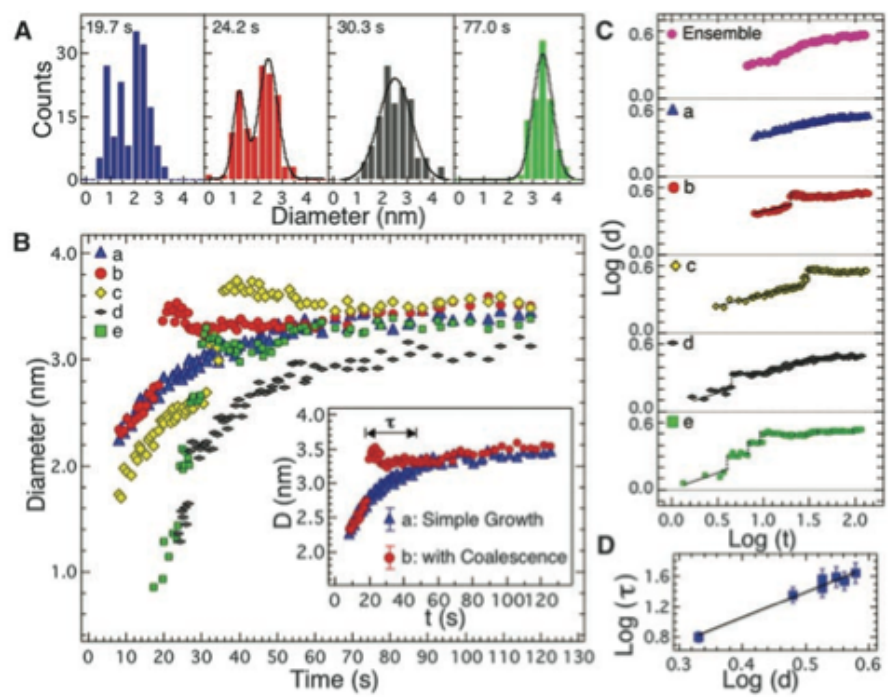
Modified approach of Ross

Use wafer-bonding to hold the two pieces together

Incorporation into a standard, 3 mm sized heating holder

- **Allows application of temperature directly to liquid**





H. Zheng, Science, **324**, 1309, 2009.

Demonstration of imaging of biological samples

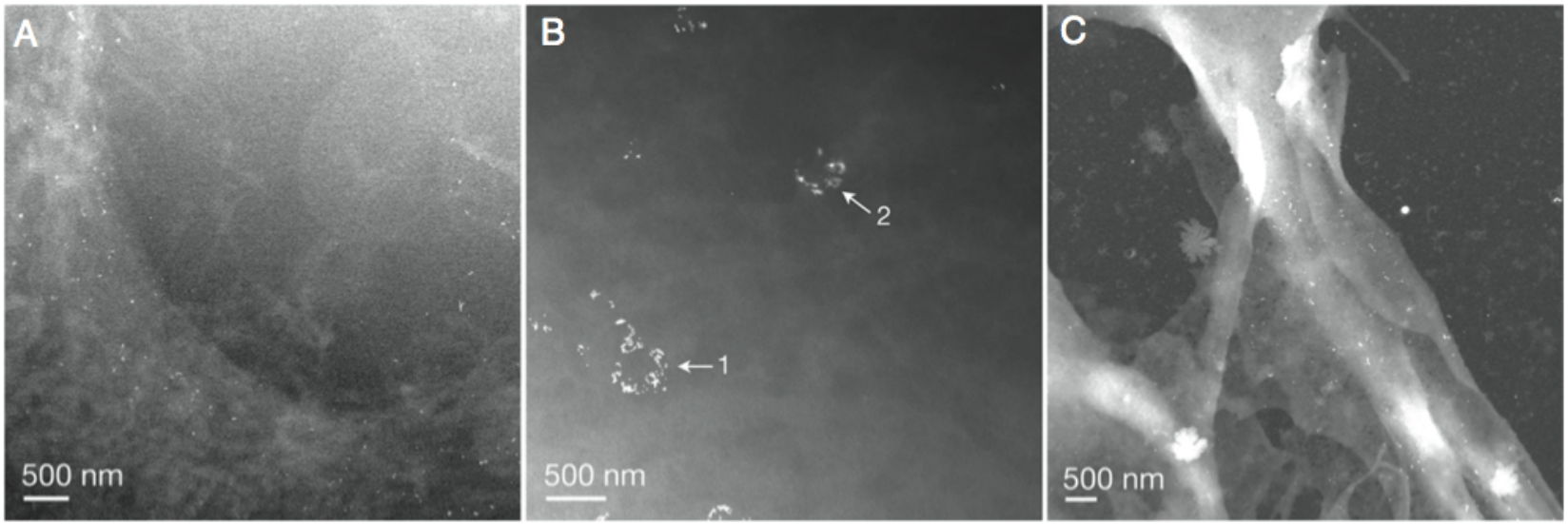


Fig. 2. Liquid STEM images of COS7 fibroblast cells labeled EGF-Au. (*A*) Image of the edge of a fixed COS7 cell after 5-min incubation with EGF-Au. The labels are visible as bright spots and the cellular material is shown as light-gray matter on a dark-gray background. The pixel size was 5.7 nm. (*B*) Image of a COS7 cell incubated with EGF-Au for 10 min and incubated in buffer (without EGF-Au) for an additional 15 min. The pixel size was 4.4 nm. (*C*) Image of the sample used in *A* recorded after the flow cell was opened and the sample was dried in air. The pixel size was 8.9 nm. Note that the salt of this sample was not removed.

Demonstrated imaging through >7 μm of liquid

Direct imaging of cells, and gold labels on cell surfaces

Commercialized product

Note: I am a co-founder of and equity holder in Hummingbird Scientific

Liquid cell TEM: areas of application

Nanoparticle nucleation, growth and self-assembly

Electrochemistry

- **Electrodeposition**
- **In-situ observations of working batteries**
- **Corrosion**

Imaging of biological samples

Imaging of soft materials

Yet to be demonstrated:

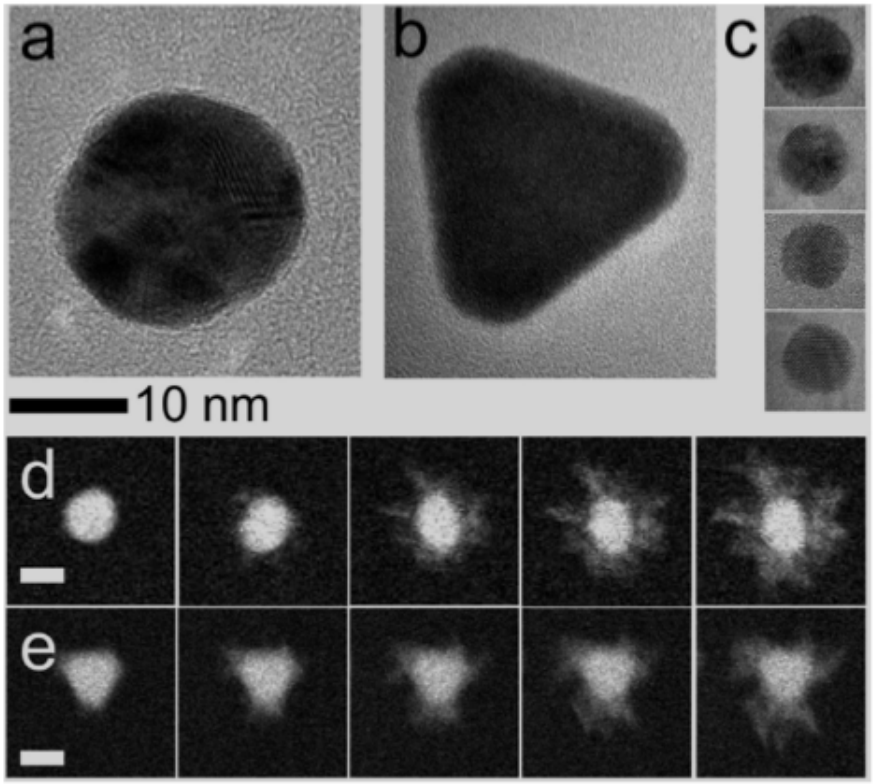
- **Electrocatalysis**
- **Photocatalysis**

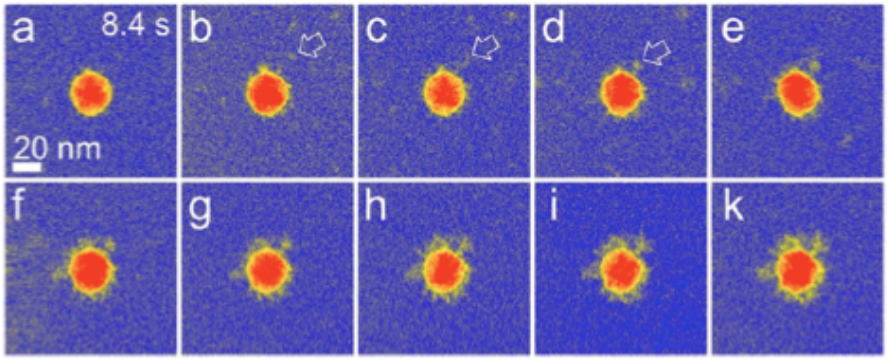
Imaging nanoparticle nucleation & growth

At the CFN we have focused on understanding core-shell nanoparticle growth

Can see such things as:

- **Homogeneous nucleation and attachment**
- **Nucleation on specific facets**
- **Kinetics of crystal growth**

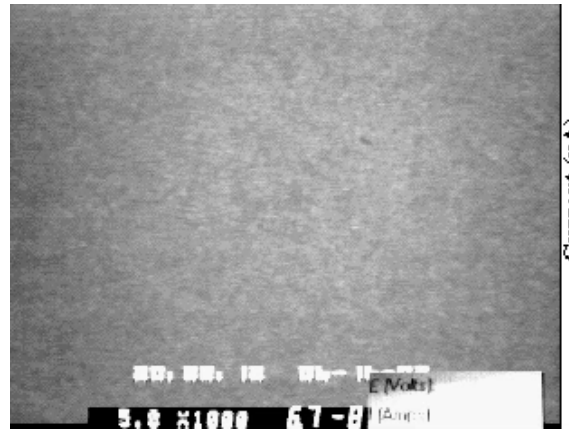


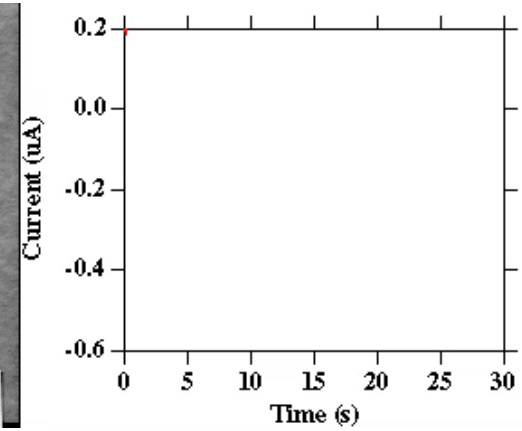


K. L. Jungjohann, et al., *Nano Lett*, Jun. 2013.

Electrochemistry

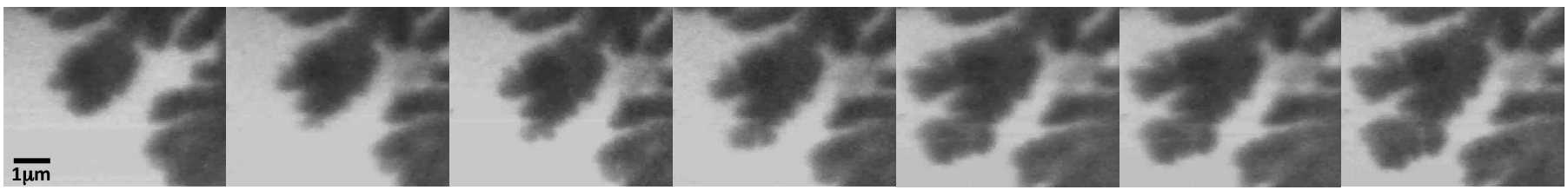
Electrodeposition of Cu on an Au electrode



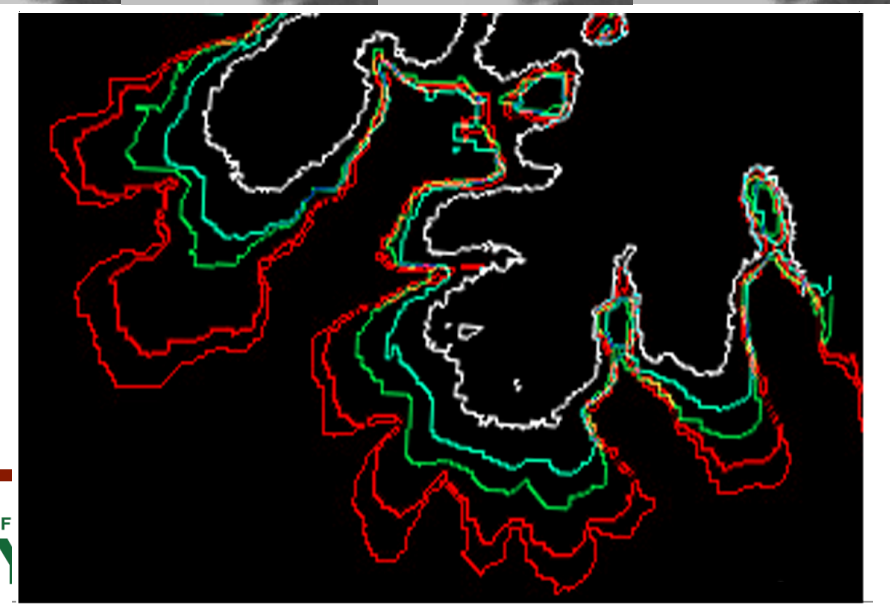


Data courtesy Frances Ross, IBM

A. Radisic, Nano Lett., 6, 236, 2006.

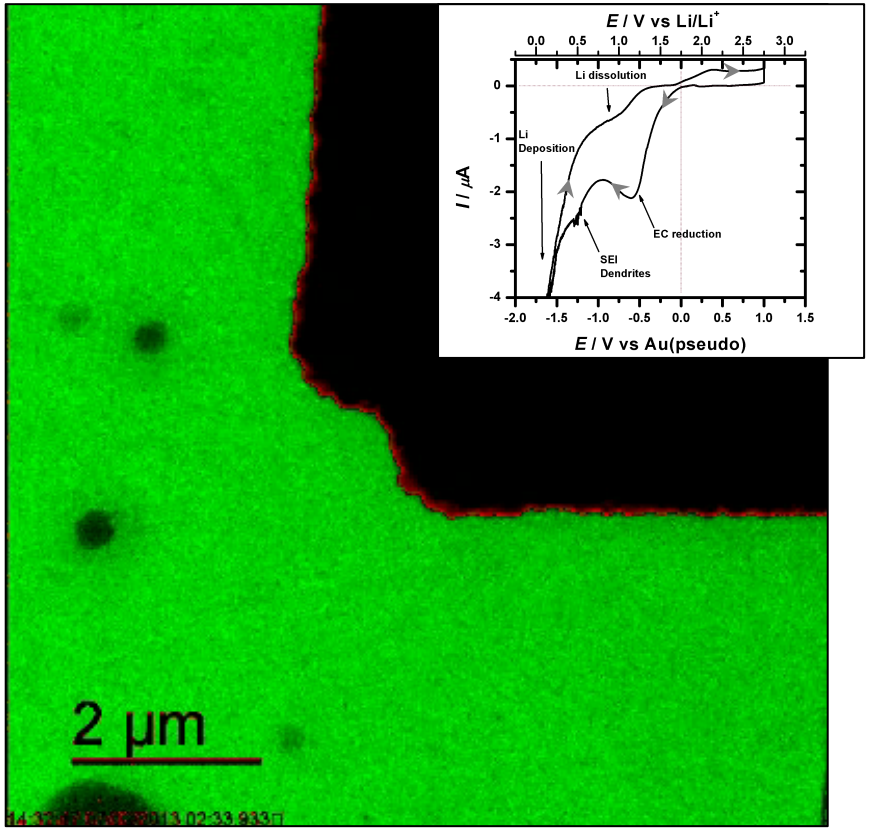


Galvanostatic growth of zinc dendrites at 40 mAcm^{-2}. Total growth rate 0.2mm/s. Stills every 8 seconds. Bright field, energy filtered imaging



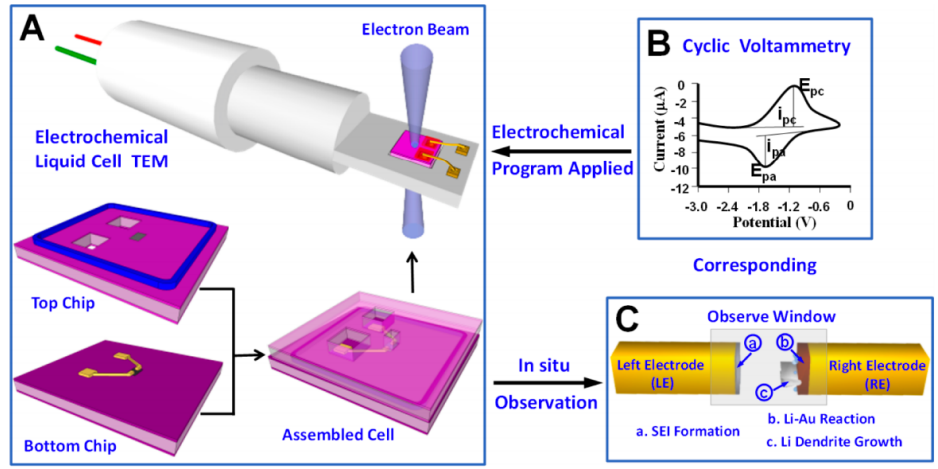
Analysis yields fractal dimensions, growth rates and branching events at different locations on the dendrite.

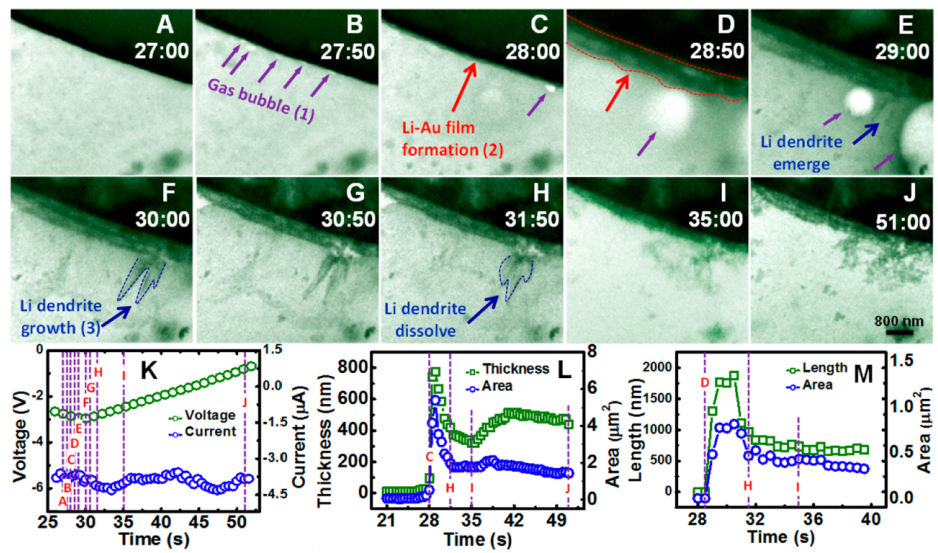
Electrochemistry



SEI Dendritic Growth at Electrode/Electrolyte Interface (1.2M LiPF6 EC:DMC)

R.L. Sacci, et al.Chem. Commun., **50**, 2104, 201450,

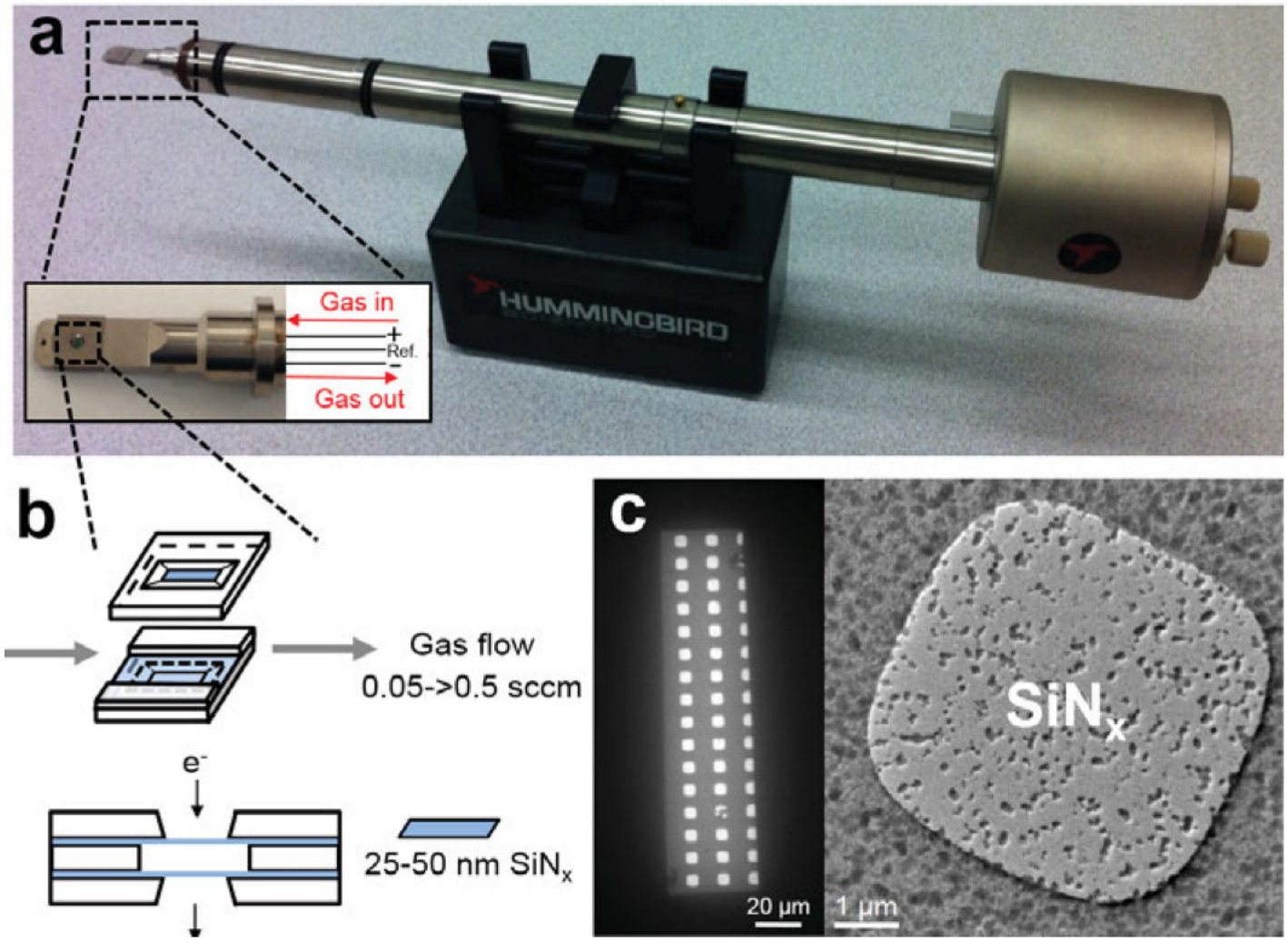




Z. Zeng, Nano Lett., **14**, 1745−1750, 2014.

Integrated gas holder

H.L. Xin, Micros. Microanal., **19**, 1558, 2014.



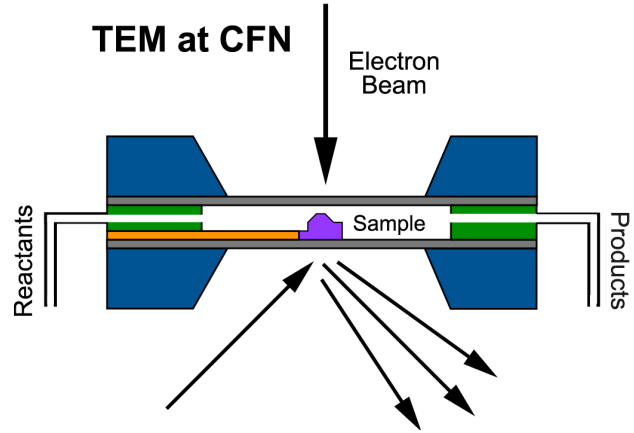
Center for Functional Nanomaterials
Brookhaven National Laboratory

U.S. DEPARTMENT OF ENERGY | Office of Science

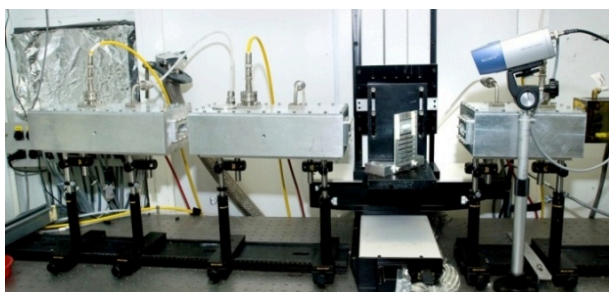
Note: I am a co-founder of and equity holder in Hummingbird Scientific

Operando & correlative experimentation

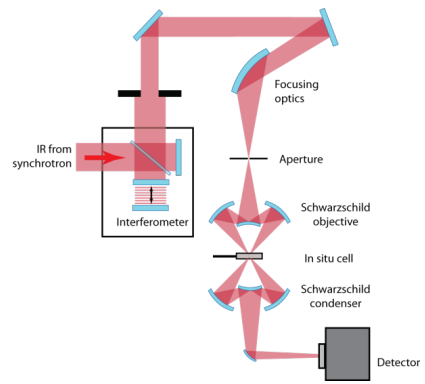
- Spectroscopy (XAS, IR), scattering (e- & x-ray diffraction) and imaging (TEM)
- Short range and long range order (EXAFS & TEM)
- Charge exchange with support (XAS, EELS)
- Core/shell structure (TEM & EXAFS)
- Reactivity studies (IR)



X-ray microprobe at NSLS



X-ray Absorption Spectroscopy



IR Microscope

Transmission Electron Microscopy

STEM imaging at atmospheric pressure

Unpublished data
(redacted)

All STEM images taken at 1 atmosphere pressure in reaction conditions

Correlative studies: electrons and photons

By measuring reactivity can directly correlate measurements of working catalysts from photons and electrons

Sufficient photon signal from the small cell, even with low brightness of NSLS-I

- High quality XANES and EXAFS
- Expect dramatic improvements at NSLS-II

Correlating data allows tracking of full range of particles sizess

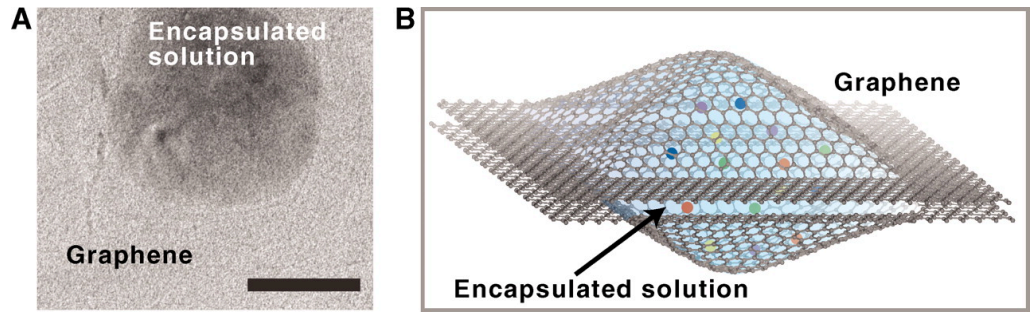
Unpublished data (redacted)

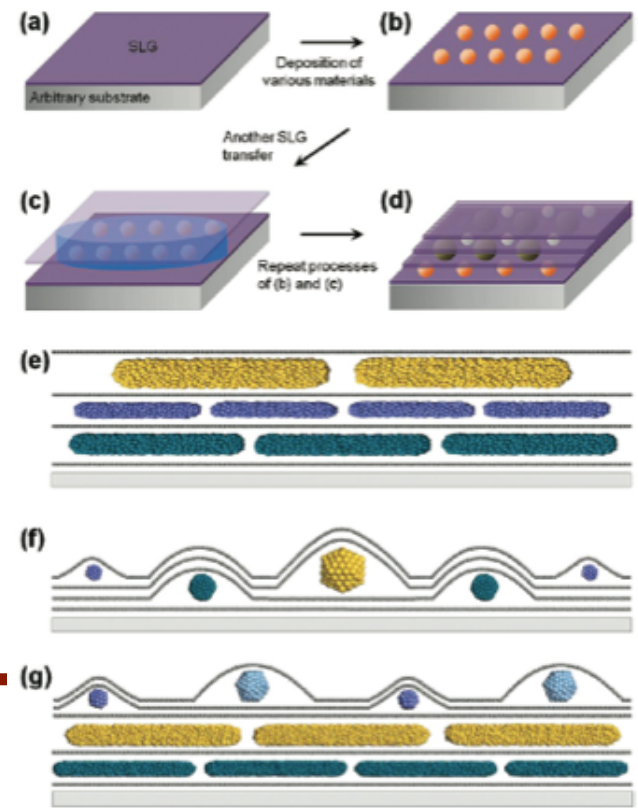
Development of thinner windows (graphene)

Basically just stick two graphene membranes together with some liquid in between

- **Leads to small bubbles of liquid being captured between the membranes**
- **Not particularly reproducible as an approach**

Development of a systematic transfer approach needed





J. M. Yuk, et al. *Nano Lett*, **11**, 3290–3294, 2011.
J. M. Yuk, et al. *Science*, 336, 61–64, 2012.

Summary

STEM & TEM are primary tools for atomic resolution characterization of materials

- Primarily done at high vacuum

Have shown three ways to go beyond this constraint

- Differentially pumped environmental TEM
- Closed-cells for liquids
- Closed-cells for gases

This is an exciting new field, with major impact on catalysis, electrocatalysis, photocatalysis