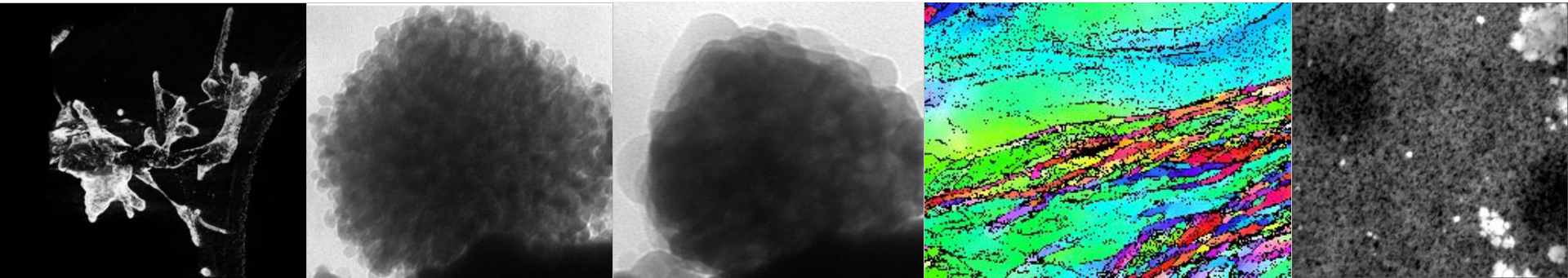


Exceptional service in the national interest



Materials Science External Review Panel - March 11-13, 2013



Advanced Microscopy Techniques for Novel Characterization and Diagnostics

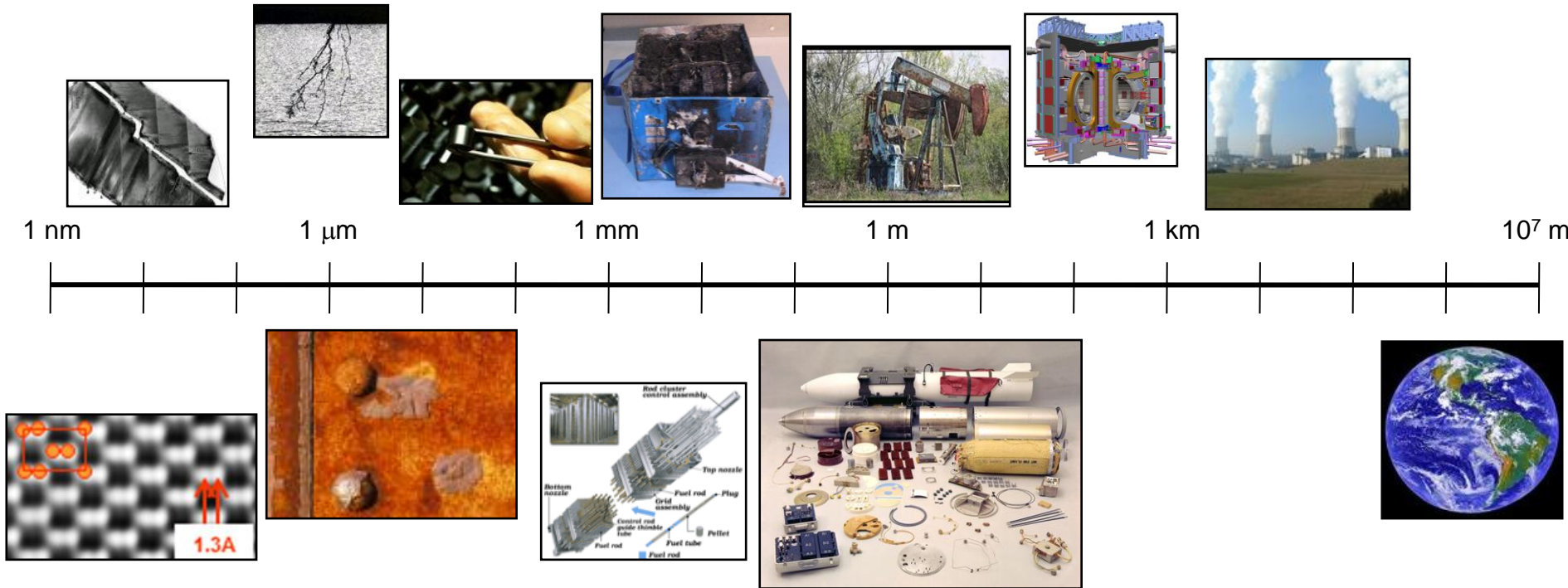
Khalid Hattar
Radiation Solid Interactions
Physical, Chemical, and Nano Science



Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Context

- To reliably predict a material's performance a detailed understanding is needed of:
 - Heterogeneity in the microstructure in:
 - All three dimensions
 - At multiple length scales
 - The structural evolution's response to the imposed environmental conditions



To obtain the necessary insight into microstructure and structural evolution, adequate characterization tools and *in situ* techniques must be developed

1. ***In situ* ion irradiation transmission electron microscope (I³TEM) in variety and combination of complex environments permits:**

- A. 3D + dose dependence = 4D information
- B. Direct correlation between nanostructure and quantifiable mechanical properties
- C. Structural stability **under** high temperature gas environments
- D. Initiation and growth of pits in metal films

2. **3D structural analysis provides greater insight**

3. **Advanced analytical techniques allow for correlation of microstructure and performance**

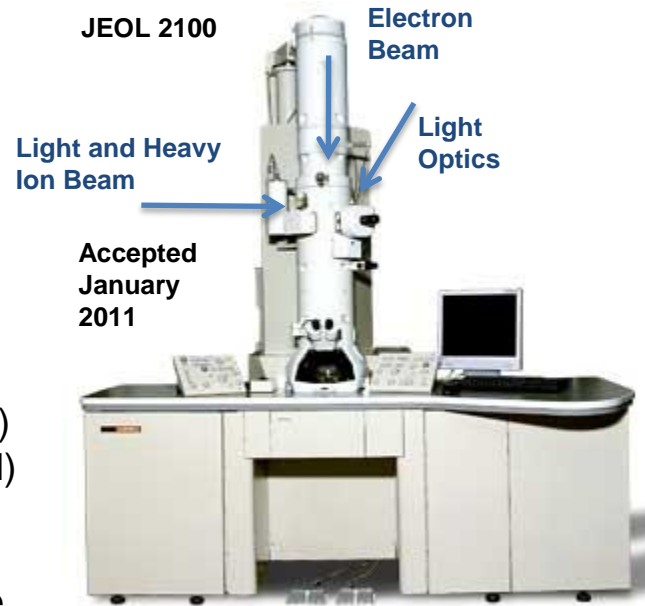
Contributors & Collaborators:

Paul G. Kotula, Ping Lu, Don Susan, Zahra Ghanbari, Jan Ringnalda, C. Chan, J. Carroll, J. Madison, M. Rye, J. Michael, J.D. Sugar, F. El Gabaly, Chueh, J. Huang, Y. Liu, J.P. Sullivan, B.L. Doyle, O. El-Atwani, D. Buller, J.A. Scott, B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, J. Sharon, B. L. Boyce, C. Chisholm, H. Bei, E.P. George, P. Hosemann, A.M. Minor, Hysitron Inc., H. Lim, C. Battaile, S.M. Hoppe, D. Sasaki, Protochips, Inc., S. Rajasekhara, N.R. Sorensen, B.G. Clark, D. Gross, J. Kacher, P.J. Cappillino, B.W. Jacobs, G. Kellogg, T. Ohta, B. Diaconescu, T. Beechem, L.R. Parent, I. Arslan, M.A. Hekmaty, D.B. Robinson & I.M. Robertson

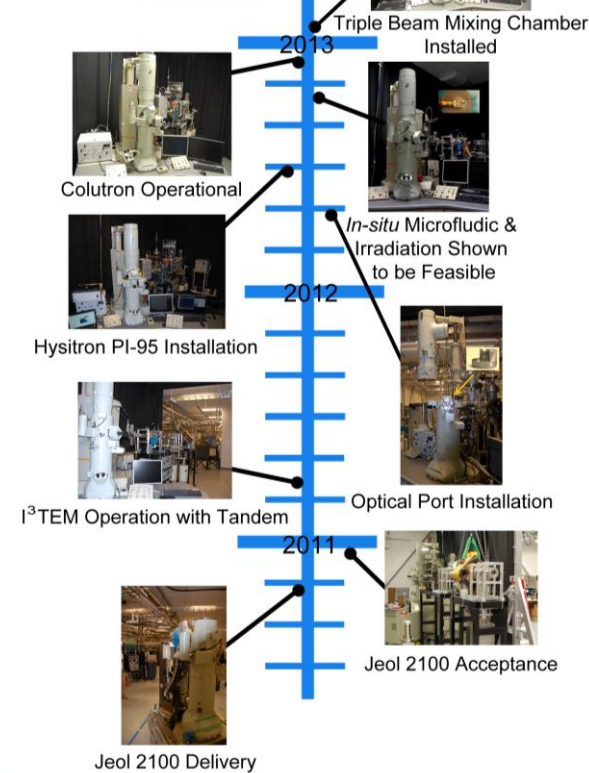
Sandia's *In situ* Ion Irradiation TEM (I³TEM)

Proposed Capabilities

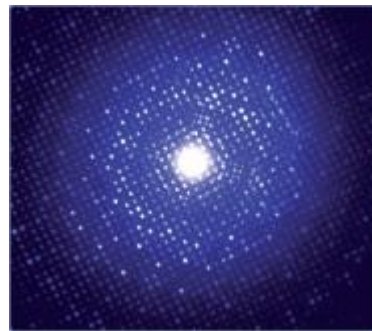
- 200 kV LaB₆ TEM
- Ion beams considered:
 - 1 MeV H¹⁺
 - 3 MeV He¹⁺ Si³⁺ Cu³⁺ Au³⁺W³⁺
 - 14 MeV Si³⁺
 - 10 keV D²⁺
 - 10 keV He⁺
- All beams hit the same location
- Electron tomography
- Nanosecond time resolution (DTEM)
- Precession scanning (EBSD in TEM)
- *In situ* PL, CL, and IBIL
- *In situ* heating and cooling stages
- *In situ* electrical measurement stage
- *In situ* quantitative mechanical testing
- *In situ* vapor phase stage
- *In situ* liquid mixing stage



TEM Expansion Timeline



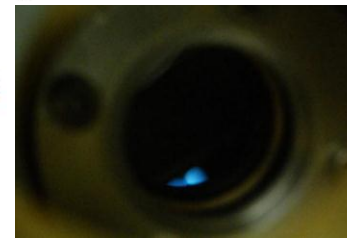
Has a unique set of dual *in situ* TEM techniques to evaluate material's response to extreme environments at the nanoscale



Single electron sensitive camera

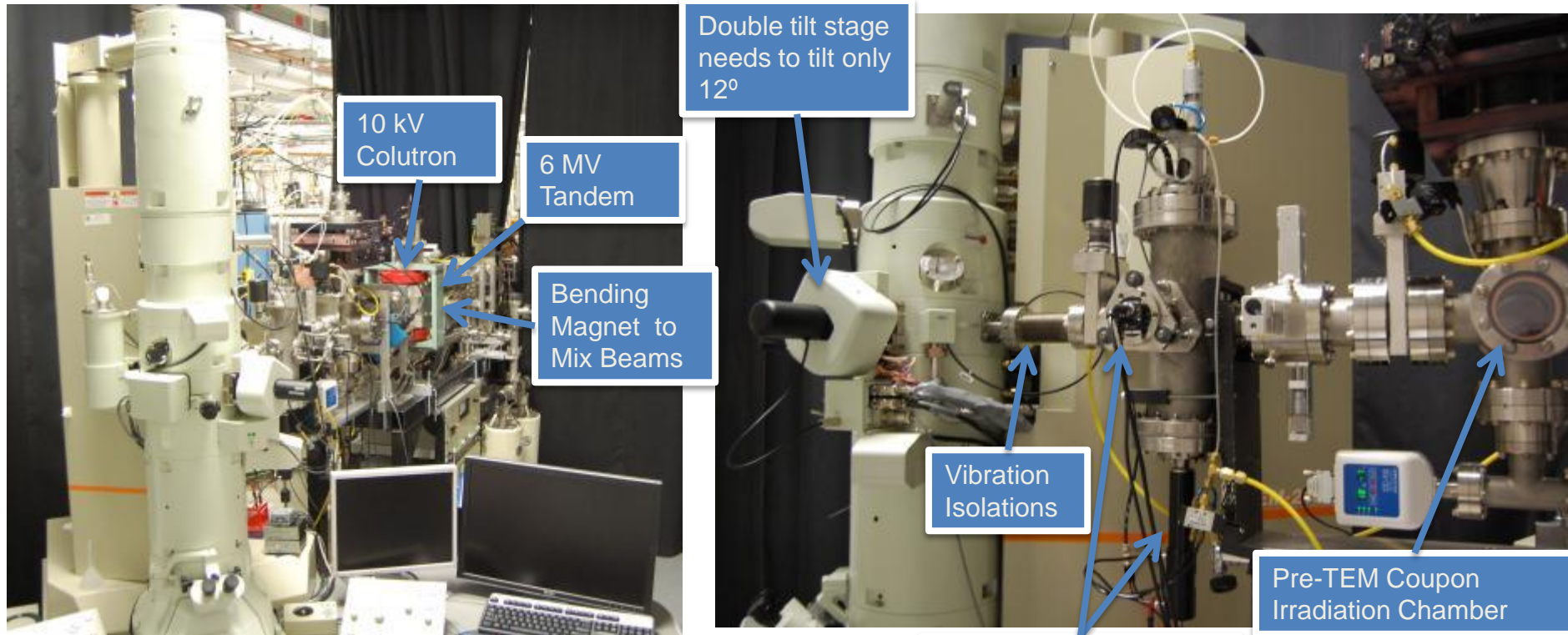


Tomography + *in situ* = 4D



First IBIL in TEM

Current Status of the *In situ* TEM Beamline

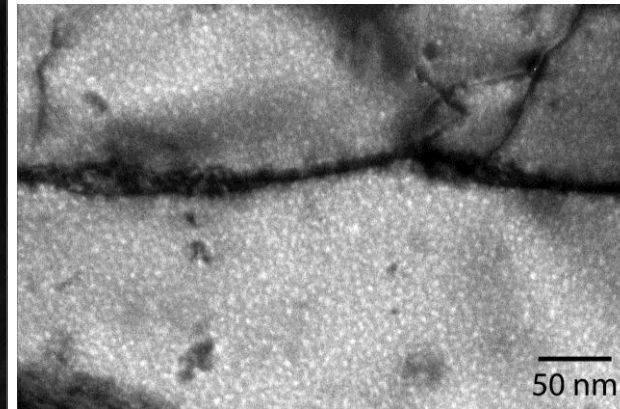
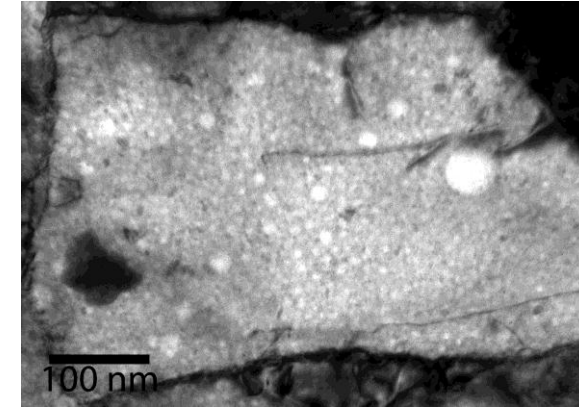
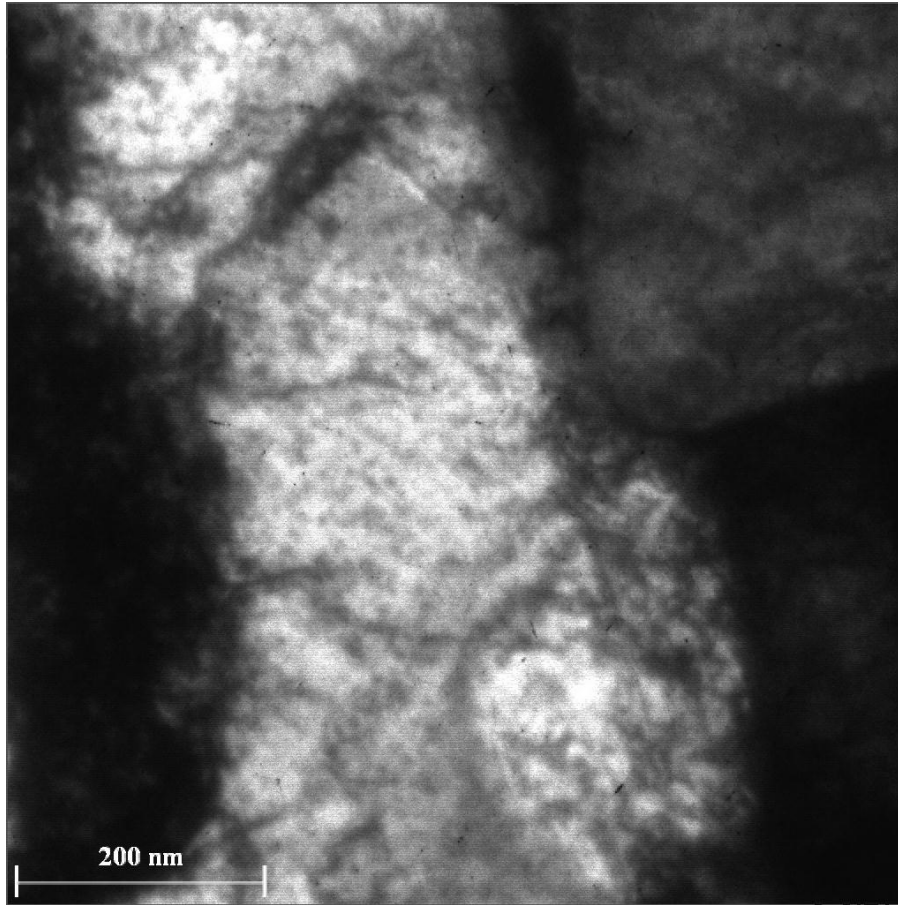


Beam burn from 14 MeV Si

Facility is operational and producing world-class results despite not being completed or optimized

What Insight into Structural Stability is Gained from I³TEM Experiments?

From NW components through proposed NE cladding to waste storage:
Understanding Radiation Damage is Essential



■ I³TEM W irradiation and He implantation of SPD-W developed for ITER applications

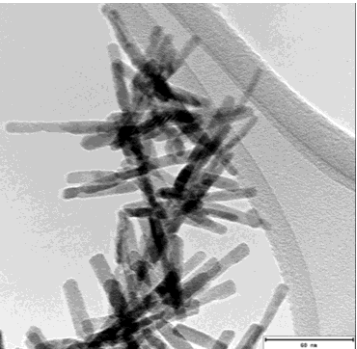
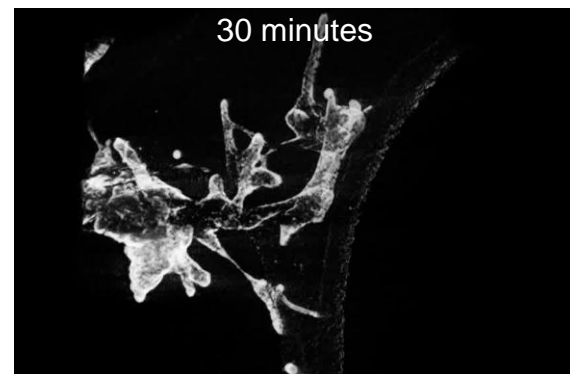
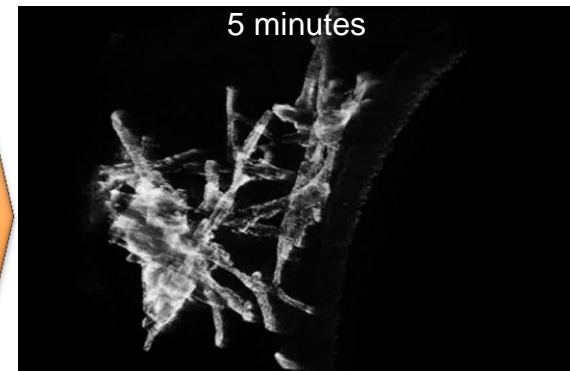
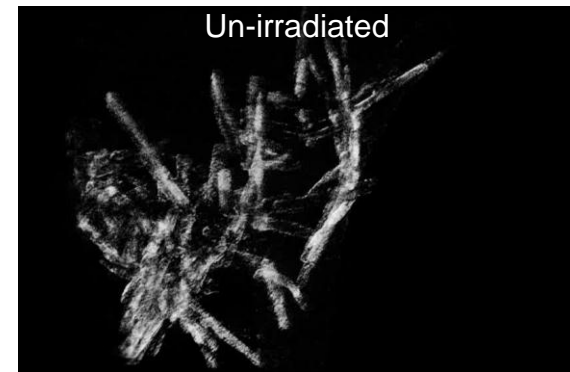
I³TEM is providing insight into:

- 1) Loop formation
- 2) Loop stability & migration
- 3) He bubble formation & distribution
- 4) Rad & structural defect interactions

Radiation Tolerance is Needed in Advanced Scintillators for Non-proliferation Applications



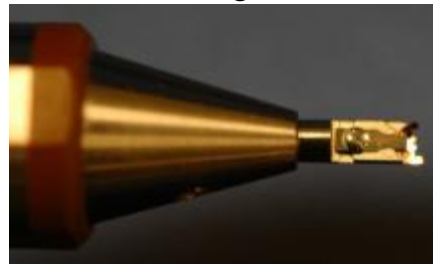
In situ Ion Irradiation TEM (I^3 TEM)



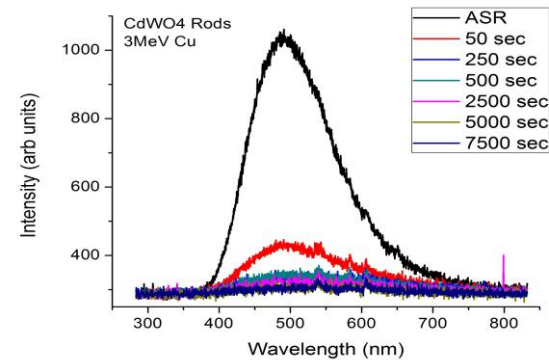
High-Z nanoparticles ($CdWO_4$) are promising, but are radiation sensitive



Hummingbird tomography stage

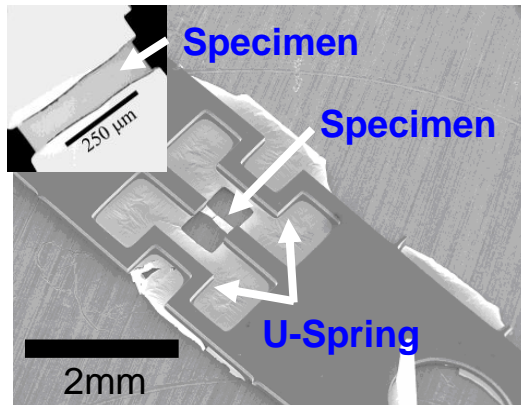


Tomography of Irradiated $CdWO_4$:
3 MeV Cu^{3+} at ~ 30 nA

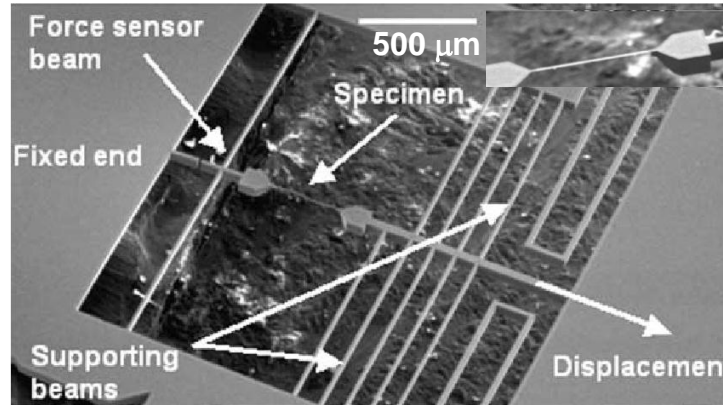


Development of *In situ* TEM Quantitative Small-Scale Mechanical Property Testing

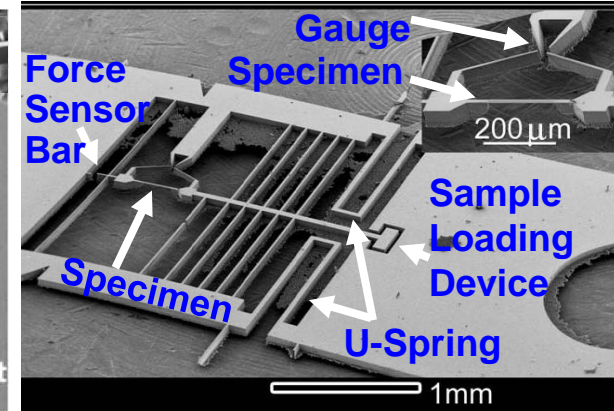
TEM-MEMS I



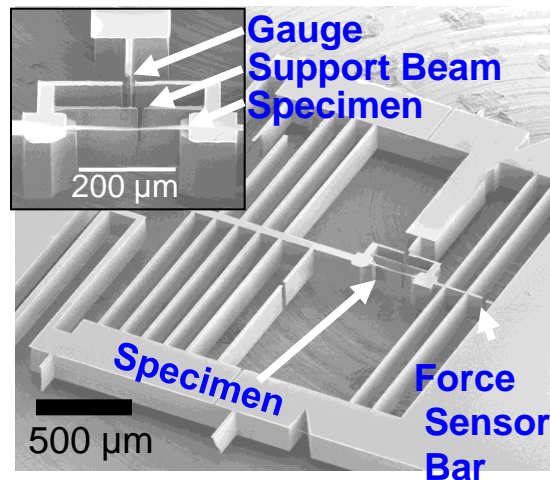
TEM-MEMS II



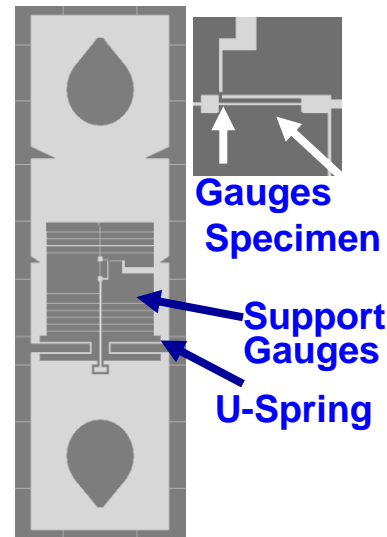
TEM-MEMS III



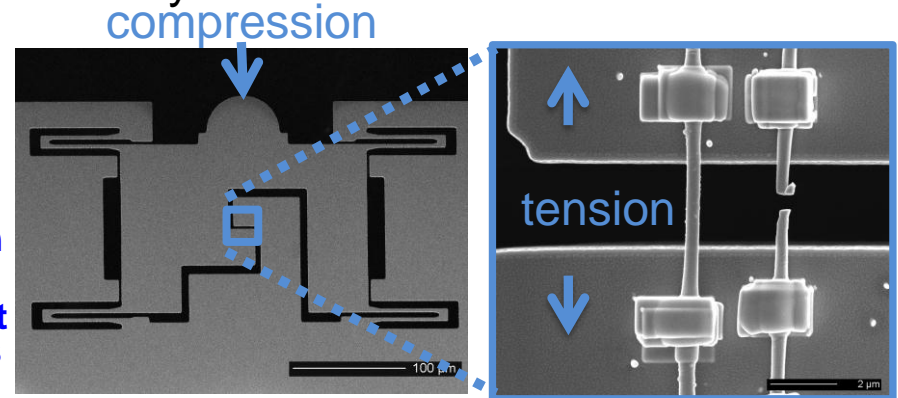
TEM-MEMS IV



TEM-MEMS V



Hysitron Push-to-Pull Device



Sandia aided in the development of quantifiable *in situ* TEM tensile experiments

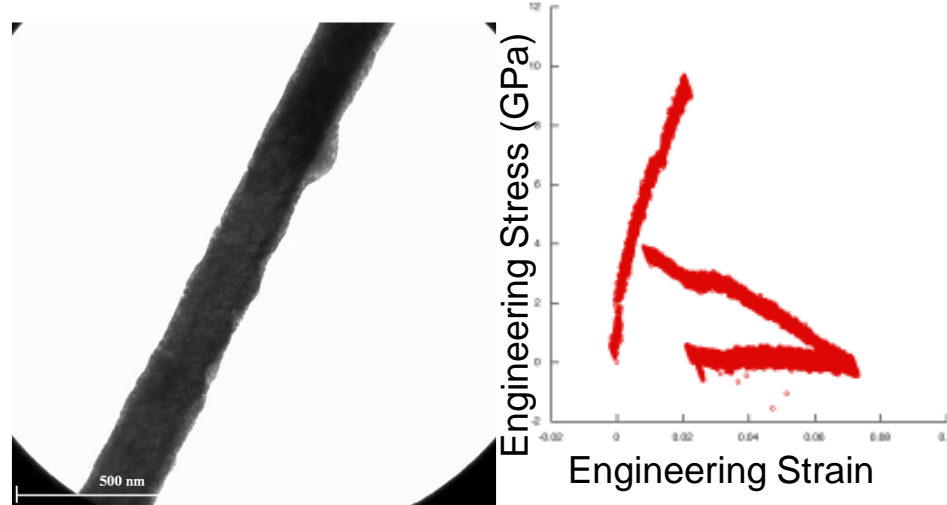
What Does *In situ* TEM Quantitative Mechanical Property Testing Provide to NW?

Radiation effect on mechanical properties

- Direct correlation of dose and defect density with resulting change in strength and ductility
- Failure of Mo-wire after 3 MeV Cu irradiation

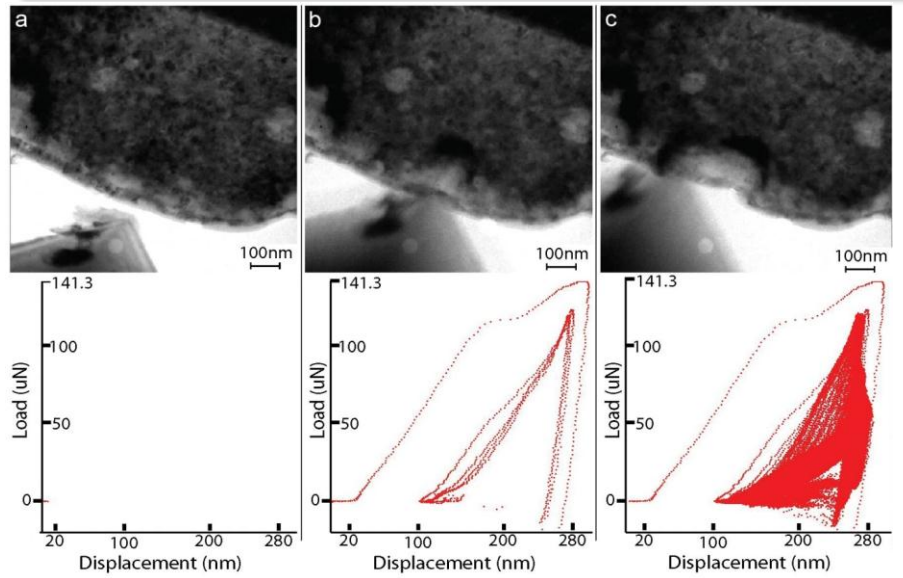
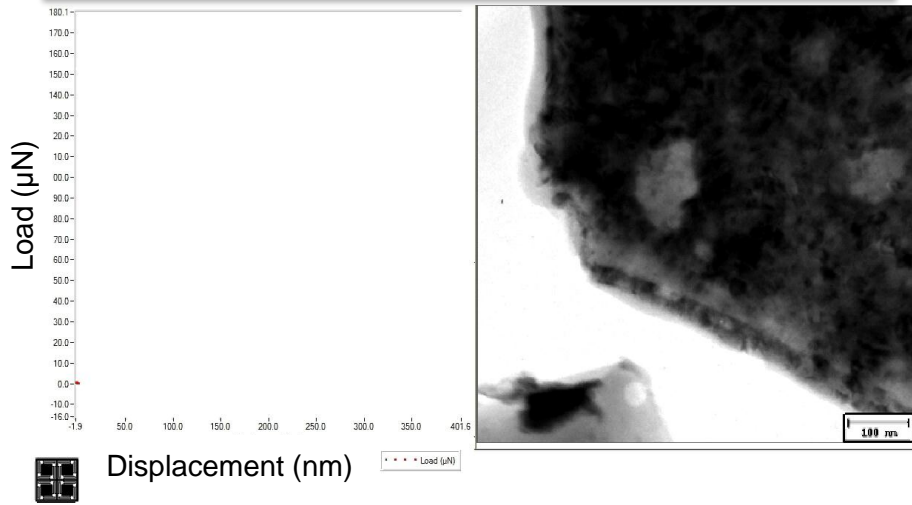
Contact and fatigue effect on structure

- Associate change in local hardness and fatigue with corresponding nanostructure
- Indent and Fatigue of nanocrystalline Cu film

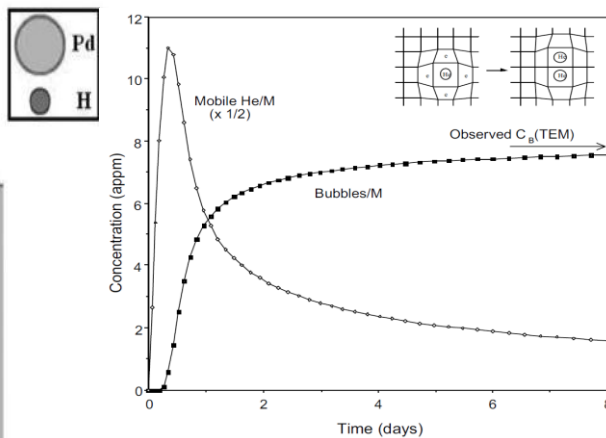
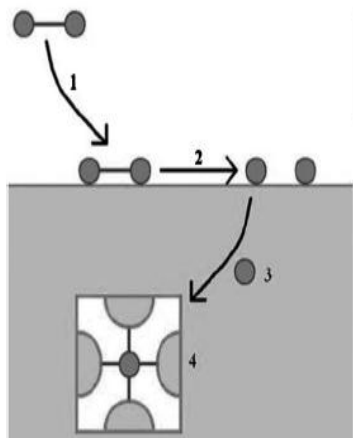


Displacement damage effect on mech. prop.

Fundamentals of contact reliability

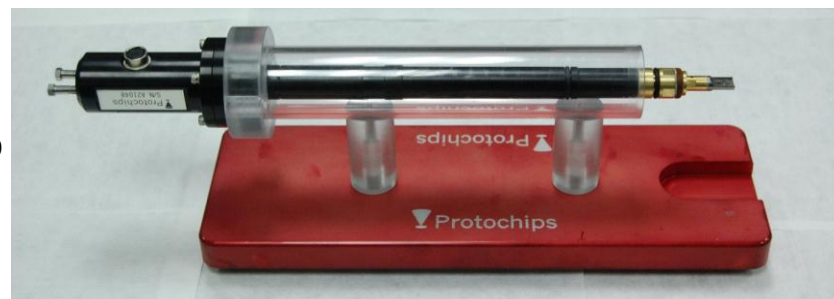


Can *In situ* TEM Address Hydrogen Storage Concerns in Extreme Environments?



Vapor-Phase Heating TEM Stage

- Compatible with a range of gases
- *In situ* resistive heating
- Continuous observation of the reaction channel
- Chamber dimensions are controllable
- Compatible with MS and other analytical tools

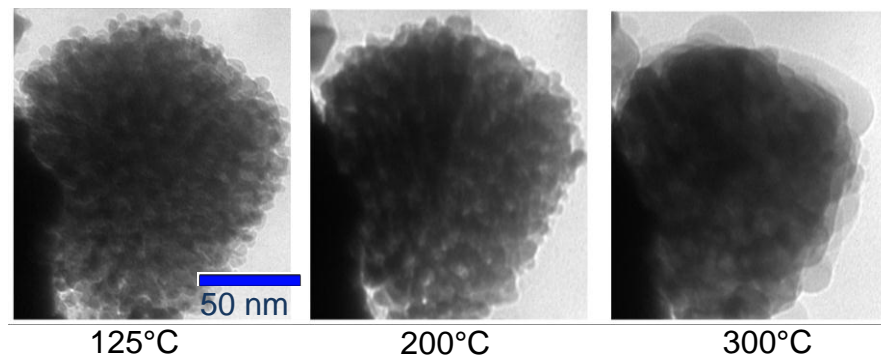
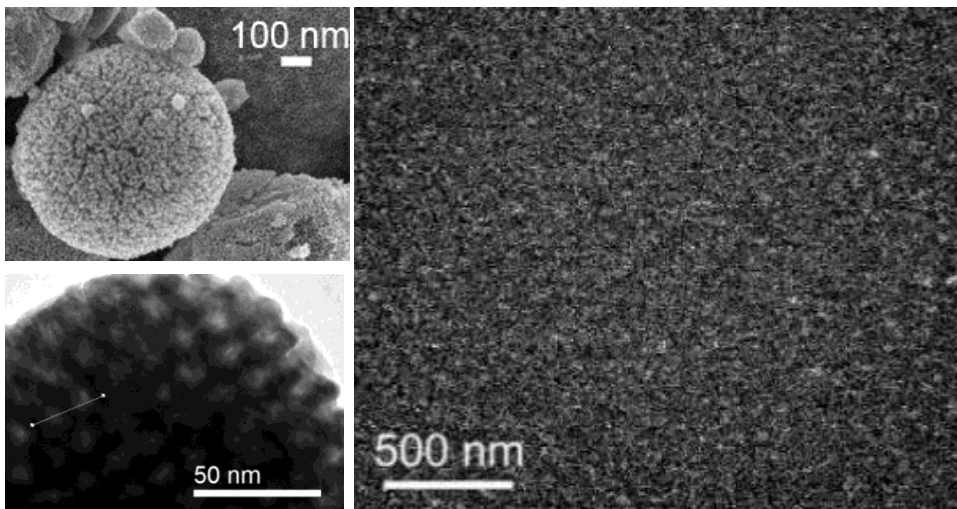


R. Delmelle, J., Phys. Chem. Chem. Phys. (2011) p.11412

Cowgill, D., Fusion Sci. & Tech., 28 (2005) p. 539
 Trinkaus, H. et al., JNM (2003) p. 229
 Thiebaut, S. et al. JNM (2000) p. 217

Harmful effects may be mitigated in nanoporous Pd

- 1 atm H₂ after several pulses to specified temp.

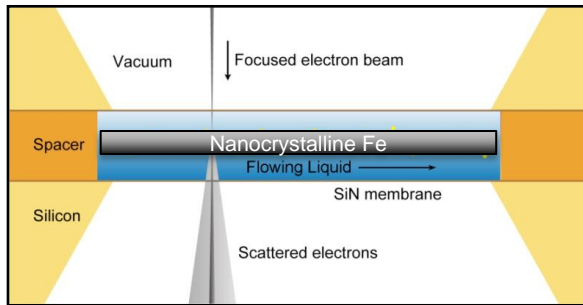


New *in situ* atmospheric heating experiments provide great insight into nanoporous Pd stability

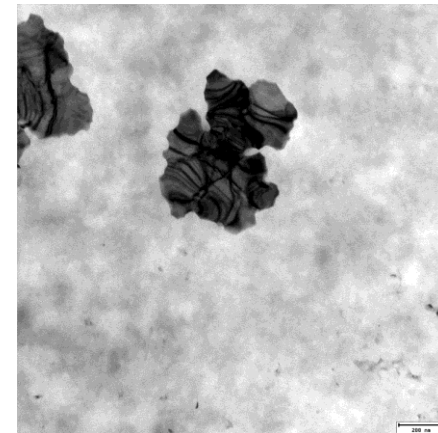
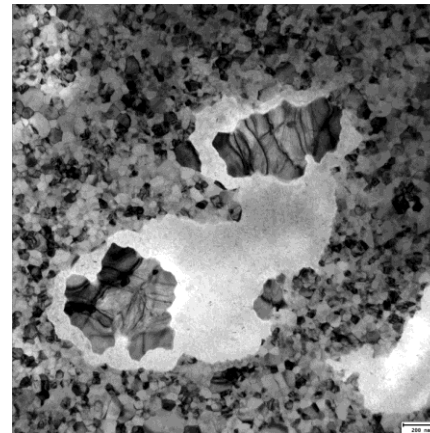
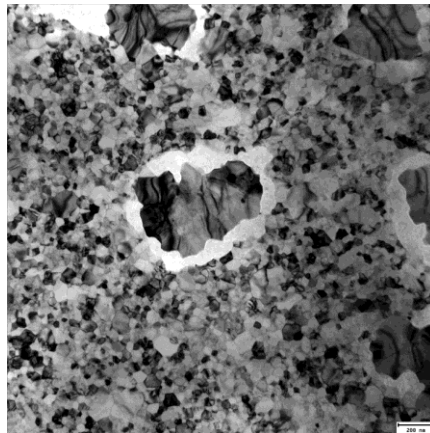
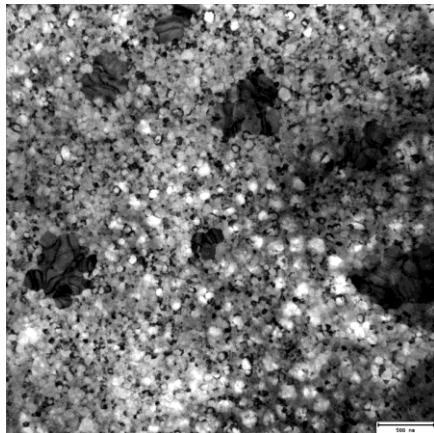
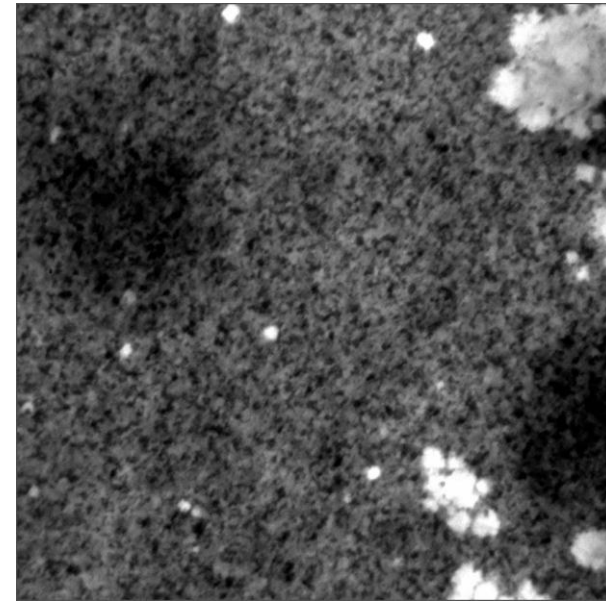
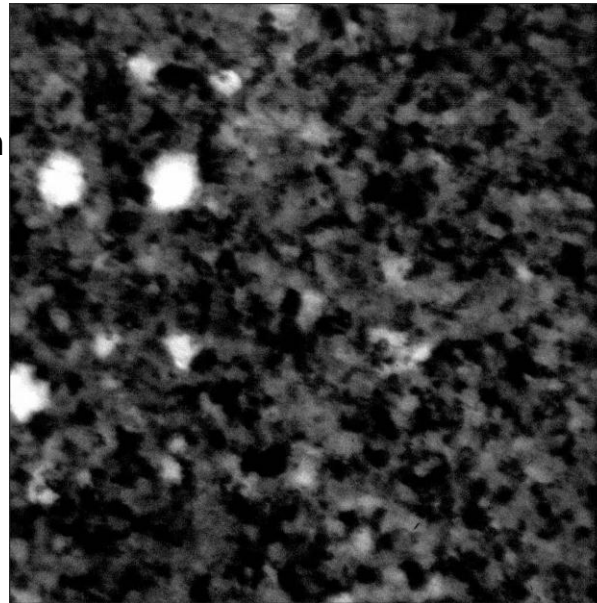
Can We Gain Insight into the Corrosion Process through *In situ* TEM?

Microfluidic Stage

- Mixing of two or more channels
- Continuous observation of the reaction channel
- Chamber dimensions are controllable



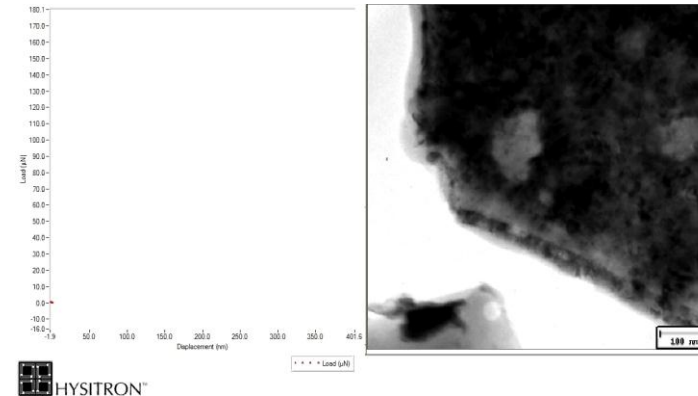
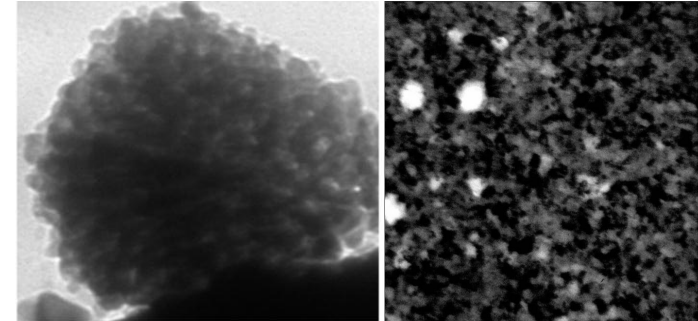
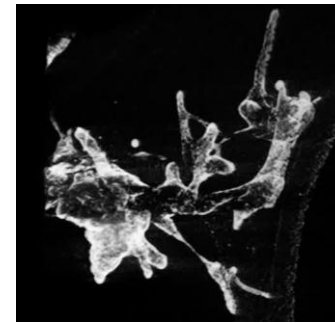
Cross-sectional schematic



Pitting mechanisms during dilute flow of acetic acid over 99.95% nc-PLD Fe involves many grains. Large grains resulting from annealing appear more corrosion tolerant

Summary & Impact of I³TEM

- Sandia's I³TEM is one of only two facilities in the US
 - Only facility in the world with a wealth of dual *in situ* capabilities
 - *In situ* irradiation from H to Au and *in situ* gas implantation
 - Eight TEM stages with various capabilities (two beta-testing)
- Attempting to elucidate nanoscale mechanisms
 - Self ion irradiation and He implantation of W-alloy being considered for ITER applications
 - Combined irradiation with tomography to understand 3D evolution in nanoscintillators
 - Developed with UIUC and Hysitron quantitative *in situ* TEM mechanical properties testing
 - Understand the effects of Hydrogen and temperature on the evolution of nanoporous Pd
 - Initial investigation into pitting on nanocrystalline Fe at the nanometer scale
- Provides a direct real time ability to evaluate a variety of extreme environments and combinations of environments



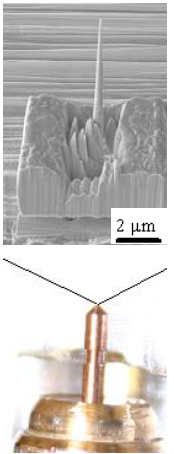
Sandia's I³TEM although still under development is providing a wealth of interesting initial observations

Contributors & Collaborators:

Paul G. Kotula, Ping Lu, Don Susan, Zahra Ghanbari, Jan Ringnald, C. Chan, J. Carroll, J. Madison, M. Rye, J. Michael, J.D. Sugar, F. El Gabaly, Chueh, J. Huang, Y. Liu, J.P. Sullivan, B.L. Doyle, O. El-Atwani, D. Buller, J.A. Scott, B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, J. Sharon, B. L. Boyce, C. Chisholm, H. Bei, E.P. George, P. Hosemann, A.M. Minor, Hysitron Inc., H. Lim, C. Battaile, S.M. Hoppe, D. Sasaki, Protochips, Inc., S. Rajasekhara, N.R. Sorensen, B.G. Clark, D. Gross, J. Kacher, P.J. Cappillino, B.W. Jacobs, G. Kellogg, T. Ohta, B. Diaconescu, L.R. Parent, I. Arslan, T. Beechem, M.A. Hekmaty, D.B. Robinson & I.M. Robertson

3D Characterization from Angstroms to Meters

AC-STEM



APT



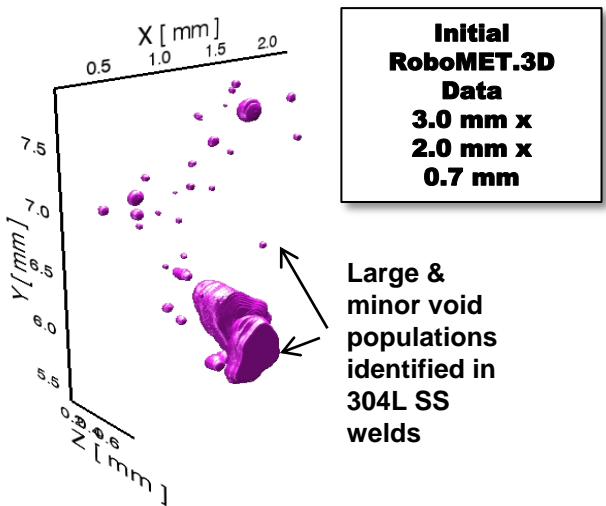
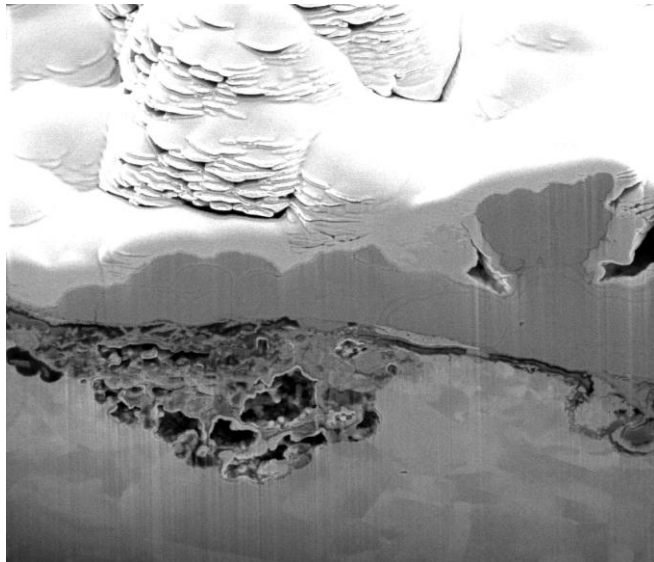
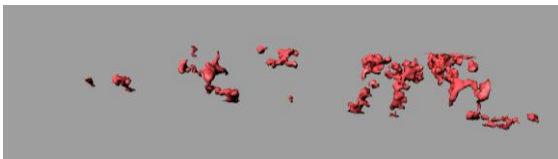
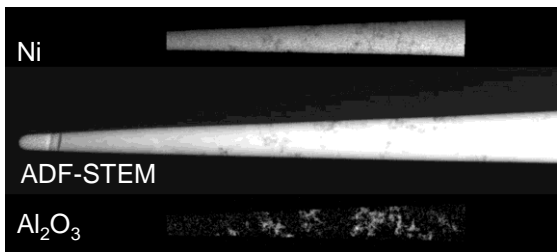
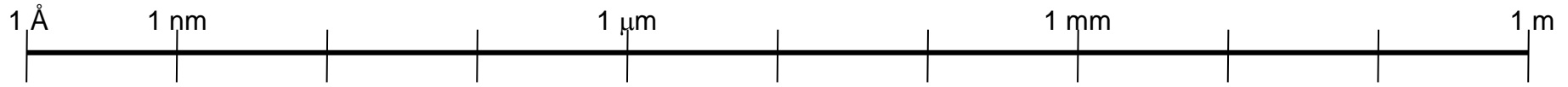
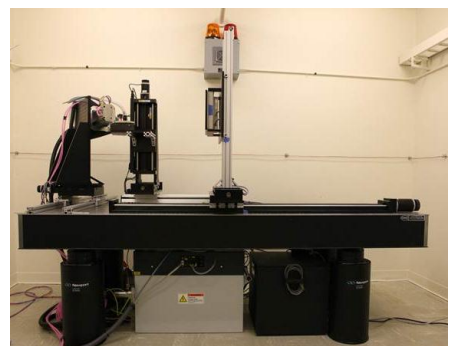
3D EBSD



Robo Met



Computed X-ray Tomography

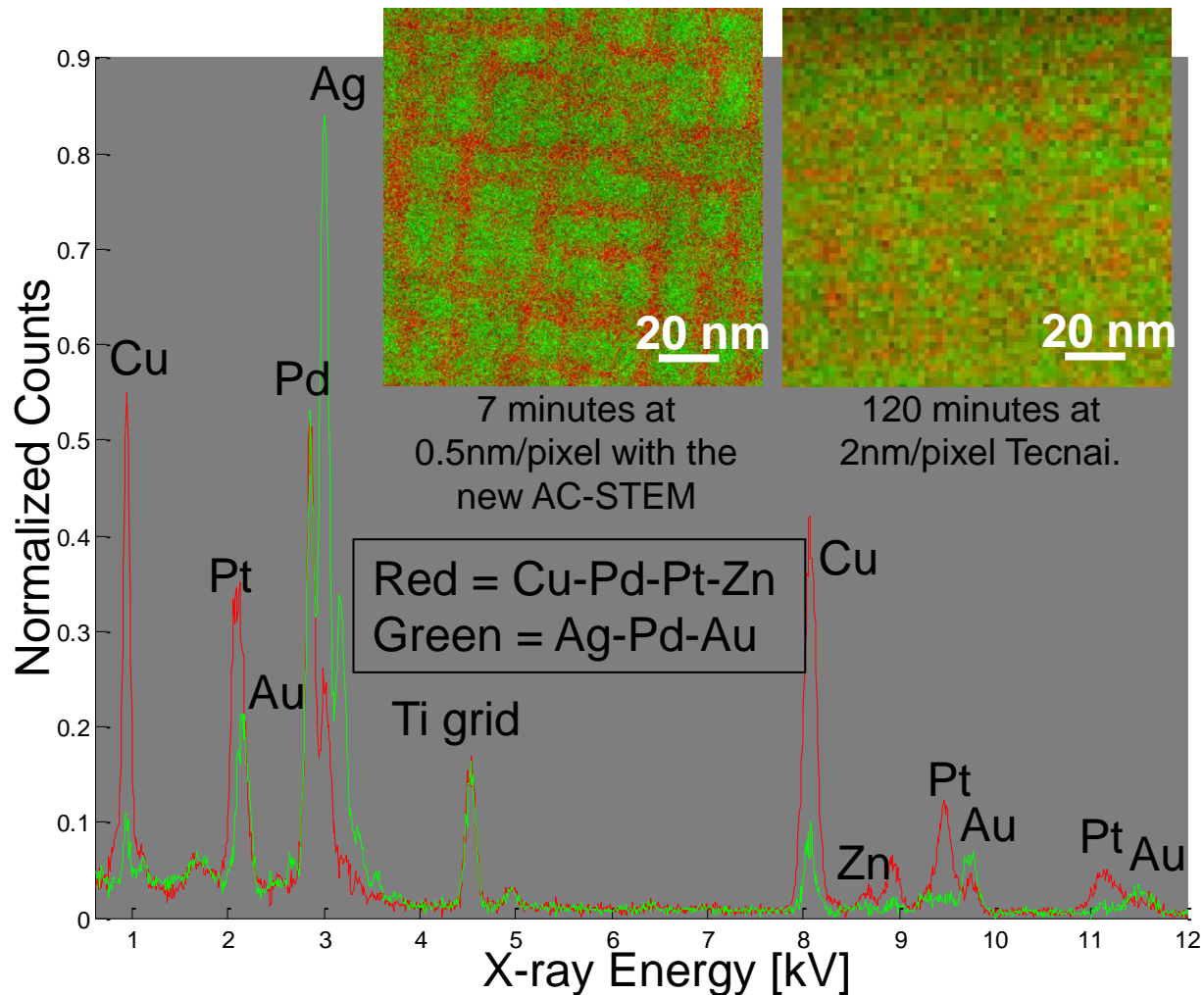
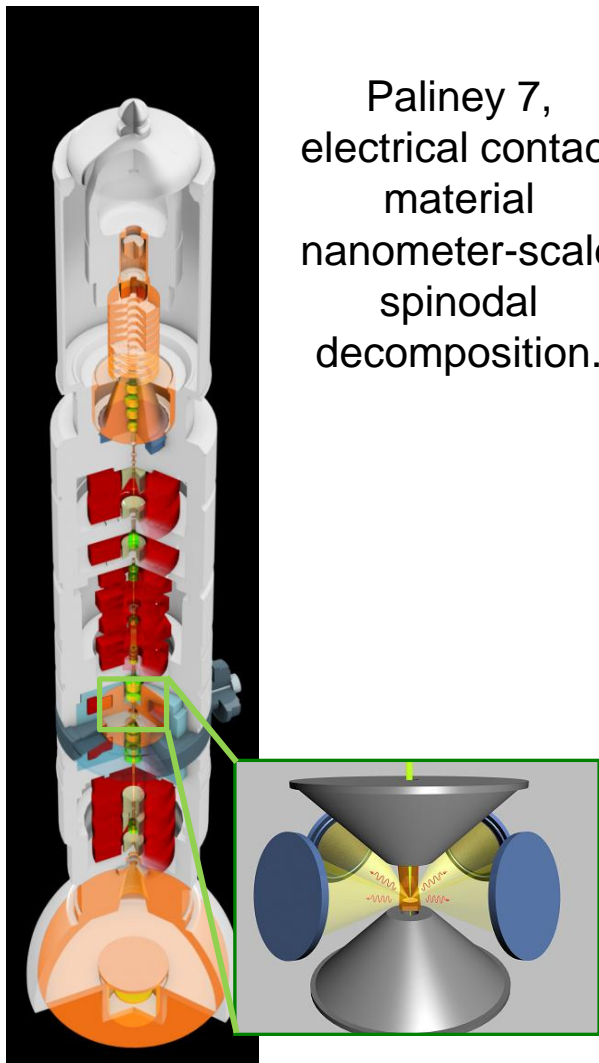


Please see poster "Atomic Geometry of Hydrogen on Aluminum" by Rob Kolasinski

3D characterization provides insight previously inferred

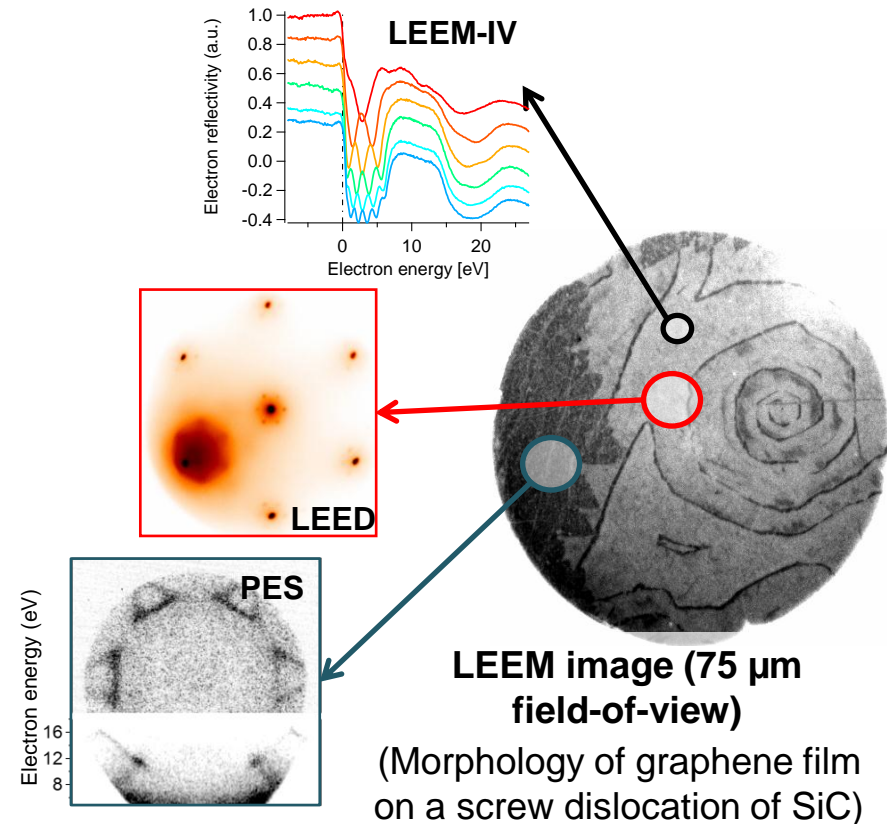
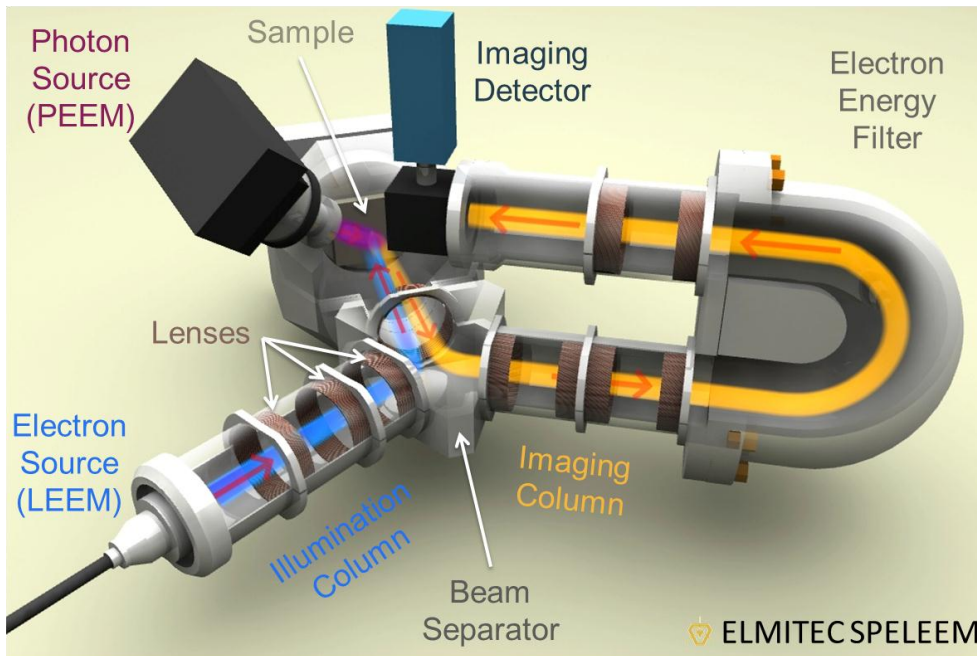
Detailed Chemical Characterization of Nanostructures

Paliney 7,
electrical contact
material
nanometer-scale
spinodal
decomposition.



The analytical power of the AC-STEM is at least 70x better than the older analytical microscope at Sandia. AC-STEM permits confirmation of a 1970s prediction.

In situ Low-Energy and Photoemission Electron Microscopy Provides Local Insight

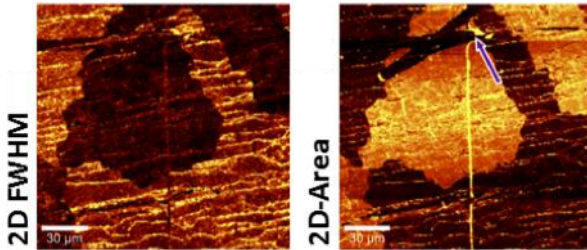


Real-time study of 2D Graphene.

- Covering wide length-scale (10nm to 100 μ m)
- Atomic-scale vertical sensitivity
- Locates and characterizes dislocations/defects
- Determines atomic structures
- Low energy electron diffraction (LEED)
- Characterizes electronic properties
- Determines unoccupied states using electron reflectivity measurement (LEEM-IV)
- Identifies occupied states using photoemission spectroscopy (PES)

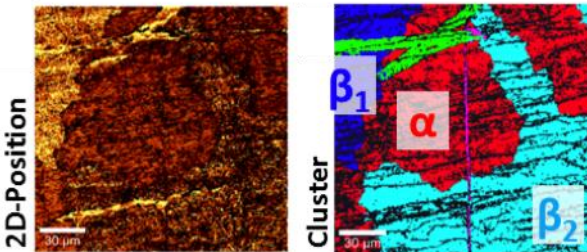
What Added Insight is Gained into Graphene Optical Properties with Combined Techniques?

Raman Imaging



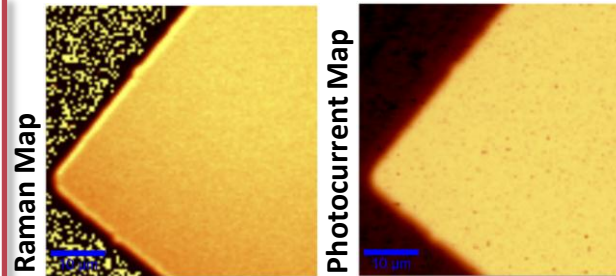
Capabilities:

- Quantify strain
- Quantify doping
- Assess defects



How does material state link to device performance?

Photocurrent



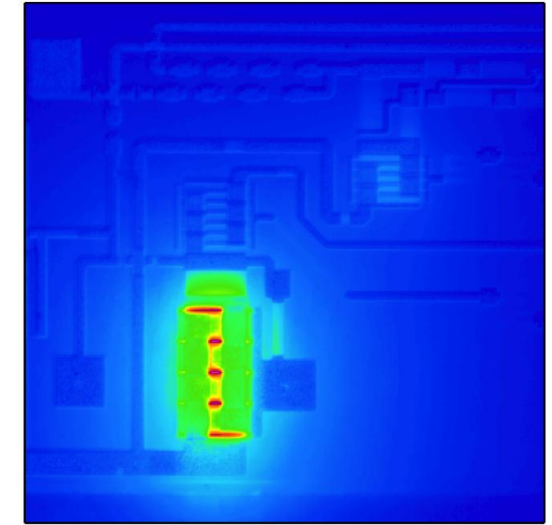
Capabilities:

- Image band bending
- Spatially resolve response
- Identify physical mechanism

Performed concurrently with Raman to link material state with performance

What mechanism is the origin of photoresponse?

IR Thermography



Capabilities:

- Temperature mapping

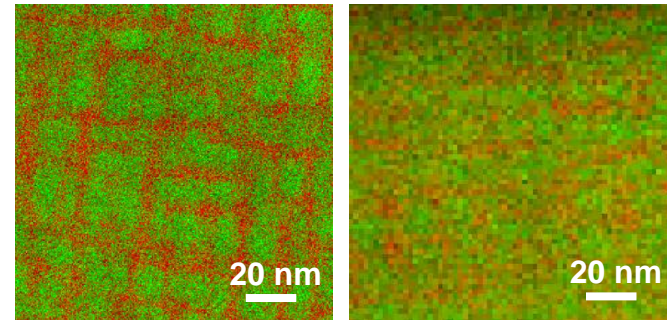
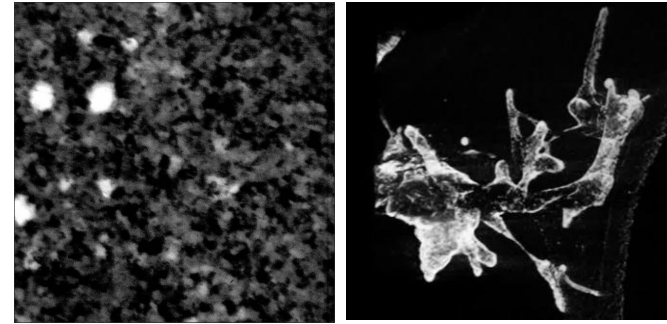
How does temperature impact performance?

Please see poster "Bilayer Graphene: Leveraging Materials Science for Mission Impact" by Thomas Beechem

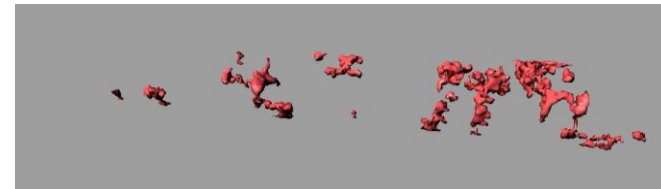
Combine Raman, IR, and photocurrent imaging to elucidate and leverage physics of adaptable graphene photodetectors.

Summary & Impact

- Sandia's I³TEM is one of only two facilities in the U.S.
- I³TEM aides in elucidating important nanoscale mechanisms
- Provides a direct real time capability to evaluate a variety of extreme and combination of environments
- AEM is undergoing a renaissance with correctors, SDDs, novel diffraction techniques, and better sources.
 - Quantitative analysis pushed to smaller volumes
 - Three decade old theories of NW components can now be proven
- Advanced microscopy can correlate properties to structures
 - Chemical distribution and active lithiation/delithiation mechanisms have been correlated to Li-ion battery performance
- Practical computed tomography is possible from nm to cm
 - Both structural and chemical information heterogeneities can be elucidated



Sandia has a suite of advanced analytical, 3-D, & *in situ* microscopy techniques to permit interrogation & understanding of material structure & evolution in a broad range of systems & environments



Contributors & Collaborators:

Paul G. Kotula, Ping Lu, Don Susan, Zahra Ghanbari, Jan Ringnald, C. Chan, J. Carroll, J. Madison, M. Rye, J. Michael, J.D. Sugar, F. El Gabaly, Chueh, J. Huang, Y. Liu, J.P. Sullivan, B.L. Doyle, O. El-Atwani, D. Buller, J.A. Scott, B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, J. Sharon, B. L. Boyce, C. Chisholm, H. Bei, E.P. George, P. Hosemann, A.M. Minor, Hysitron Inc., H. Lim, C. Battaile, S.M. Hoppe, D. Sasaki, Protochips, Inc., S. Rajasekhara, N.R. Sorensen, B.G. Clark, D. Gross, J. Kacher, P.J. Cappillino, B.W. Jacobs, G. Kellogg, T. Ohta, B. Diaconescu, L.R. Parent, I. Arslan, T. Beechem, M.A. Hekmaty, D.B. Robinson & I.M. Robertson

Posters in Novel Characterization & Diagnostic Tools & Techniques Thrust:

Presenter	Org.	Poster Title
Thomas Beechem	1114	Bilayer Graphene: Leveraging Materials Science for Mission Impact
Mike Brumbach	1819	HAXPES at the National Synchrotron Light Source and Characterization of Aging in Hard Gold Contacts
Dave Jones	2555	A Novel Pressure Transducer Array Detector (PTAD) as a High-Resolution Diagnostic for Energetics
Rob Kolasinski	8252	Atomic Geometry of Hydrogen on Aluminum

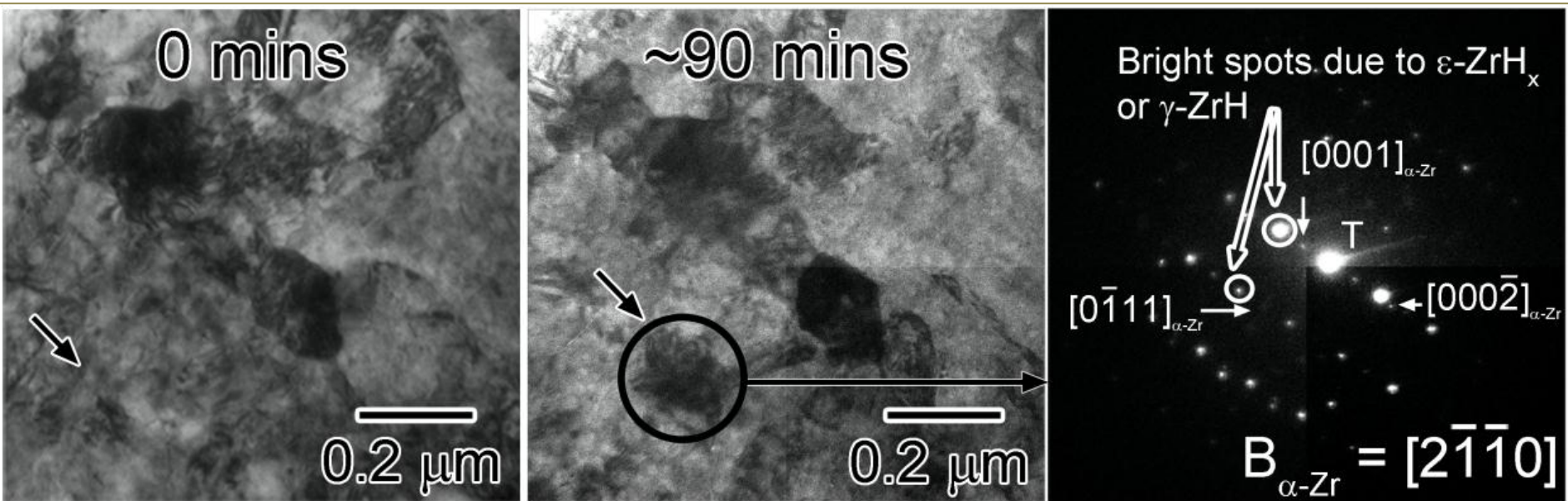
In situ Observation of Hydride Formation in Zirlo

Absolute hydrogen pressure: 327 torr (~ 0.5 atm),

Ramp rate: 1 $^{\circ}\text{C}/\text{s}$

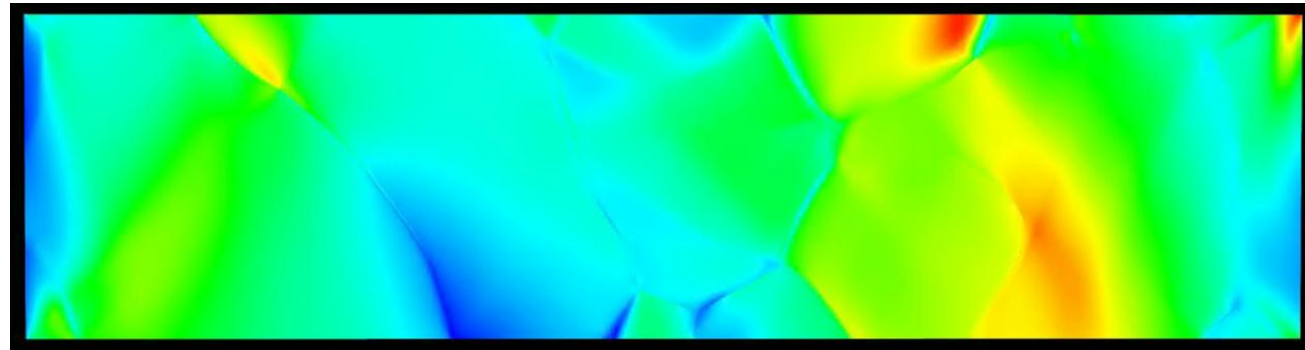
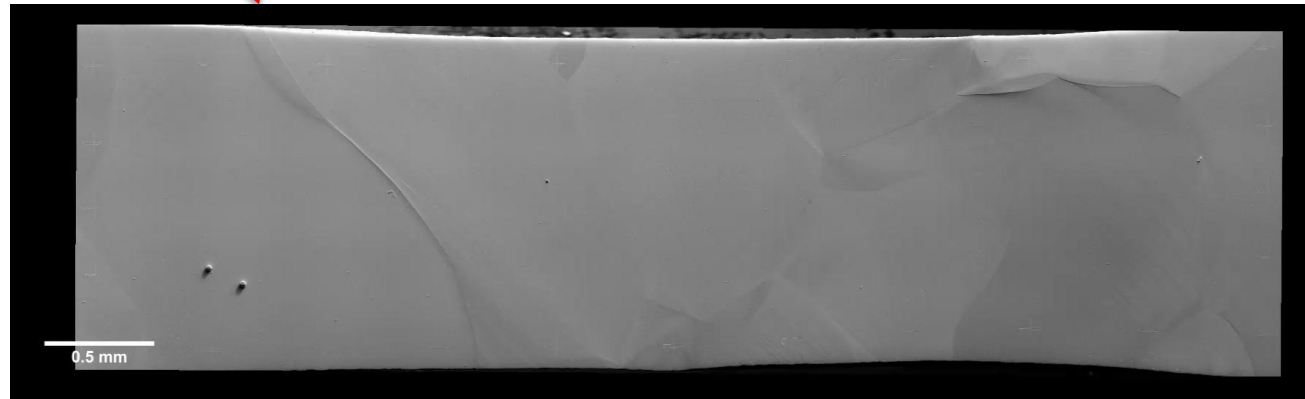
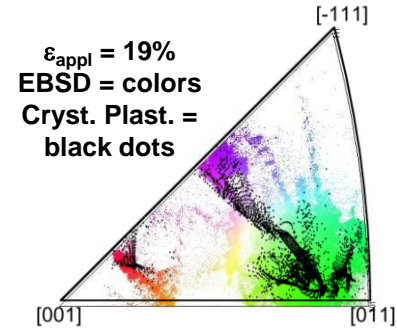
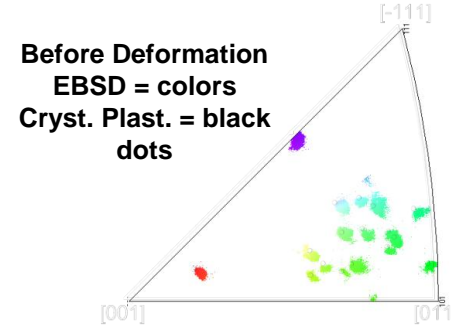
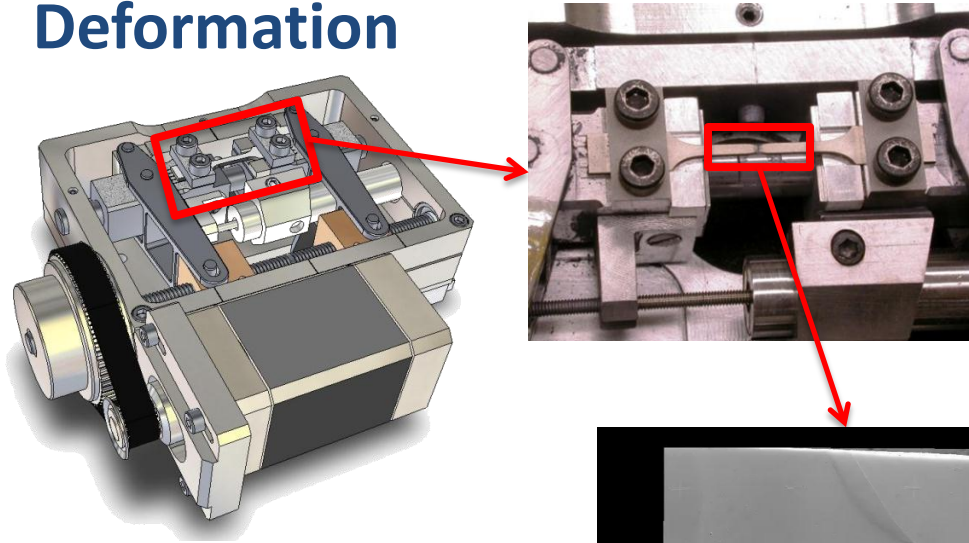
Final temperature: ~ 400 $^{\circ}\text{C}$

Dwell time: ~ 90 mins



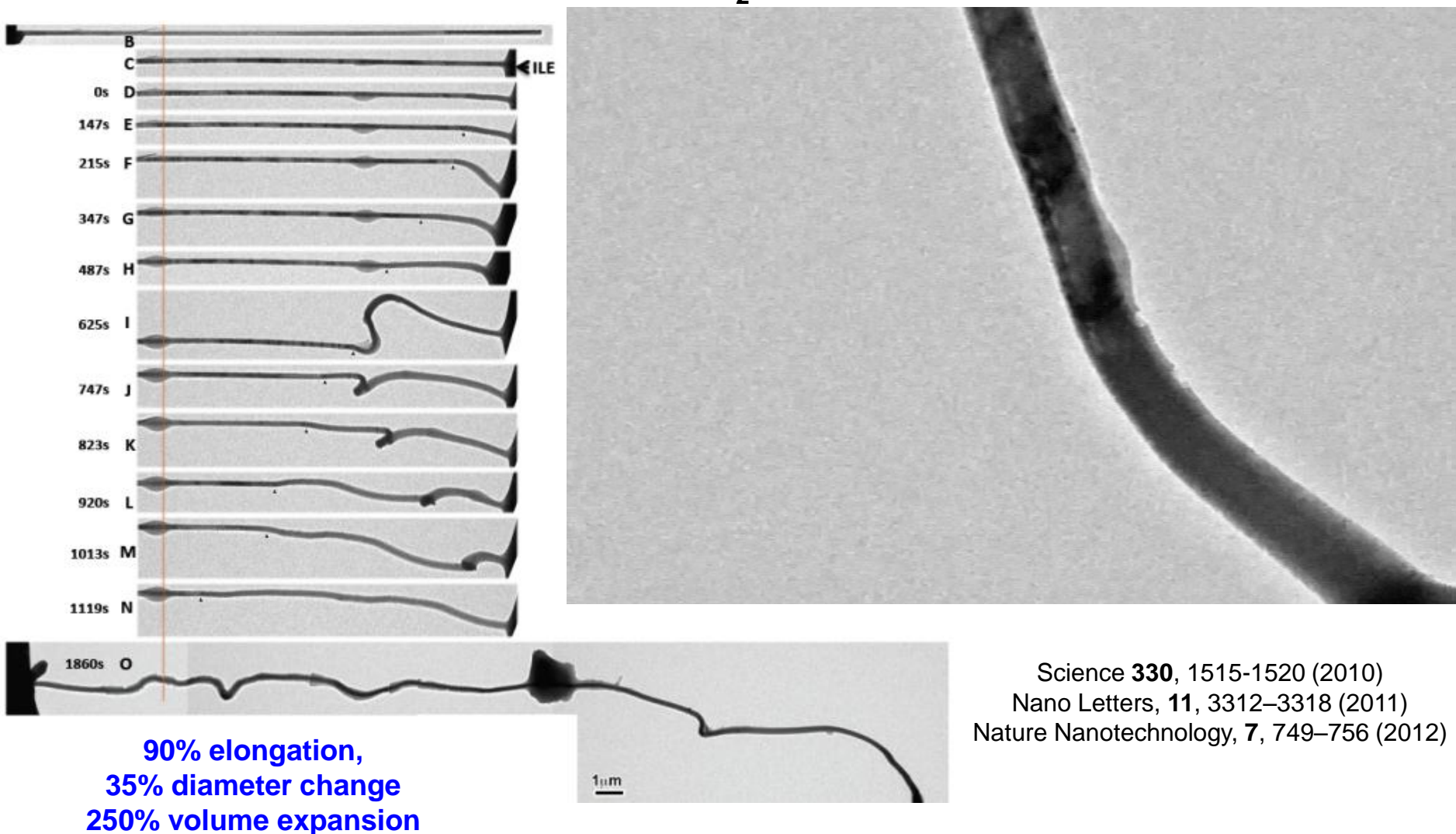
Hydride formation was shown for the first time by use of a novel TEM gas-cell stage at elevated temperature and hydrogen pressure

In situ SEM Loadframe Allows Direct Observation of Local Deformation

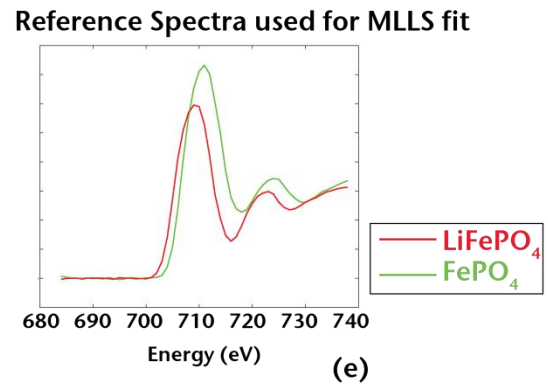
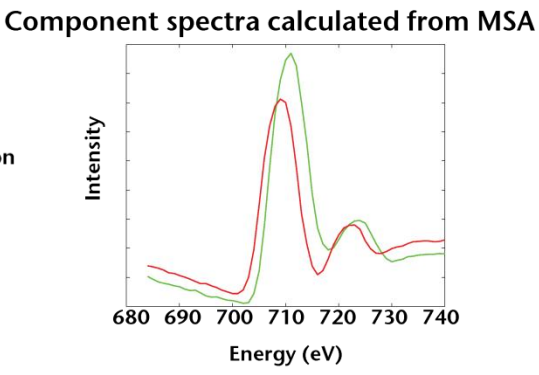
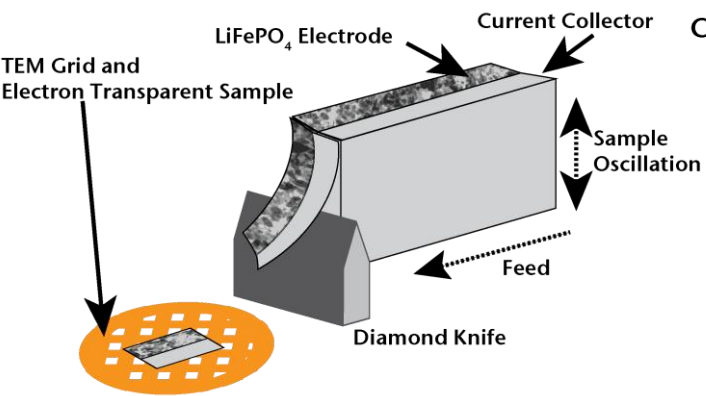
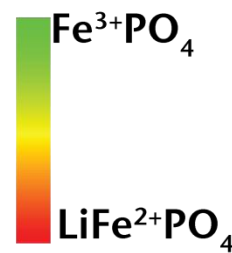
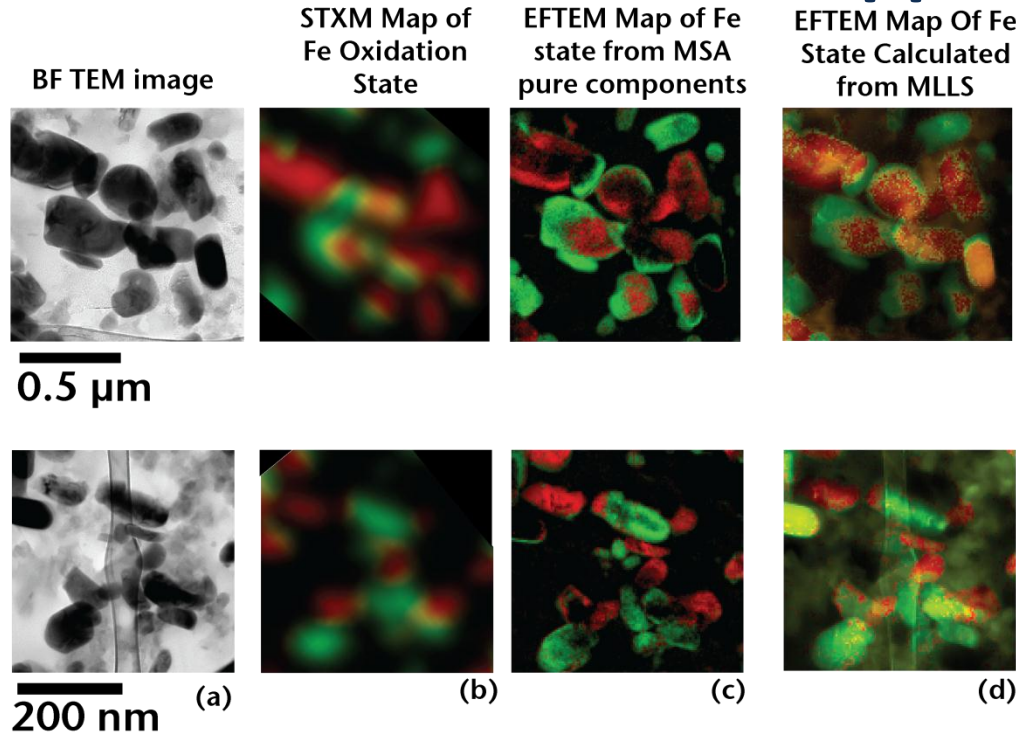
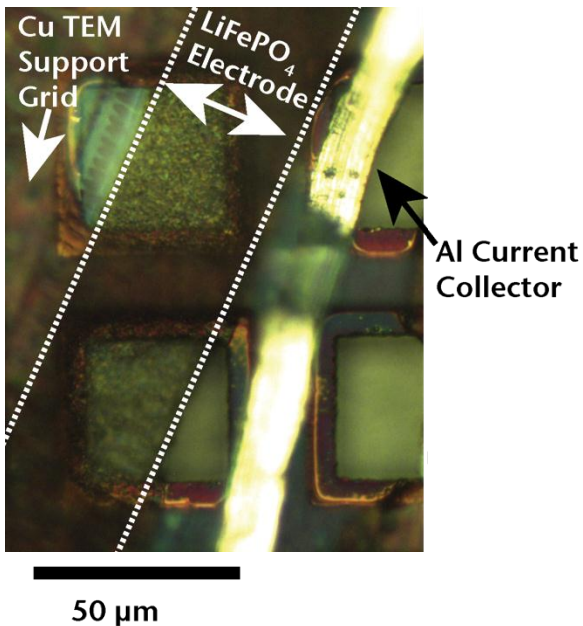


In situ SEM loading provides quantitative observation of failure processes to inform a microstructural-scale failure criterion

Lithiation of SnO₂ Nanowire

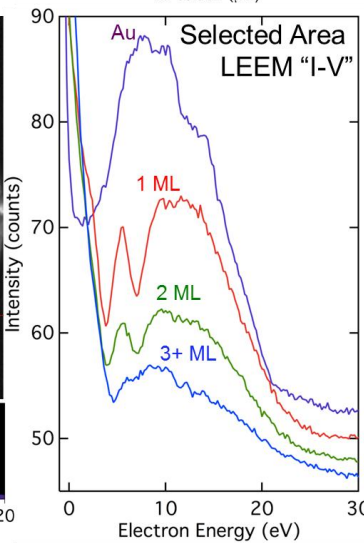
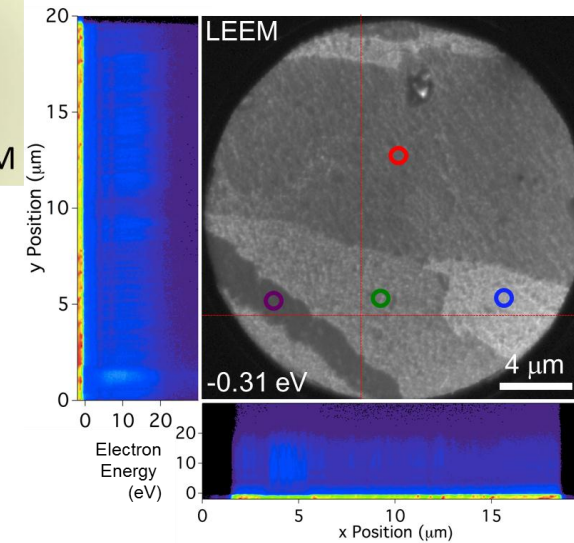
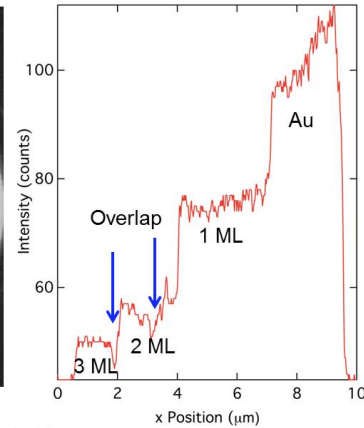
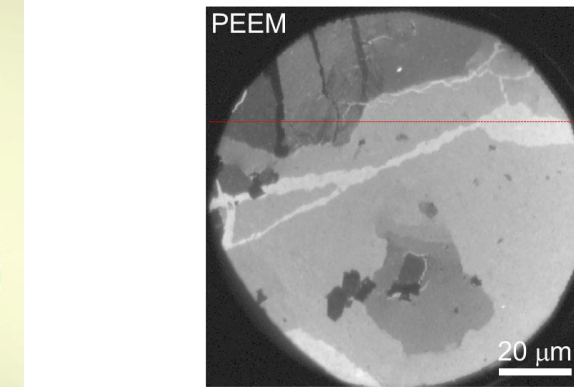
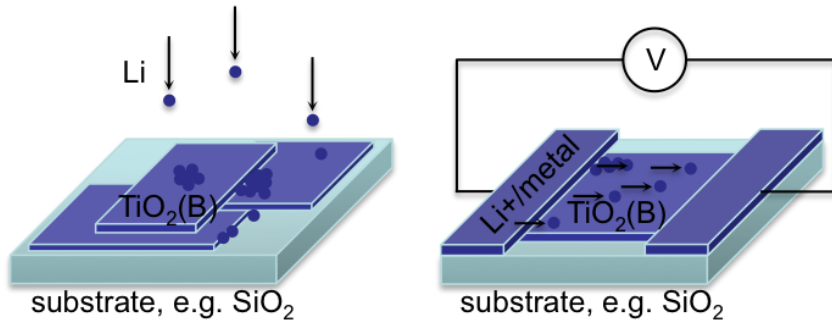
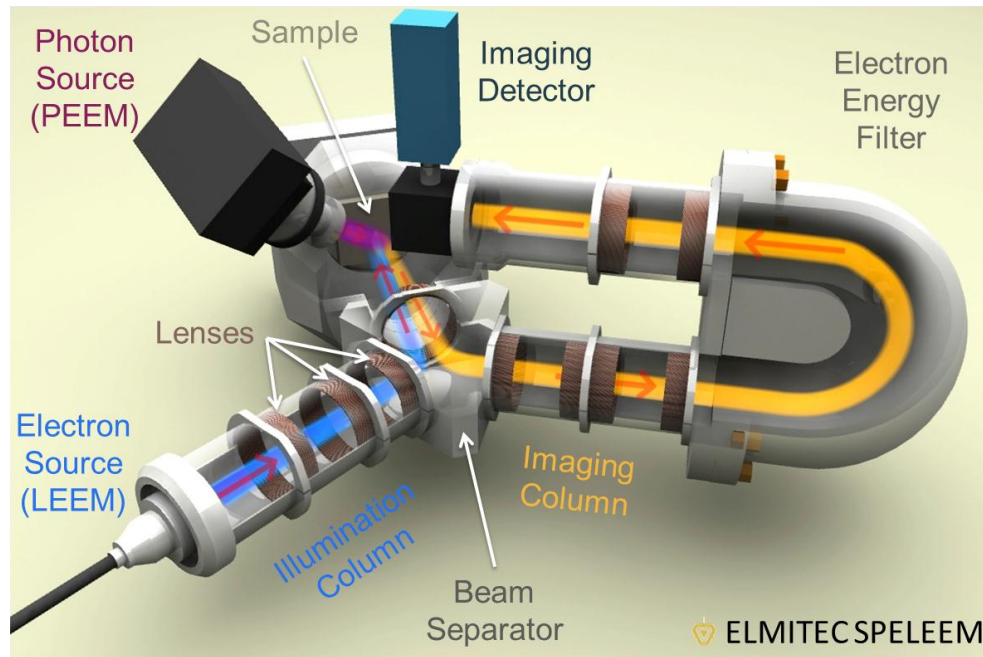


Combining TEM and STXM Chemical Mapping



These images compare the spatial and depth resolution of the techniques.

In situ Low-Energy and Photoemission Electron Microscopy



Real-time study of lithiation and delithiation processes on/in TiO₂.