SAND2011-2871C

New Ion Beam Lab: Capabilities Applicable to MOFs

Current and Potential Research Directions

April 8, 2011

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2009-2801P

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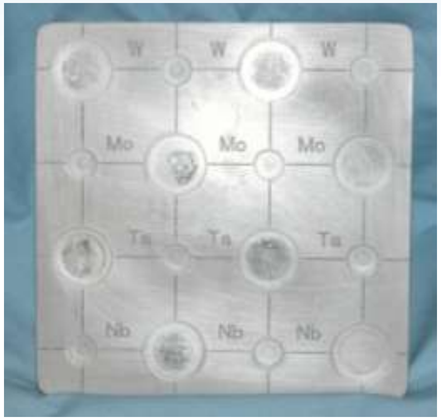
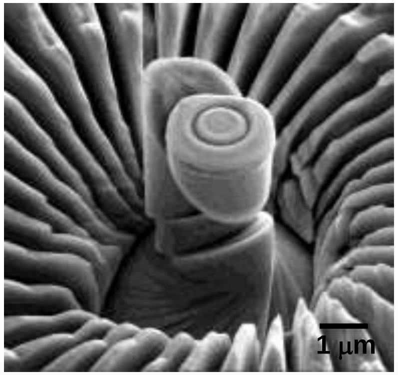
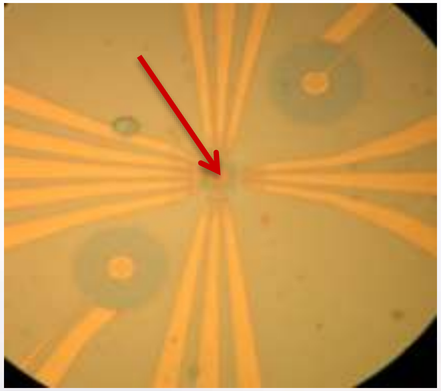
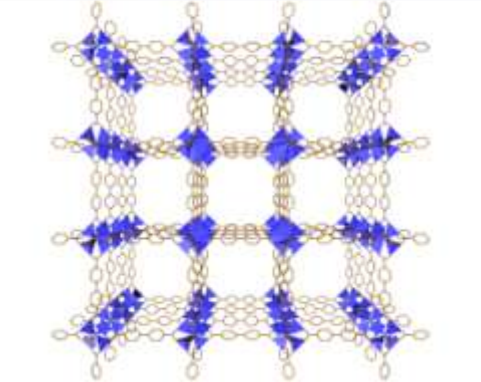
Outline

1. **Versatile Capabilities Available at the New Ion Beam Lab**
   - Micro-ONE
     - Nuclear Cladding Materials
     - Scintillators
   - In-situ Ion Irradiation TEM
   - Nanoimplanter
2. **Future Directions for Advance Scintillator Characterization**









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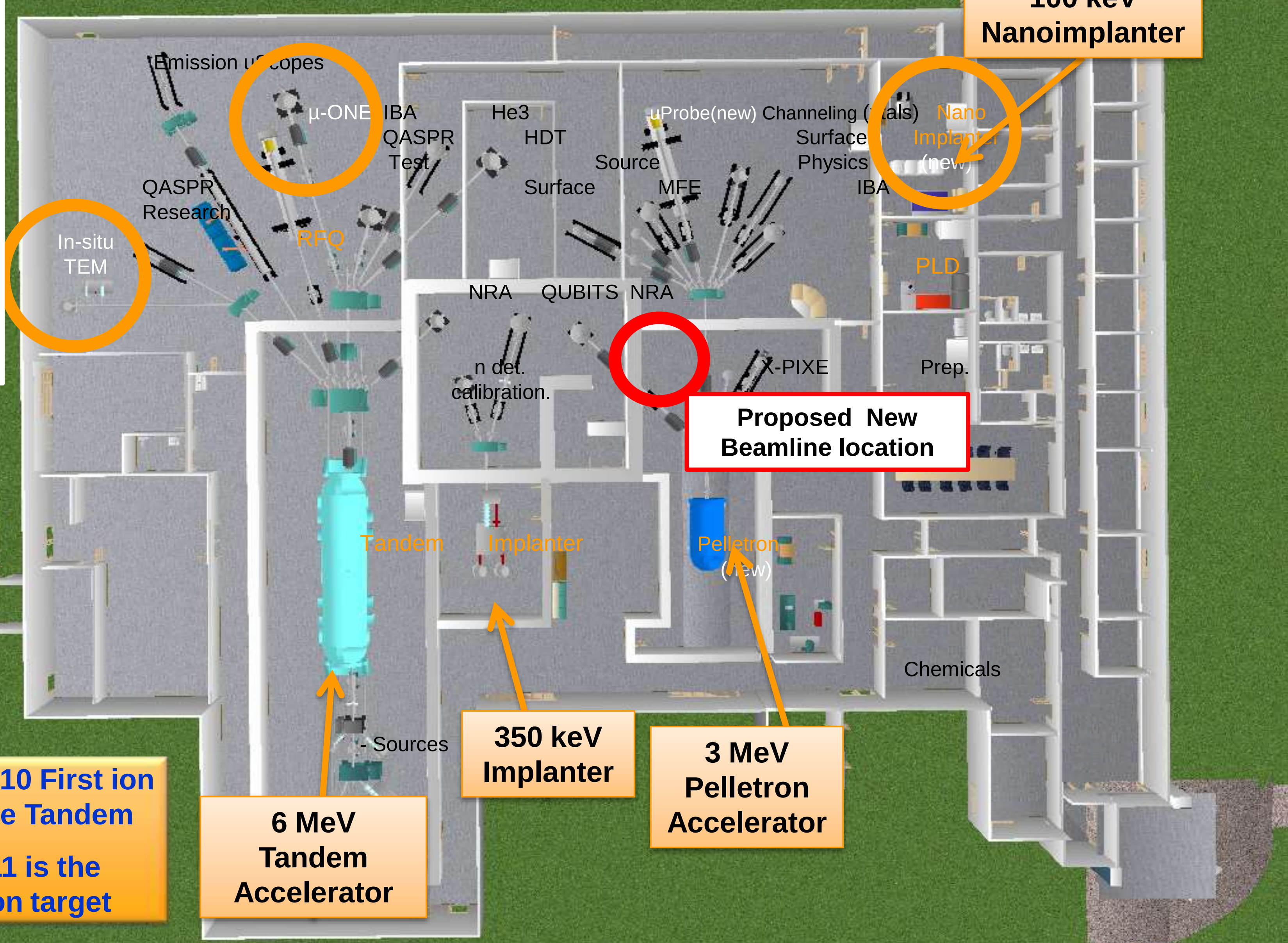
New Ion Beam Laboratory

New Facility
laboratory space
1850 m^2
office space
650 m^2
Old Facility:
1300 m^2 total

Building: $20M
Equipment: $11M
Total: $40M



June 15th, 2010 First ion beam on the Tandem

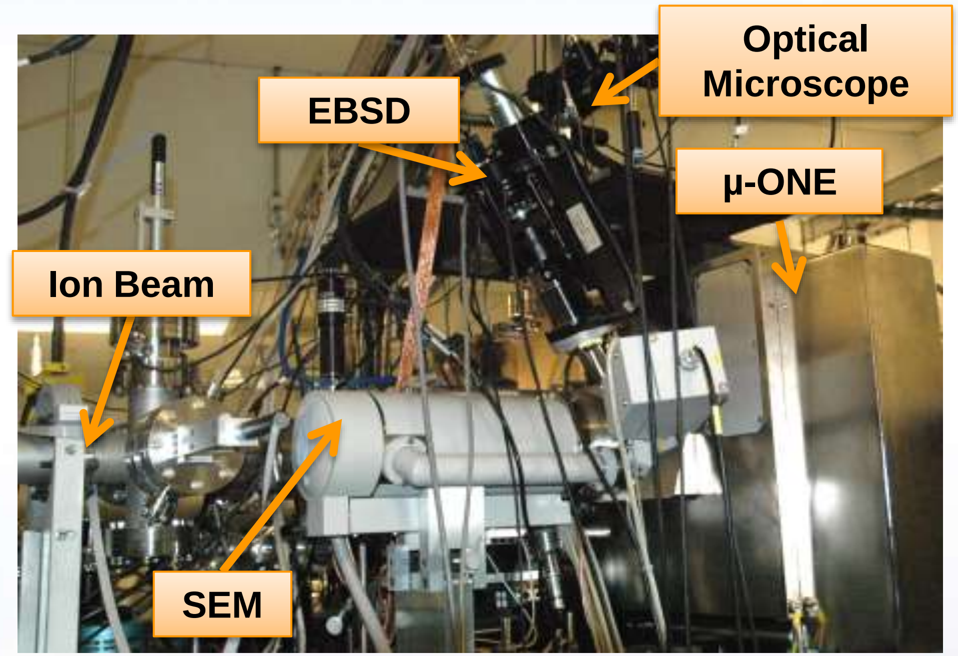
June 2011 is the completion target

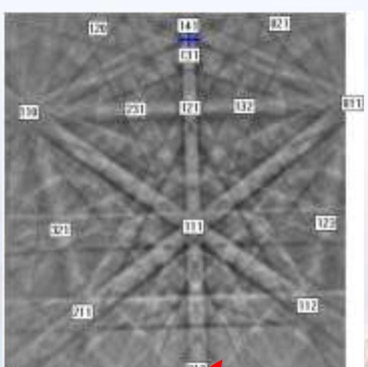
Micro-ONE Capabilities

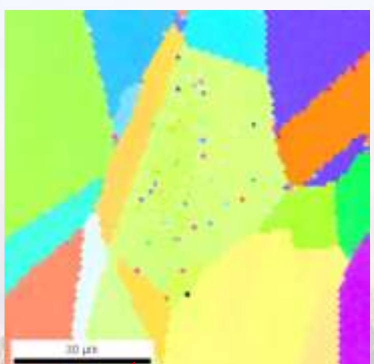
Micro-ONE = Micrometer resolution Optical, Nuclear, and Electron Microscope

Micro-ONE capabilities

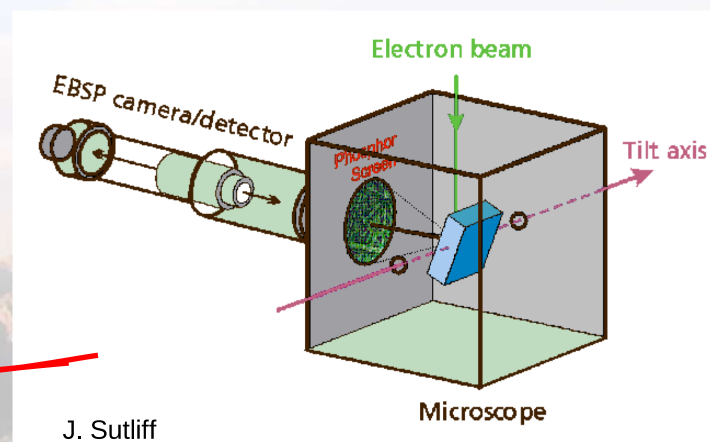
- Beam size: < 1µm (~ 0.5 µm)
- Current: single ions to 10,000 ions/s
- Ions: H, He, heavy ions
- Energy: (q+1)*6 MeV for heavy ions
- Scan size: ~ 100x100 μm^2
- Stage position with 50 nm resolution
- Fast blanking capabilities
- Navigation based on GDS II files
- IBIC and TRIBIC capabilities
- EBSD mapping







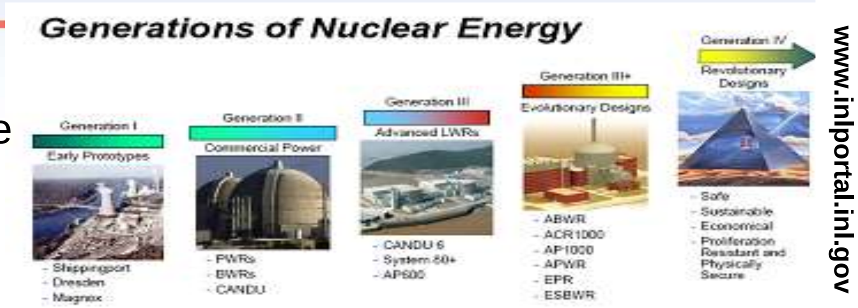
First EBSD Pattern and Map obtained with this system

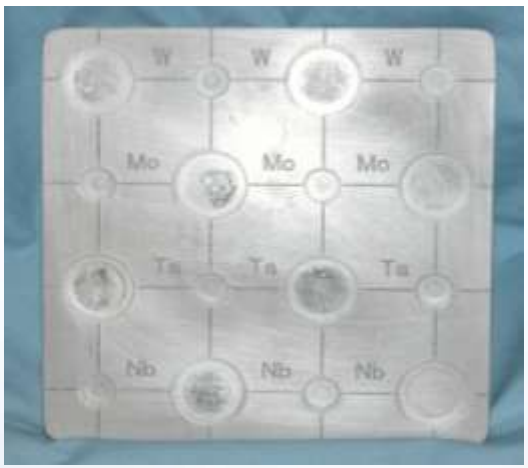


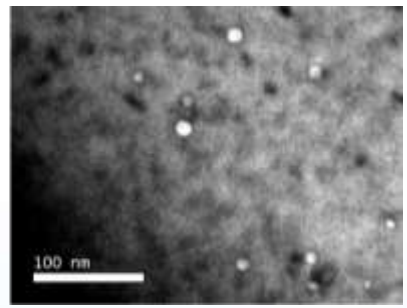
Will allows parallel imaging of changes in microstructure: grain size, phase transformations.

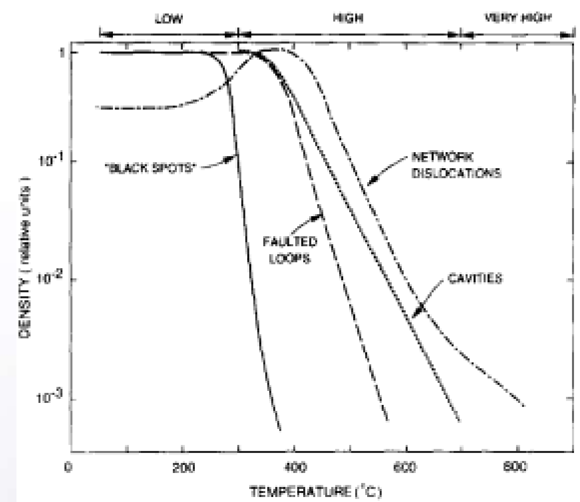
Sandia's Approach to Rapid Material Validation for Advanced Materials Necessary for New Reactors

- Advanced Materials are Needed
- Several Theories exist for the desired microstructure
- New materials have been made
- Current Neutron fluxes require decades for testing









Microstructural Characterization (XTEM)

Mechanical Properties (small-scale testing)

Local Composition (Diffusion Couples) + Local Microstructural Control (Ion Irradiation)

Validating Comparison to Neutron Irradiation Experiments + Investigation into new materials

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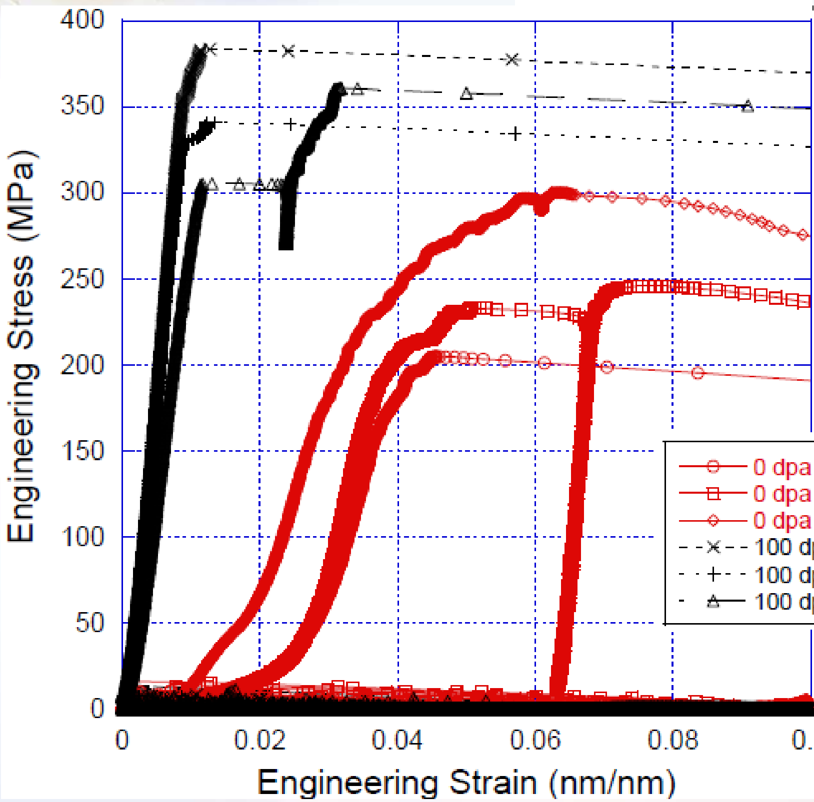
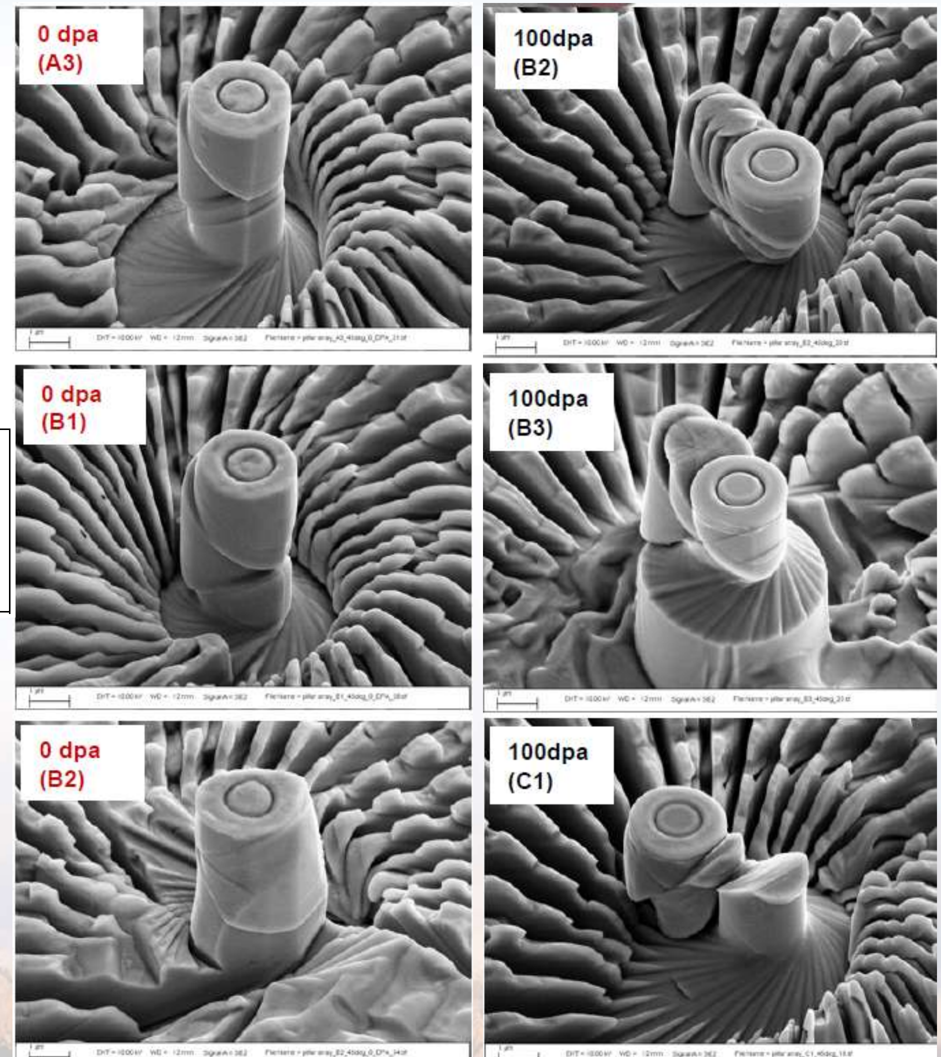
Micropillar Compression of Irradiated Cu





Increased strength and decreased ductility is seen in the Irradiated pillars

Collaboration with Brad Boyce

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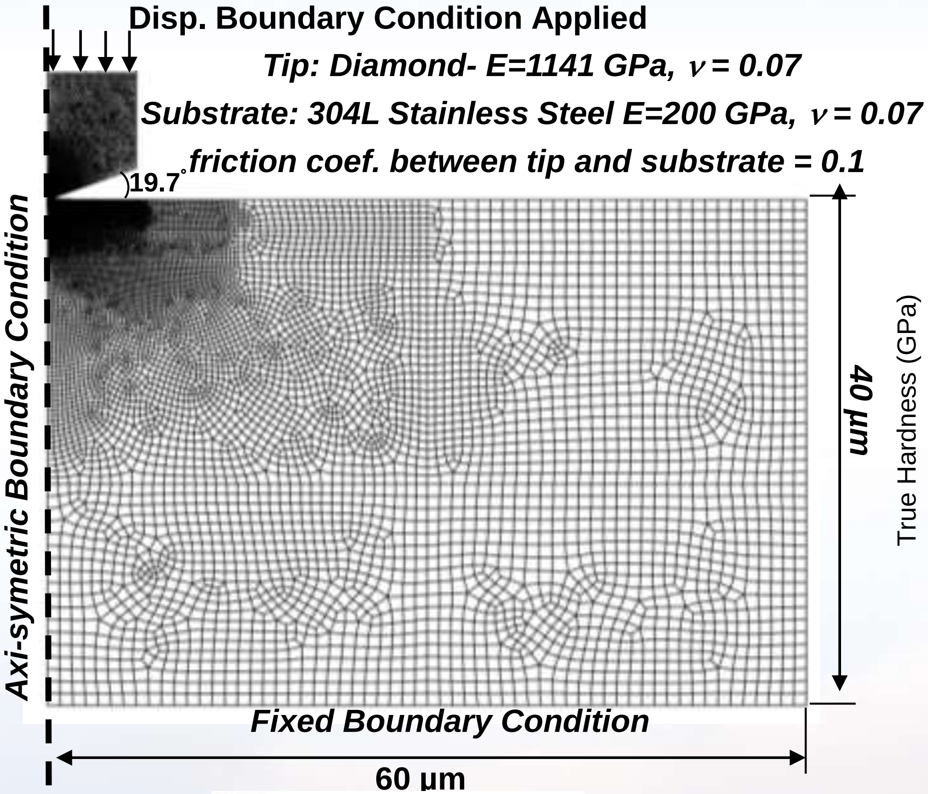
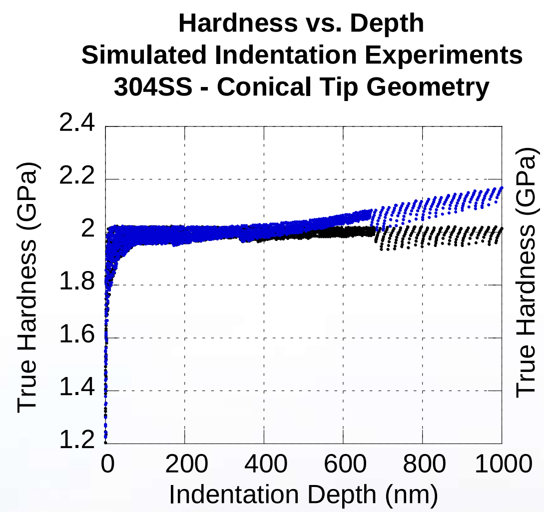
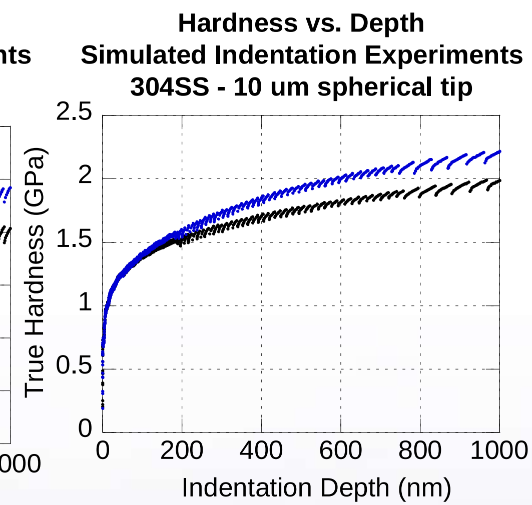
Finite Element Simulations of Indentations into Ion Irradiated Steels

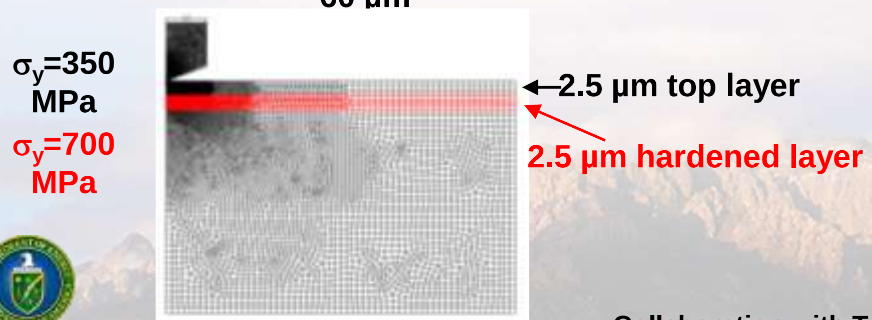






Without hardened subsurface layer

With hardened subsurface layer



Deviations due to ion irradiation are expected from both spherical and conical indentations

Collaboration with Tom Buchheit

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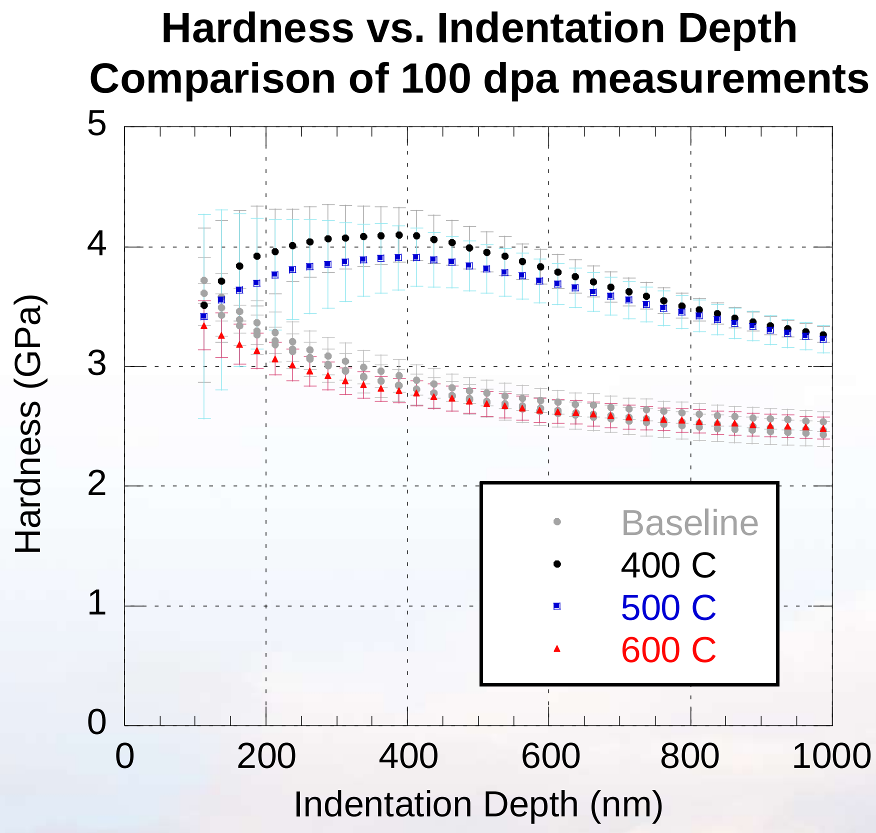
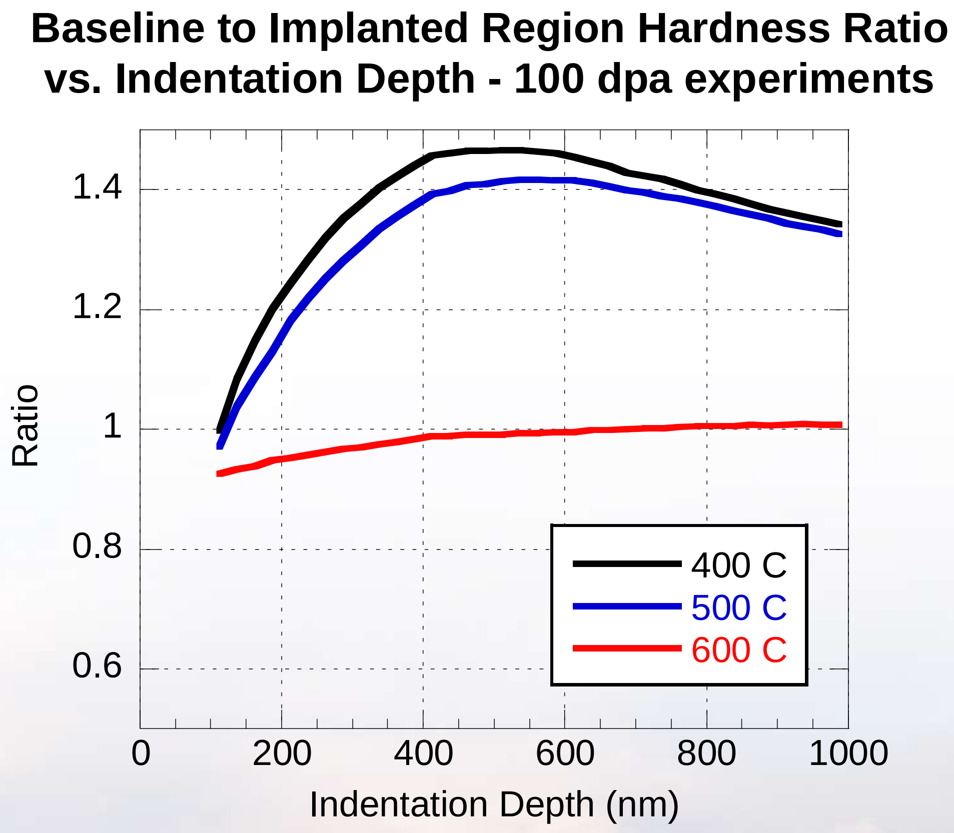
Berkovich Indentation of 100 dpa Irradiated Samples



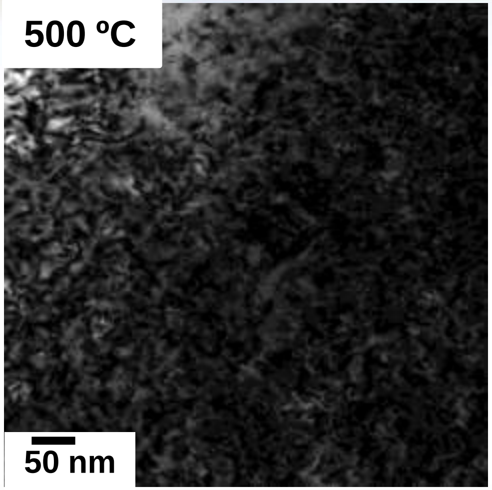


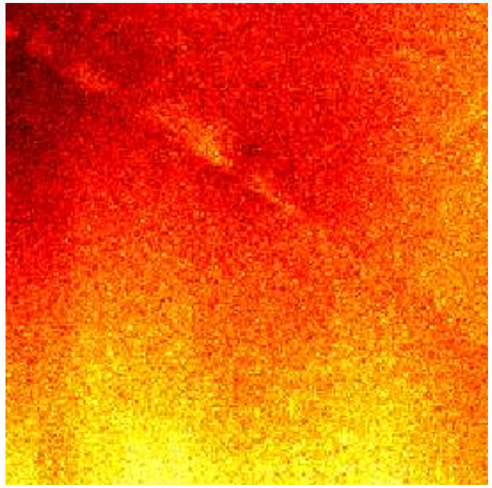
At 100 dpa, the hardness difference between 400 ºC and 500 ºC sample and the control microstructure has increased.

Collaboration with Tom Buchheit

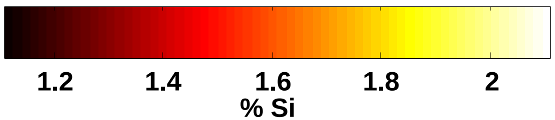
Microstructural Evolution between 500 ºC and 600 ºC

316L Stainless Steel: 100dpa, 20 MeV Nickel Ions

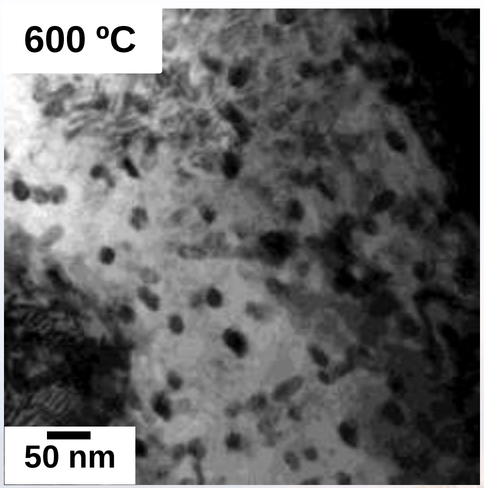


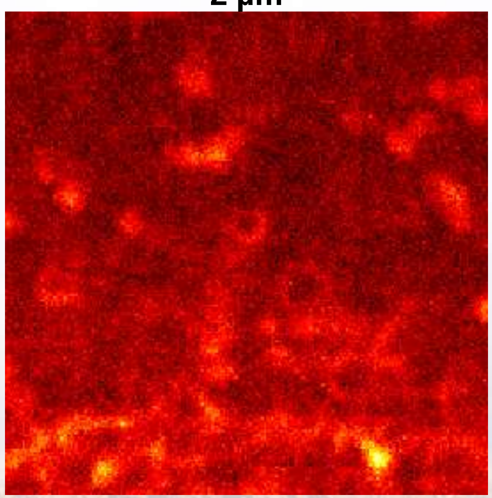


2 µm

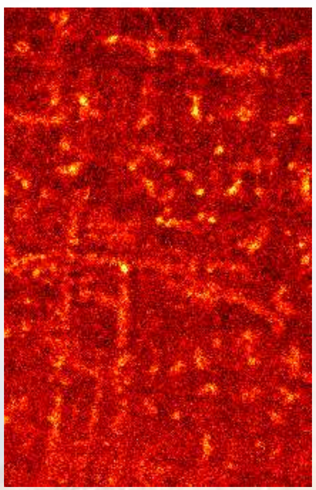


- Large number of small defects present in the irradiated region
- No significant segregation of either the Ni or Si constituents



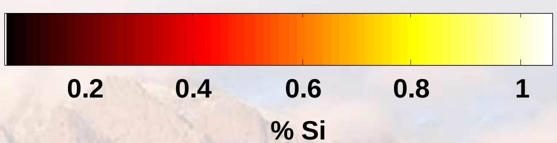


500 nm



1µm x 2µm

- Voids are formed and are self-ordered
- Significant segregation of either the Ni or Si constituents



Ni and Si rich regions appear to self-organize and sometimes surround voids at 600 °C, but not 500 °C

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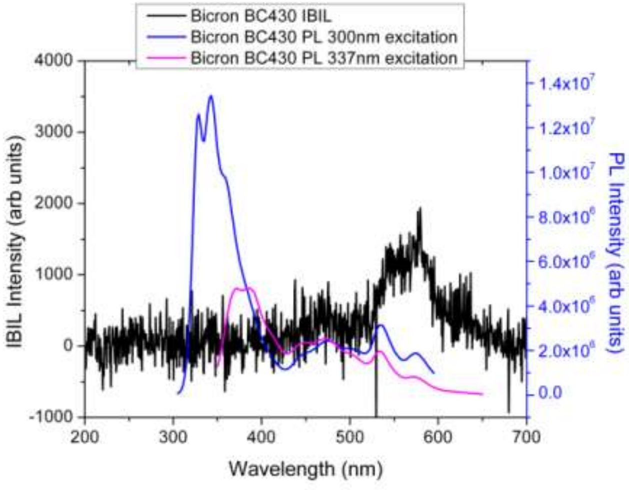
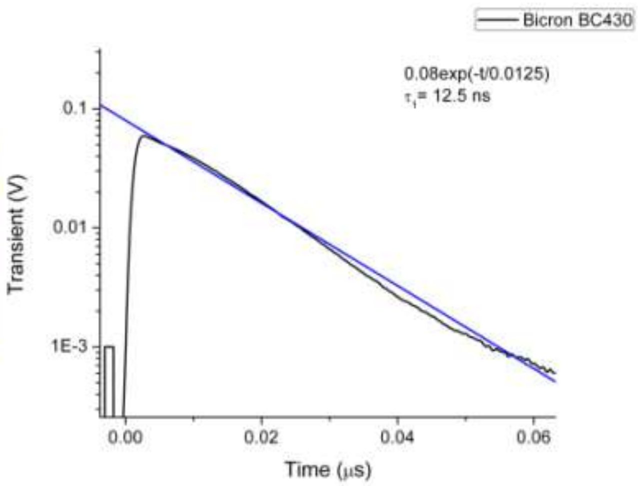
IBL Current Capabilities for Ion Beam Induced Luminescence Studies

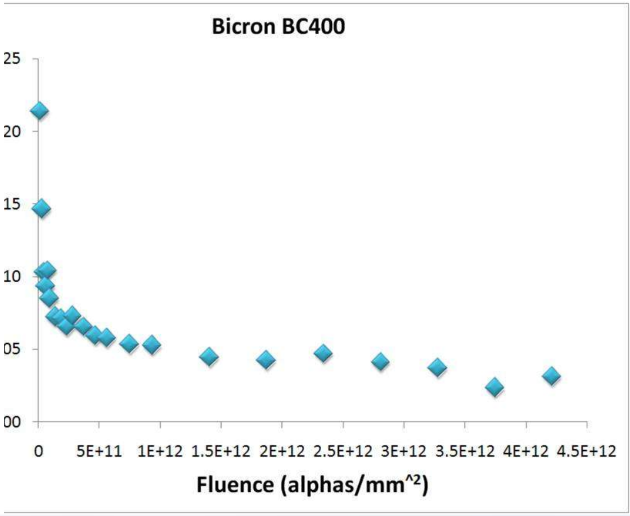
Spectrometry



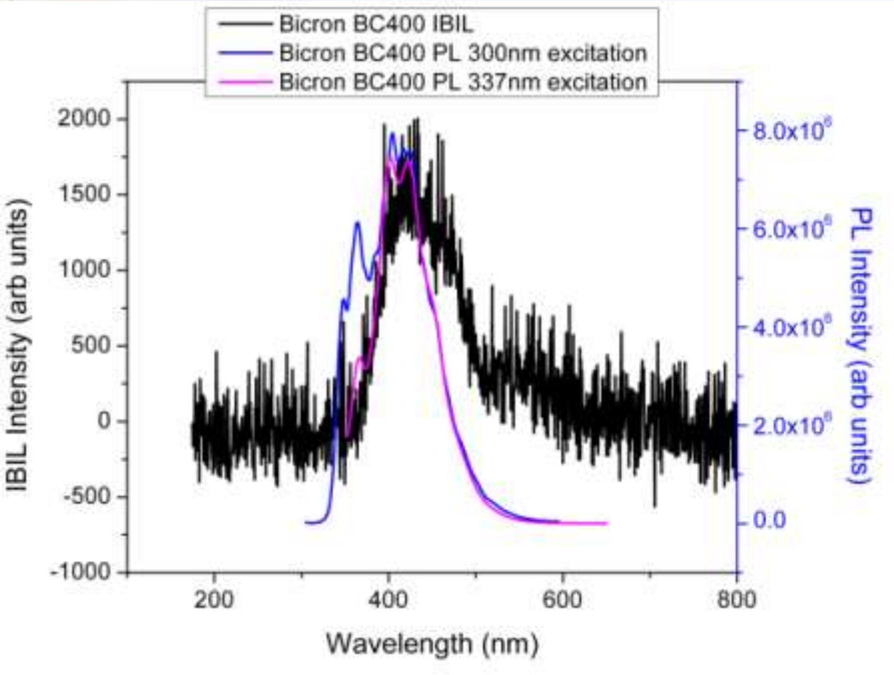
Decay Time

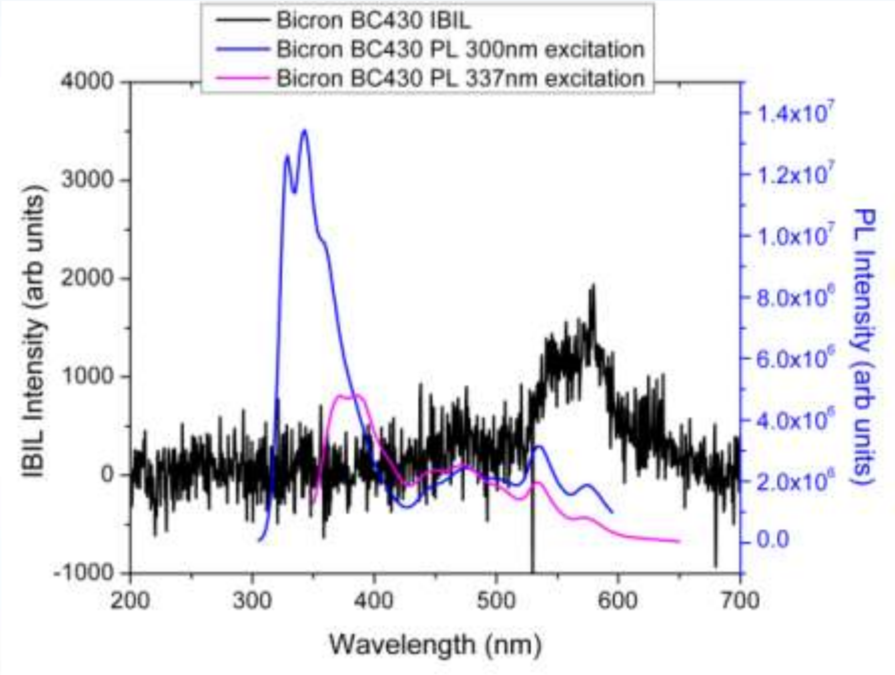


Radiation Hardness



Spectroscopy of a Model System: Bicron

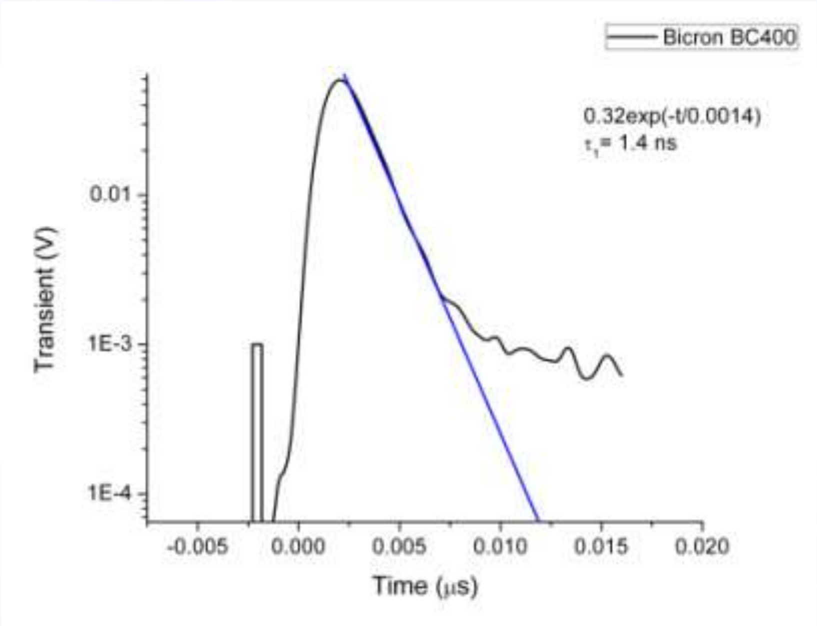


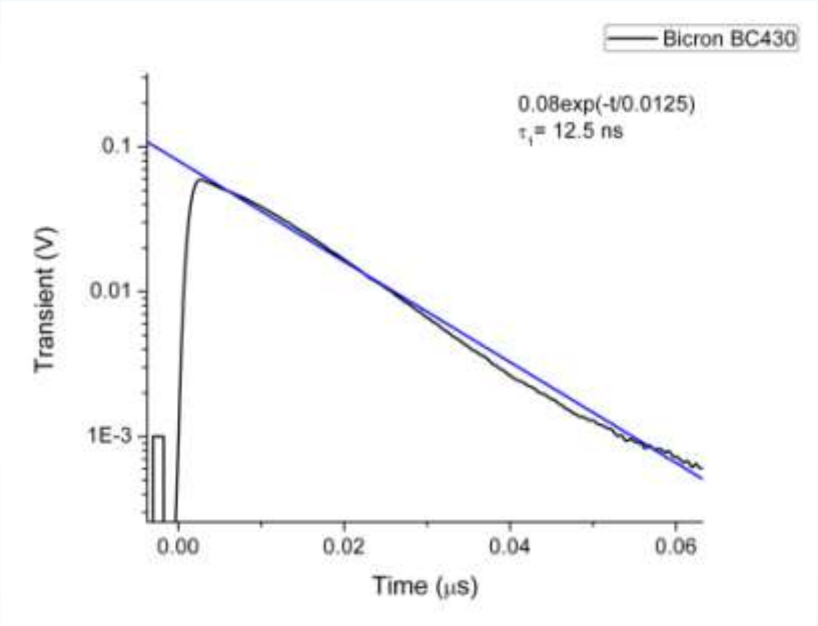


- **BC400 is a blue-emitting organic scintillator**
- **Excitation wavelength can affect emission spectrum**
- ***Disadvantage: E*****mission wavelengths will overlap air luminescence**

- **BC430 is marketed as a red-emitting organic scintillator**
- **With PL, see very intense UV emission**
- ***Advantage:* Red emission could be useful - avoid air luminescence**

Decay Time of a Model System: Bicron

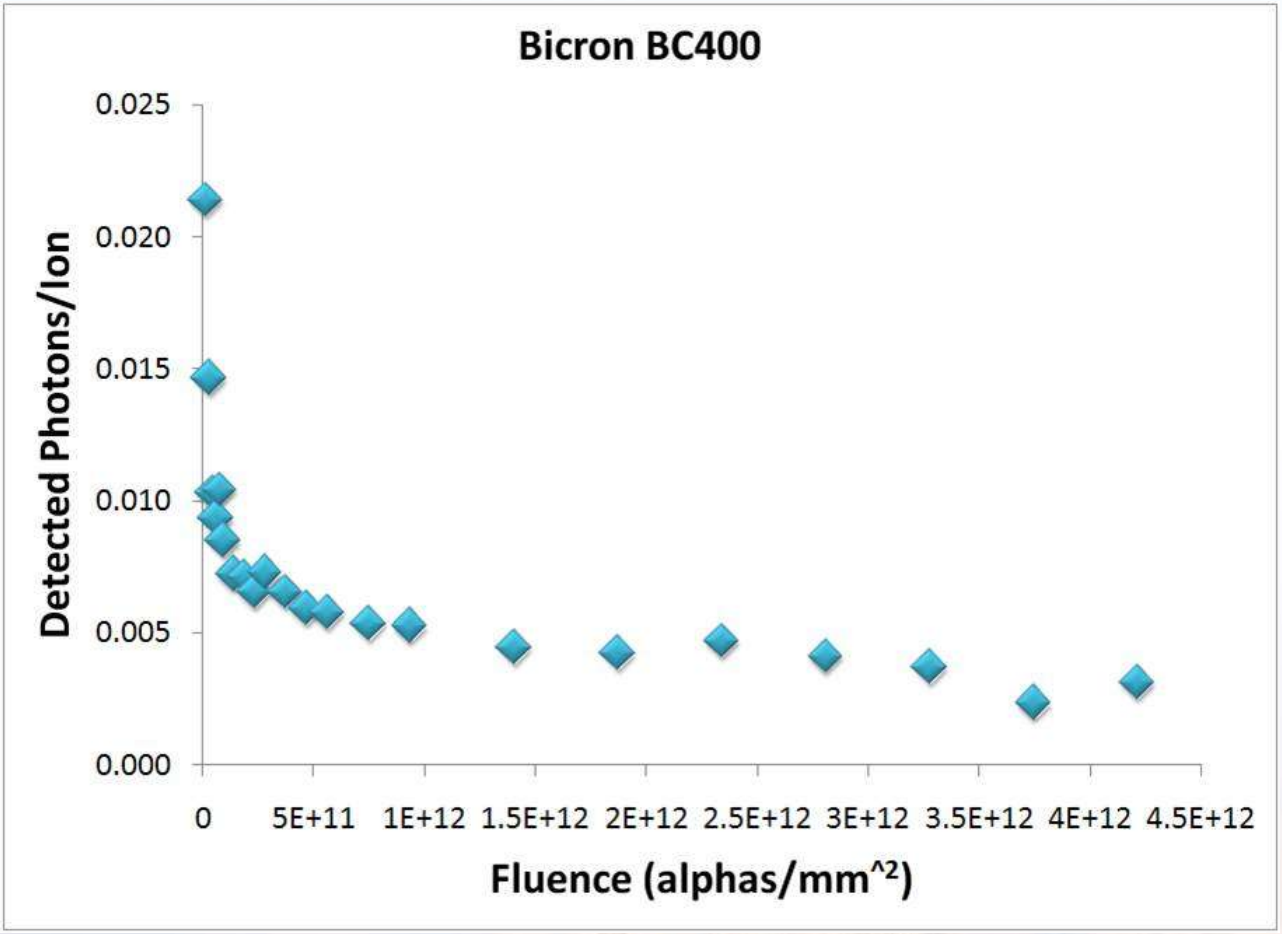




- ***Advantage:*** **BC400 has a very fast decay time**
- **Reported : 2.4 ns**

- ***Advantage:*** **BC430 also has a very fast decay**
- **Reported : 16.8 ns**

Radiation Damage in a Model System: Bicron



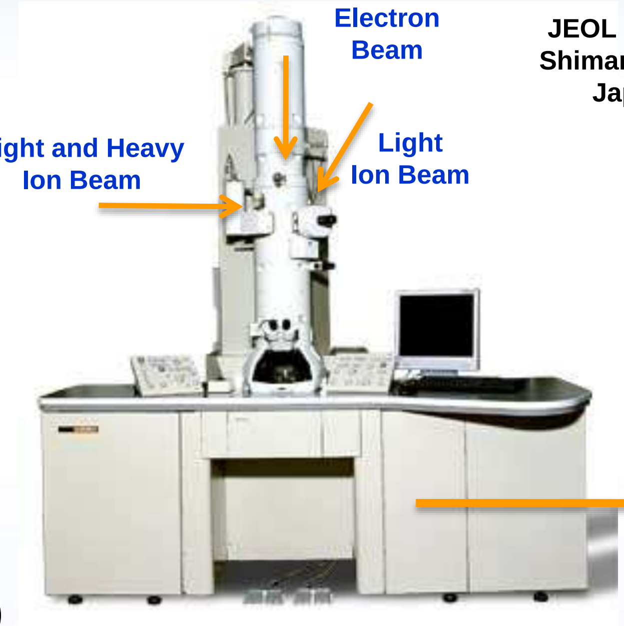
- ***Disadvantage:*** BC400 and BC430 both demonstrate high sensitivity to radiation damage

Bicron exhibits very low photons per ion ratio and significant radiation damage

In situ Ion Irradiation TEM

Proposed Capabilities

- 200 kV LaB_6 TEM
- Ion beams considered:
  - Any Ion produced by the Tandem
  - 250 keV D^{2+}
  - 250 keV He^{+}
  - All beams will hit same location
- *In situ* vapor phase stage
- *In situ* liquid mixing stage
- Tomography
- Nanosecond time resolution (DTEM)
- Procession scanning (EBSD in TEM)
- *In situ* PL, CL, and IBIL
- *In situ* heating and cooling stage
- *In situ* electrical measurement stage
- *In situ* straining stage

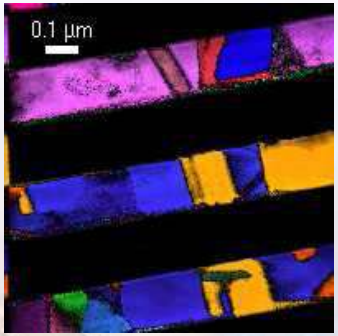


JEOL 2010 at Shimane Univ. Japan

1 in the US (ANL)
11 world-wide

TVIPS

Hummingbird



Nanomegas

We are at the beginning stages of planning. Many potential additions for an *in situ* triple beam facility are being considered

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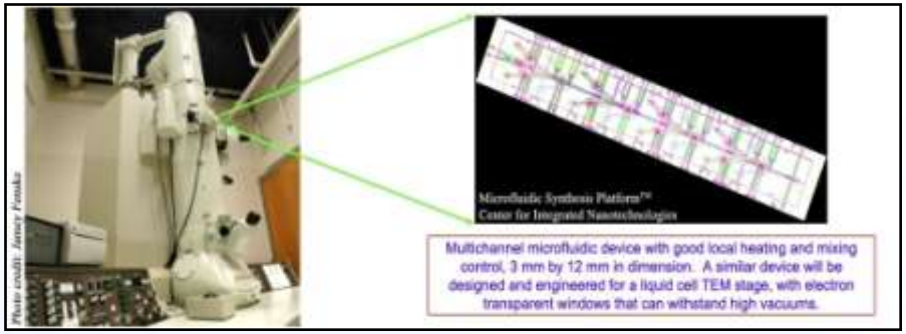
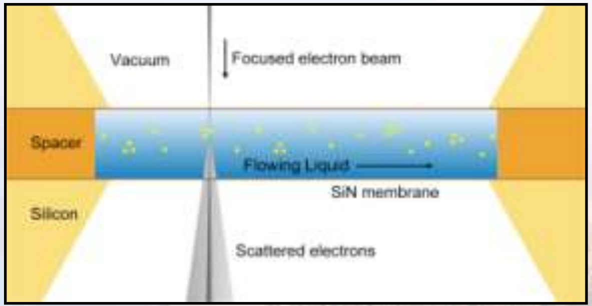
In Situ TEM Fluid Flow Stages

Microfluidic Stage

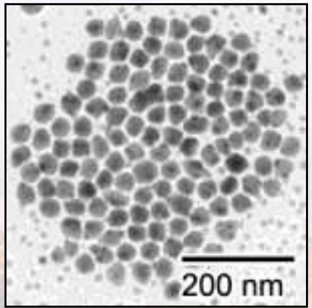
- Mixing of two or more channels
- *In situ* resistive heating
- Continuous observation of the reaction channel
- Chamber dimensions are controllable



Picture of a TEM and schematic of a microfluidic chip



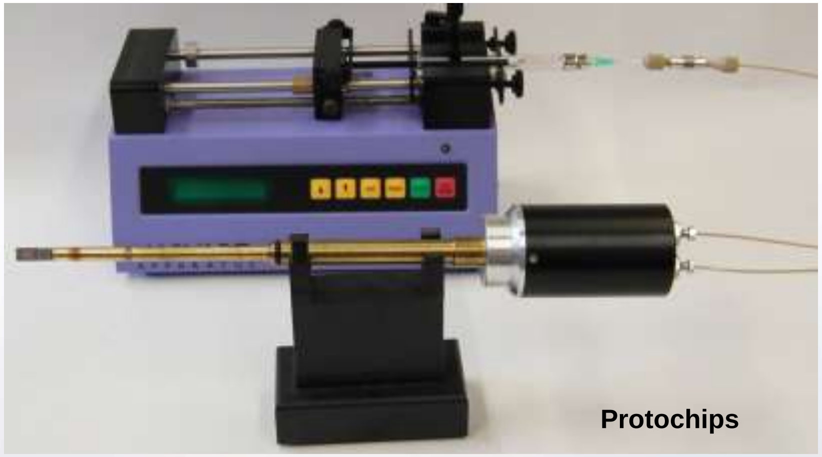
Cross-sectional schematic of liquid cell



Au Nanoparticles

Vapor-Phase Stage

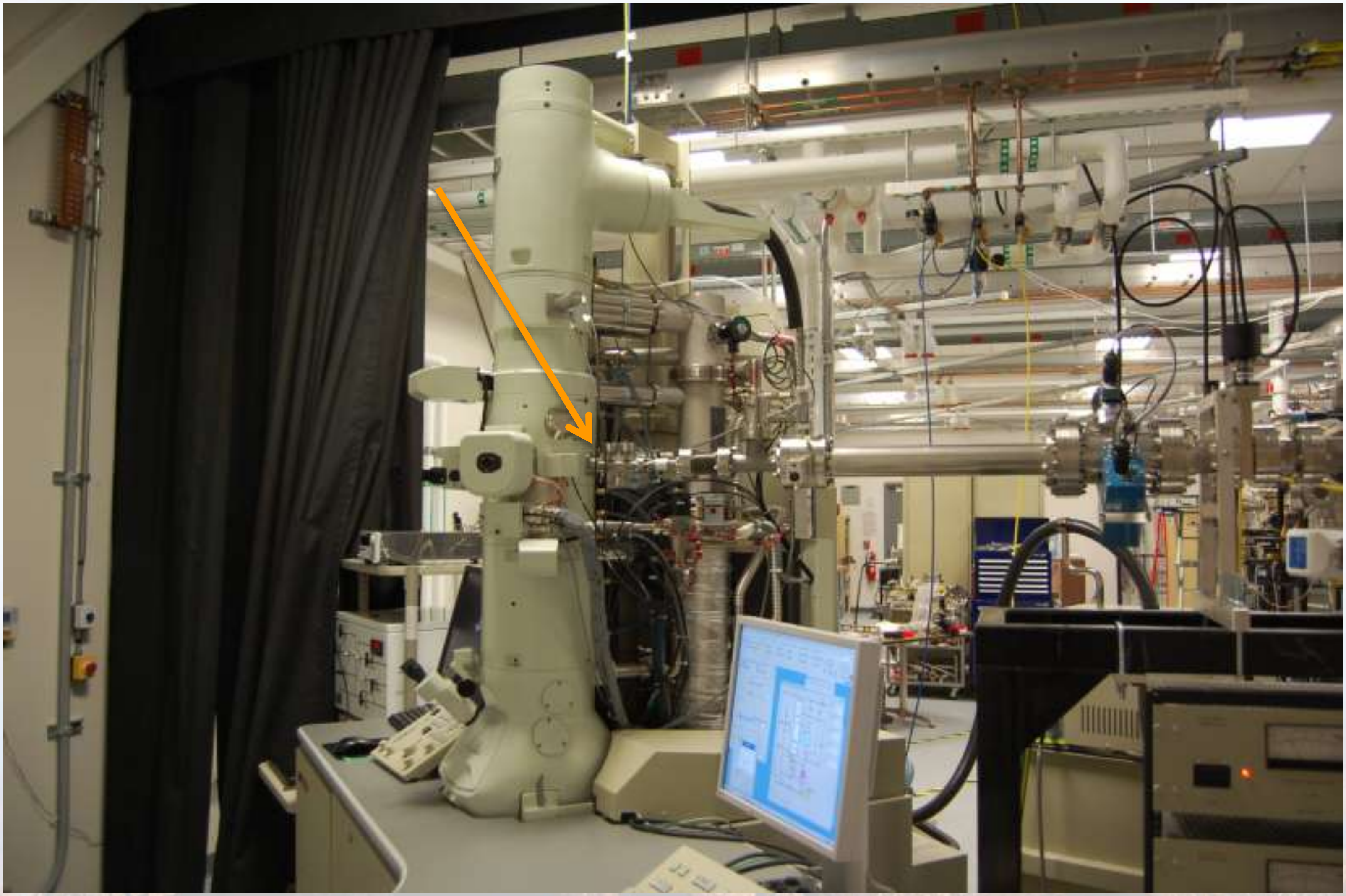
- Compatible with a range of gases
- *In situ* resistive heating
- Continuous observation of the reaction channel
- Chamber dimensions are controllable
- Compatible with MS and other analytical tools



- Initial use for corrosion studies of dry nuclear waste storage

Stages alone provide new research opportunities and even more when combined with ion beams

Current Status of the In-situ TEM Beamline



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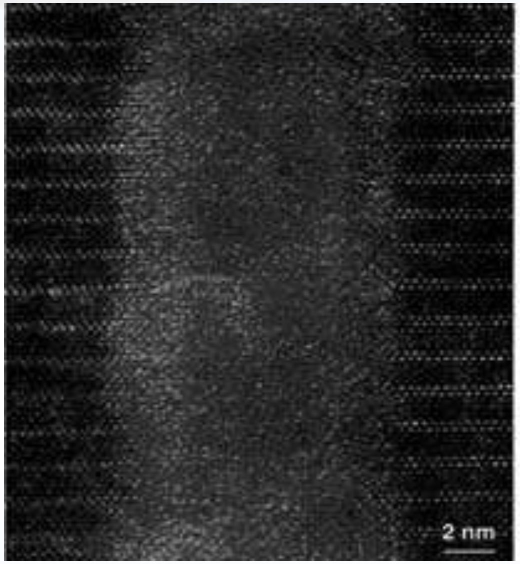
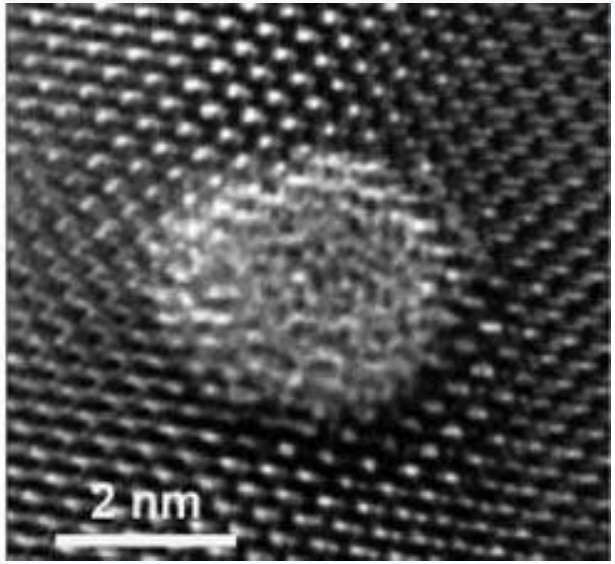
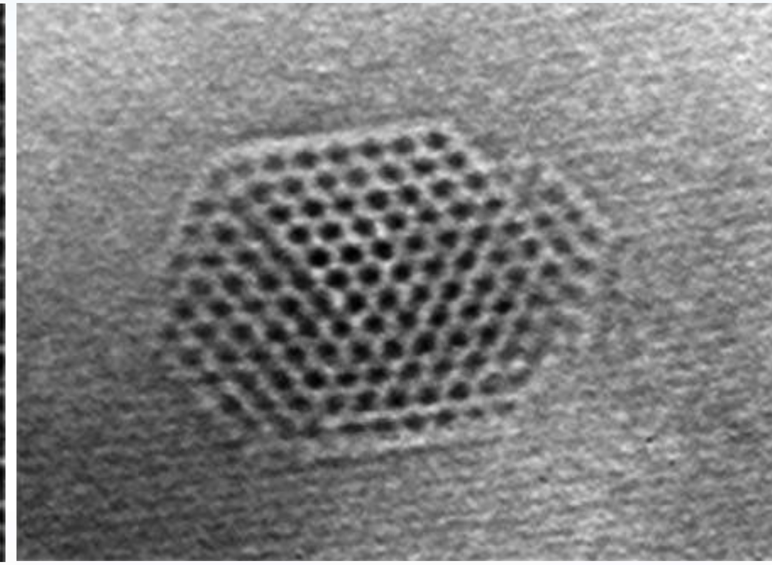
Unique Structures from Ion Implantation







Channeling Tracks

- Cross-section HRTEM
- Single amorphous tracks in High-T_c Superconductor $Bi_2Sr_2CaCu_2O_8$

- Plan-view HRTEM
- Single amorphous tracks in Zircon $ZrSiO_4$

Solid Xe

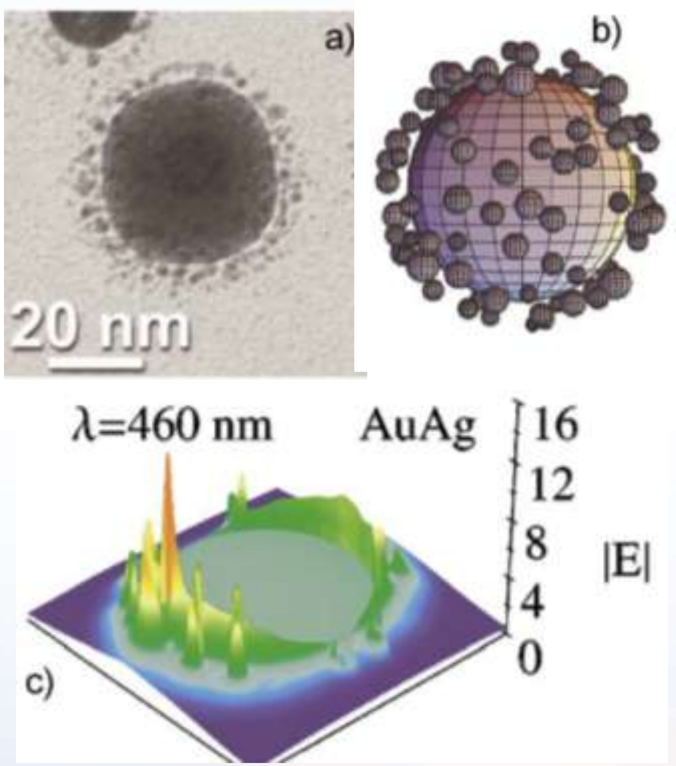
- Xe implanted into Al
- Xe crystalline at RT
- At standard pressure
  - Boiling point is -108.12° C
  - Melting Point is -111.7° C

Unique nanostructures can be formed

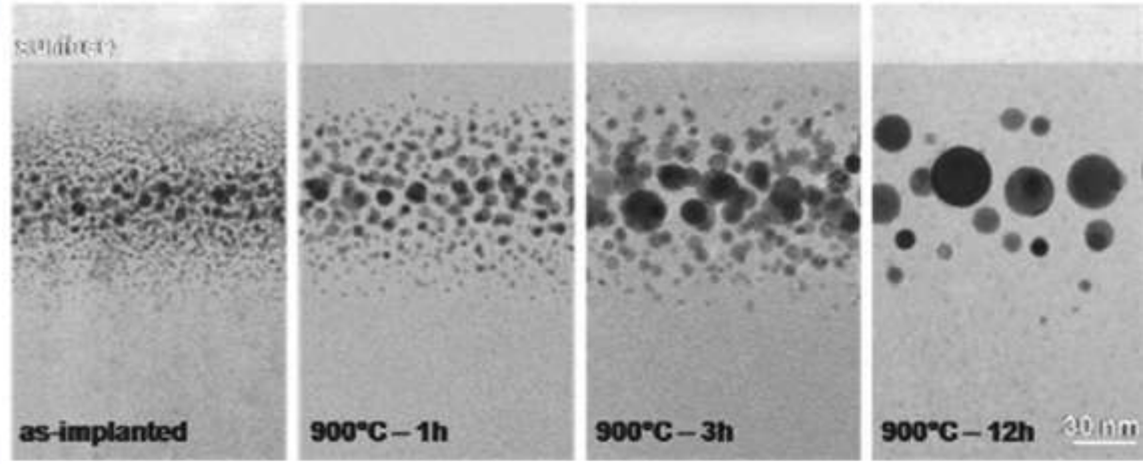
Helborg et al. “Ion Beams in Nanoscience and Technology”

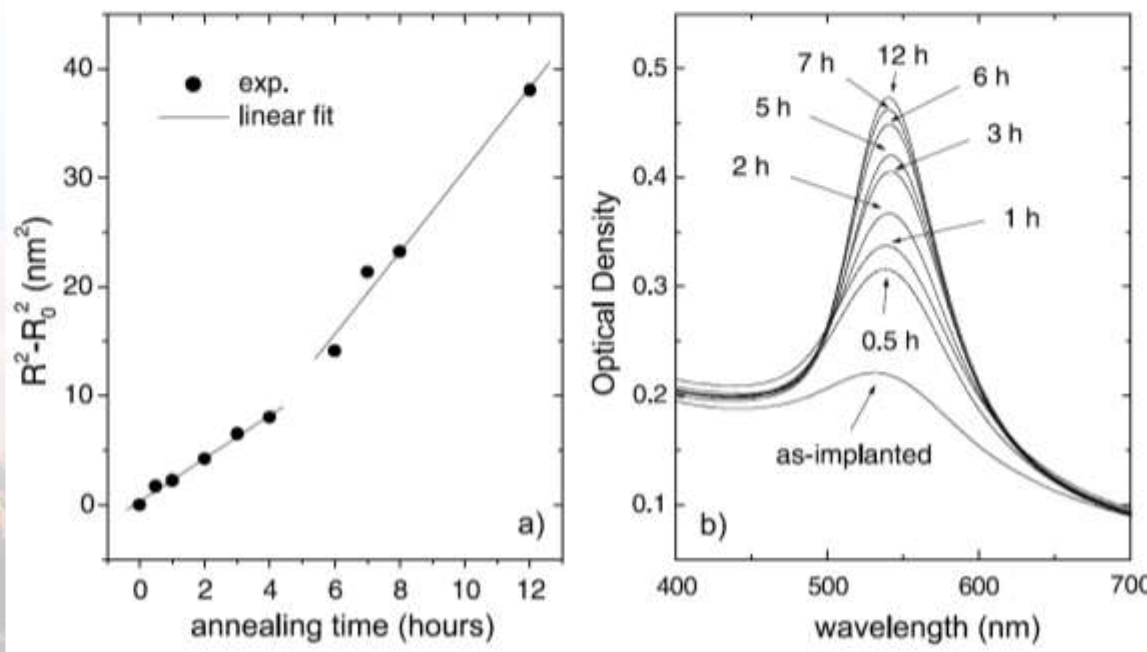
Ion Beams and Optical Properties in Nanoparticles

Sateltie structure from He into AuAg produce red shift



Au implanted as a function of annealing condition and resulting absorption spectrum





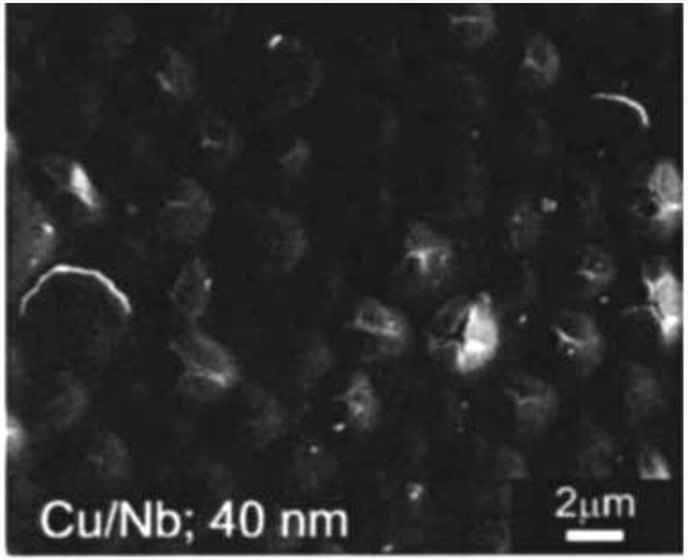
Optical properties can be tailored by irradiation of nanoparticles or annealing of irradiated zones

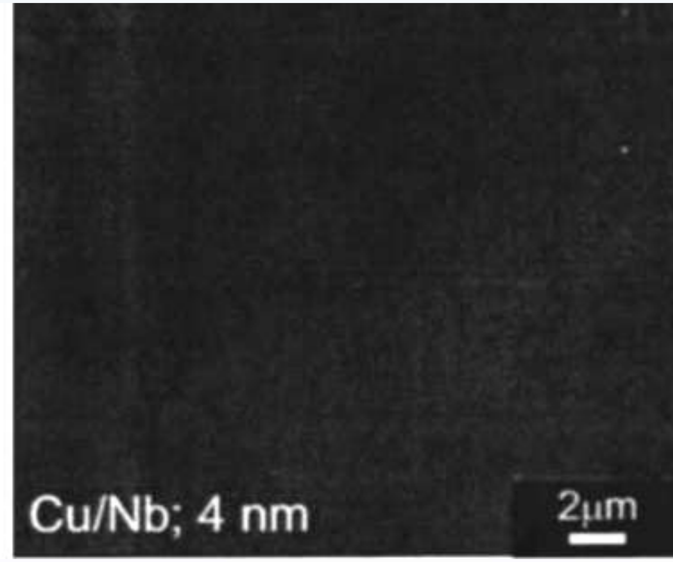
H. Bernas "Materials Science with Ion Beams"

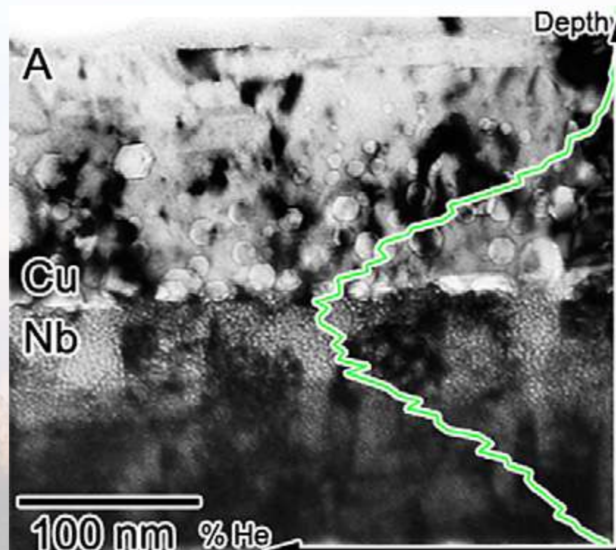
Neutron Damage Simulation in Metals

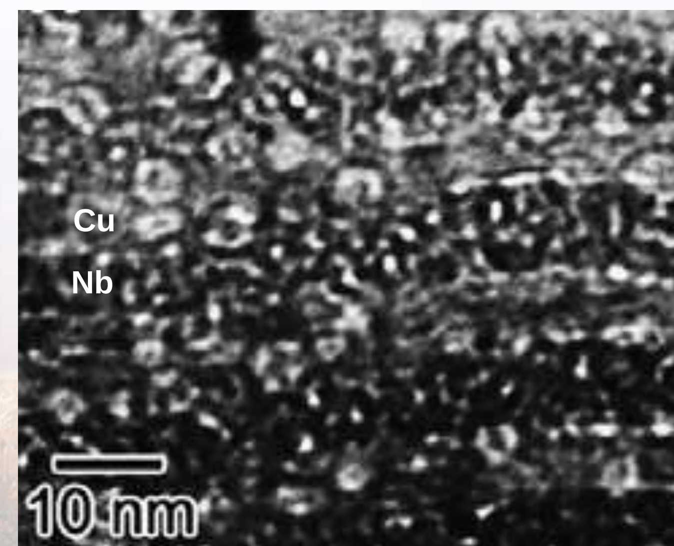
- **Many materials systems are being considered.**
- **Interface engineering is providing a potential solution**
- **Copper-niobium nanolamellars provide a plethora of interfaces that readily distribute damage**

Significantly enhance testing with in-sit ion beam irradiation



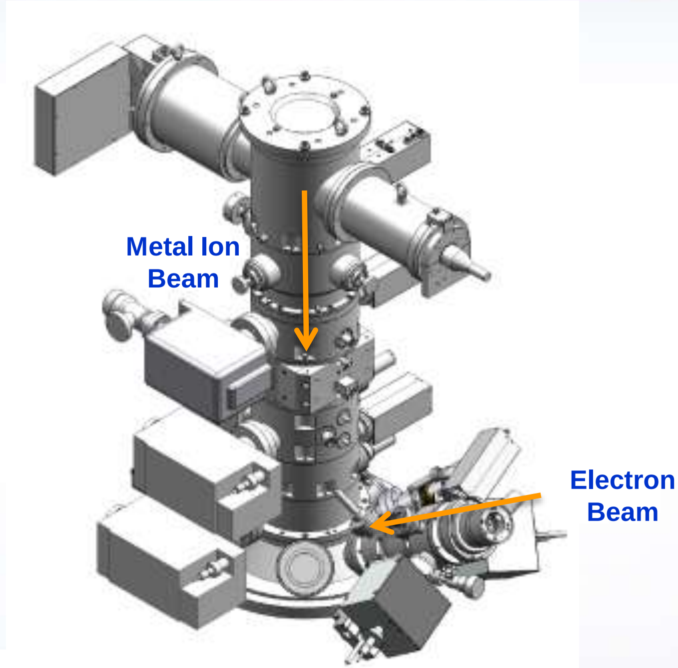


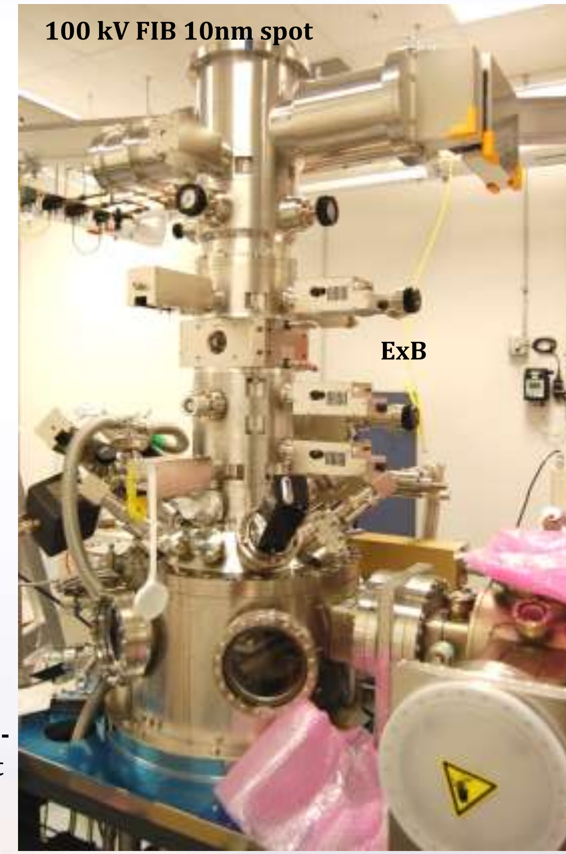




Nanoimplantor

- Multiple liquid metal ion source (LMIS)
- *E* x *B* filter
- Ion column with a maximum accelerating voltage of 100 kV
- 10 nm spot size
- High-resolution SEM
- 4 manipulators with 10 nm resolution and low current measurement capabilities

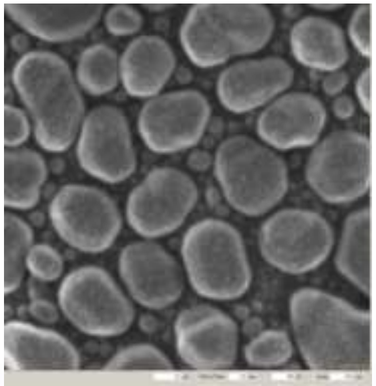




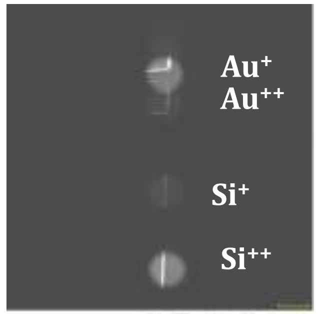
These capabilities greatly exceed the capabilities of commercially available Ga^{+}-based dual-beam FIB systems in terms of irradiation doses, ion species, and nanofabrication.

Nanoimplanter first results and projects

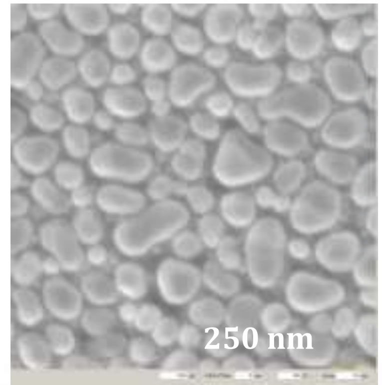
Imaging and machining with 100 keV Ga



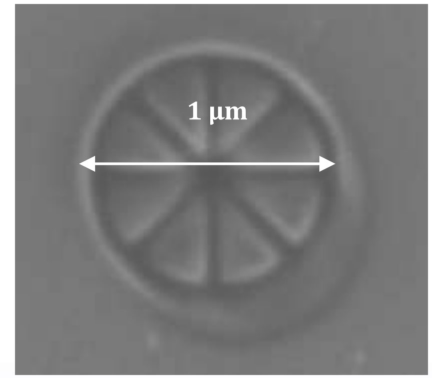
SNL Fabricated AuSi LMIS

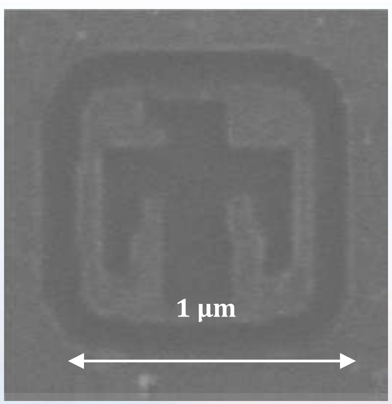


200 keV Si^{++} Beam



100 keV Au^+ Beam





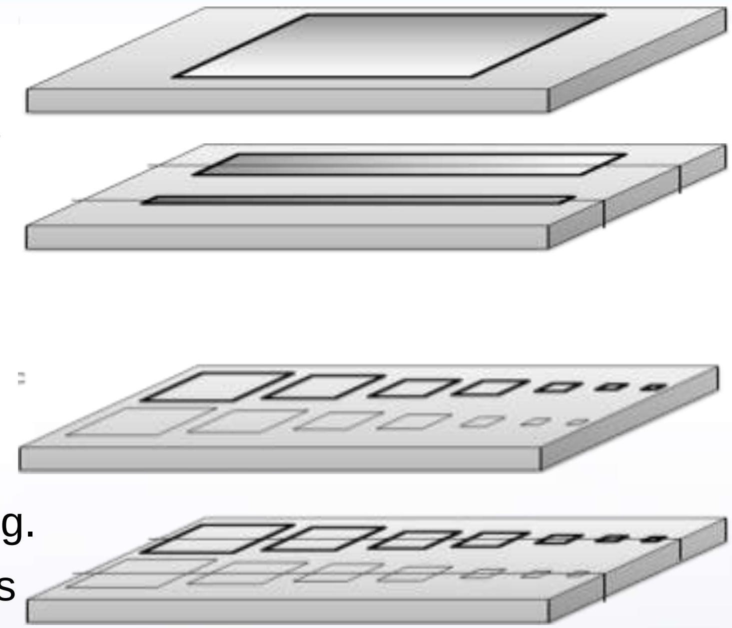
Single Ion Implantation

- Donor implantation for Quantum Computing
- Color Centers in Diamond (single photon sources)
- Magnetic impurities in GaAs nanostructures

Rapid prototyping

- Nanoelectronics – deterministic doping for next generation of semiconductor devices
- Fabrication of novel semiconductor devices (implantation), MEMS structures (milling)
- Nanostructural modifications of material systems

Local Control of Structural Defects



- **Local Control of Grain Boundaries**

•Control of ion species, energies, and beam size permit local rearrangements of interfaces and grain boundaries.

• The altered region surrounding various grain boundary types are controlled via the size and duration of self-ion implantations.

• Length scales associated with solutes will be investigated by tailored heavy ion implantation.

- **Deformation of Confined Volumes**

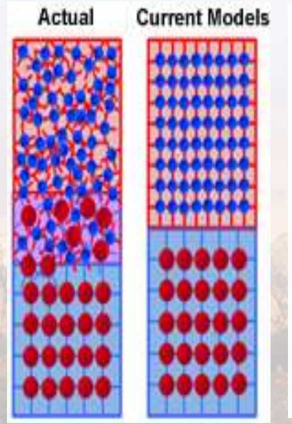
•Diffusion couple Ion beam will be used to confine the area of thin films down to a few nanometers prior to mechanical testing.

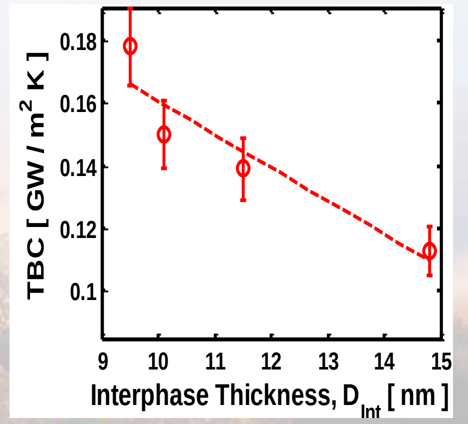
• This confinement can encapsulate identified defect structures in the film including: grain boundaries and particles.

• This will provide an alternative method to FIB milling for the production nanostructues

- **Controlling Interfacial Structure and Properties**

•Determination of thermal transport across interfaces as a function of local disorder



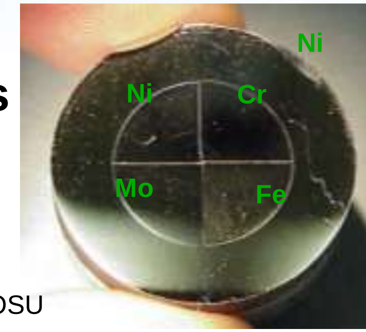


Additional Applications of Future Capabilities

- **FIB beyond**
  - Ga$^+$ ion beam

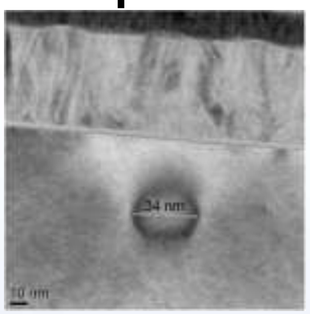
Collaboration with D. Gianola at Univ. of Penn.

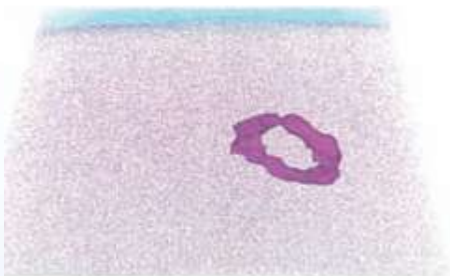
- **Combinatorial Irradiation Studies**



Collaboration with J.-C. Zhao at OSU

- **Nanostructured Sub-surface Composition Control**



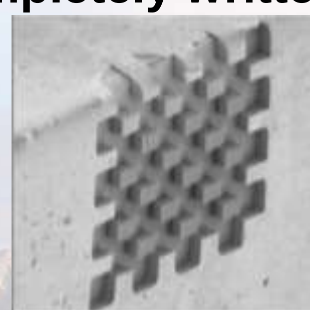


Thompson et al. Science **317** 1370

- **Study of the long term stability of glass for nuclear waste**

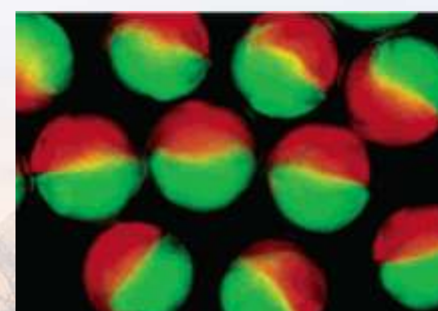
Collaboration with A. L. Billings at SRNL

- **Completely written structure**



Gomez-Mrilla et al. J. Micromec. MicroEng. **15** 706

- **Janus Particle Fabrication**



Shepherd et al. Langmuier 2006

- **And many more…**

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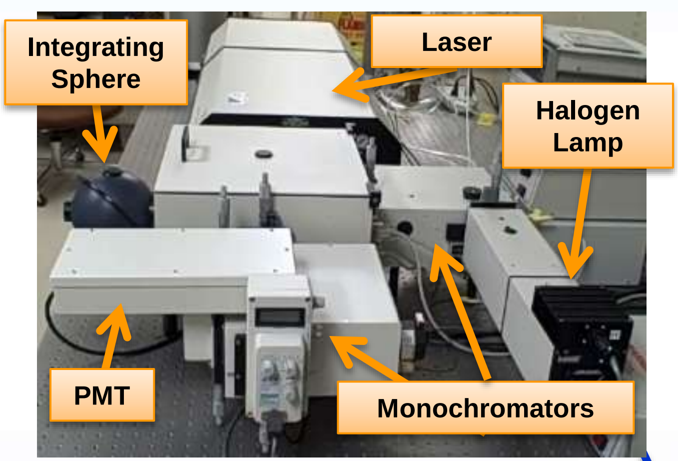
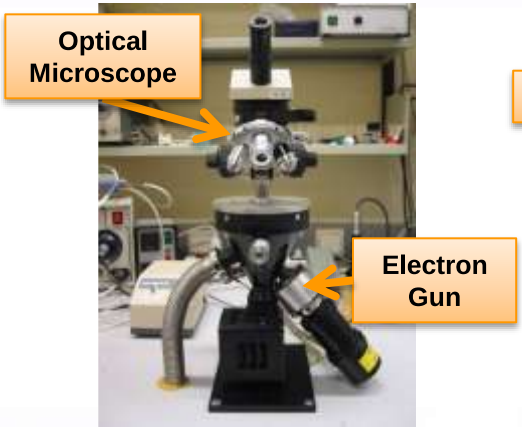
Proposed Integrated System on Dedicated Ion Beam Line

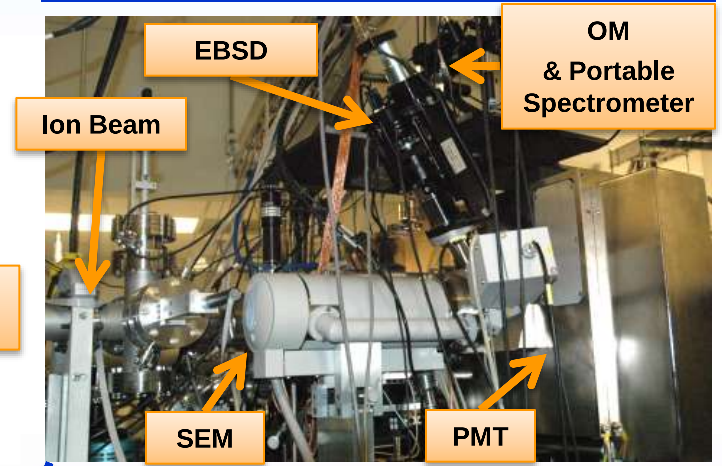
Photoluminescence



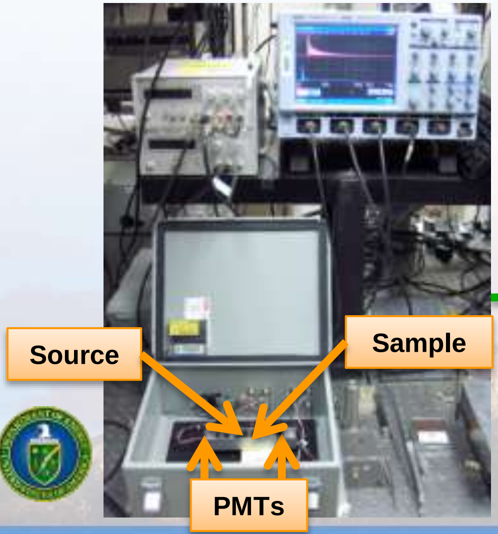
Cathodoluminescence



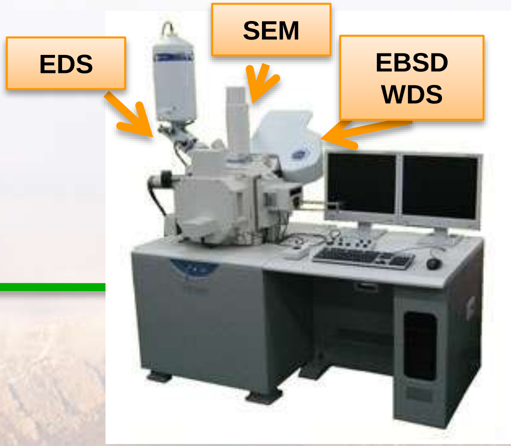
Ion Beam Induced Luminescence



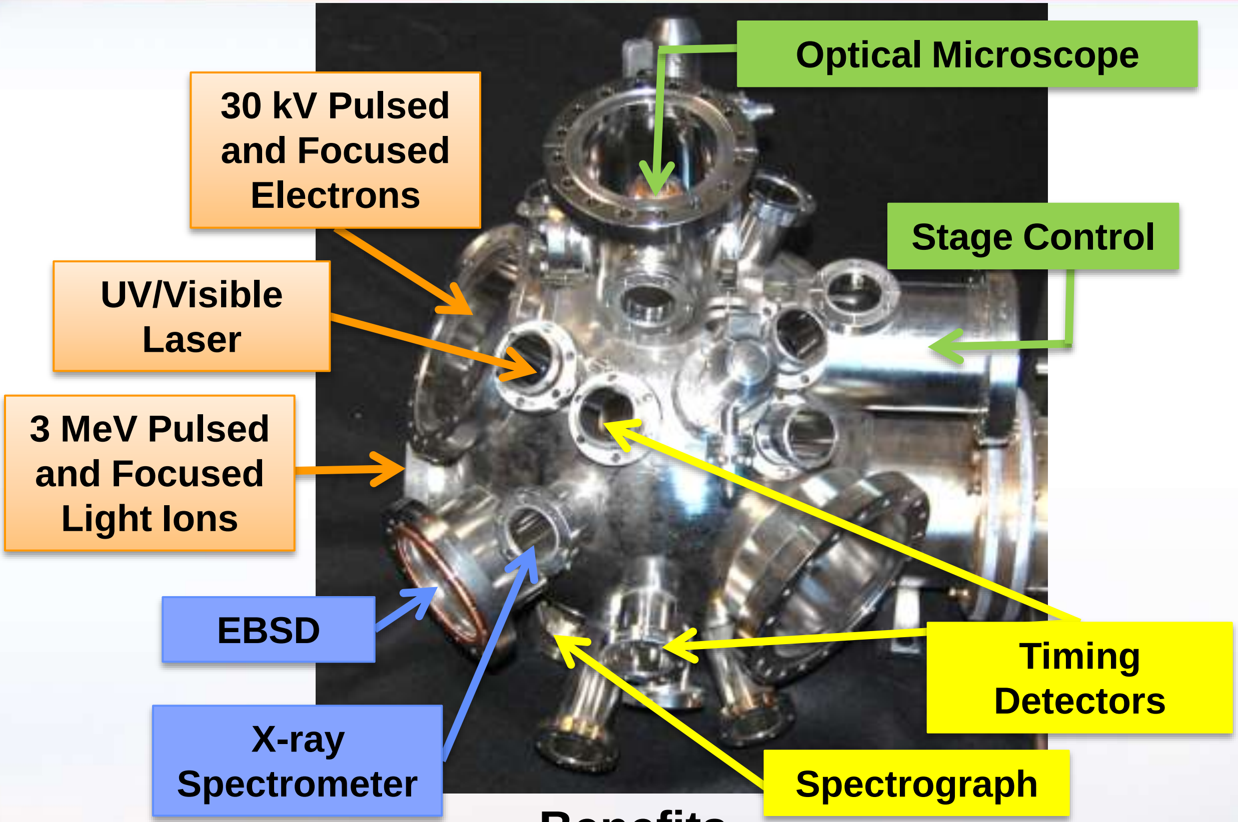
Timing Measurements



Microstructural Characterization



Ten Measurements in one Experiment!

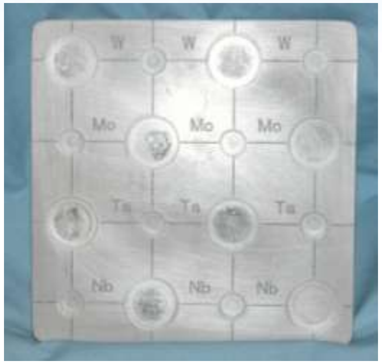


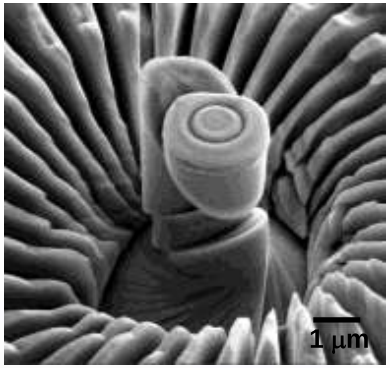
Benefits

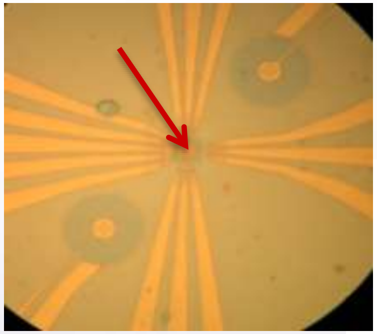
- Timing & spectroscopy of luminescence induced by ions, electrons, photons, & ɣ
- A unique *user facility* permitting advanced testing on scintillating materials
- Development of and publications on novel radiation detection materials
- *Rapid & fundamental validation* of advanced materials for current: NA-22, LDRD, and CRADA projects

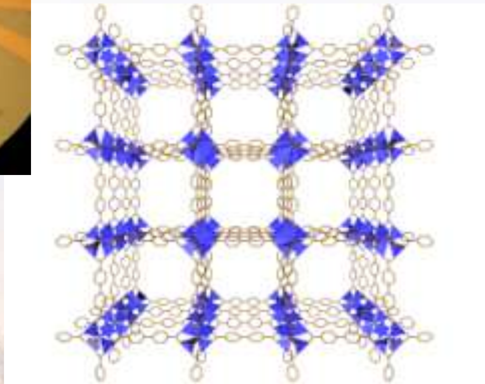
Conclusions

- Current techniques permit simulation of neutron exposure to MOF structures
- Developed a wide suite of end stations, which provides great versatility in the in-situ ion irradiation capabilities
- The development of a new Pelletron end station provides great advantages for scintillator research









Acknowledgements

- All staff and technologists of the IBL at SNL
- Many staff and technologist in 8000, 1800, and 1100 for helpful advice

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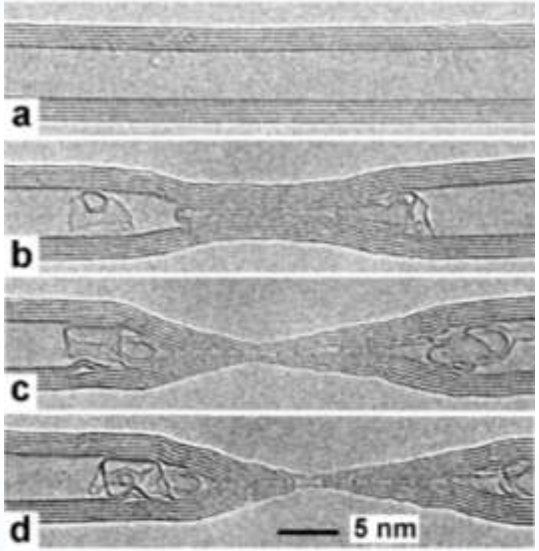
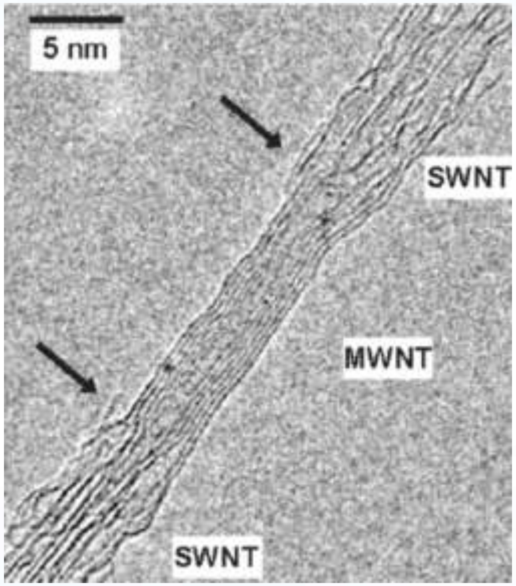
Radiation Damage in CNT

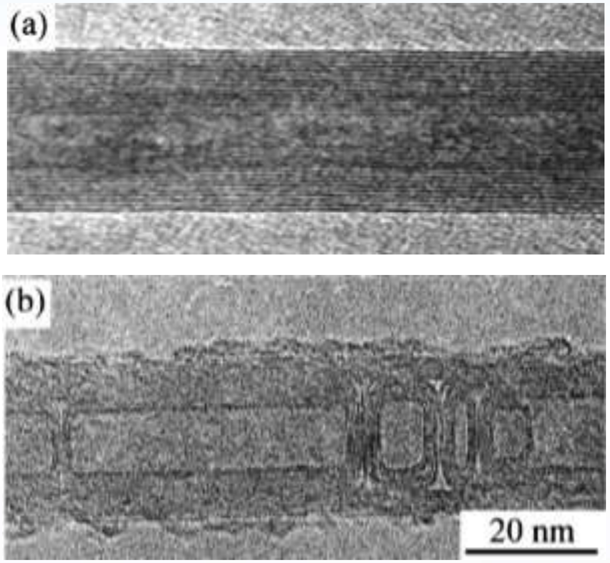
Extension & SWNT Formation



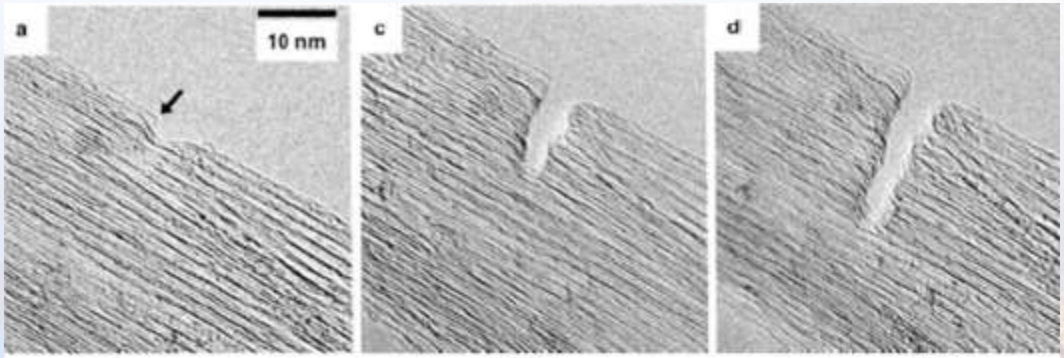
MWNT production from SWCNT bundles



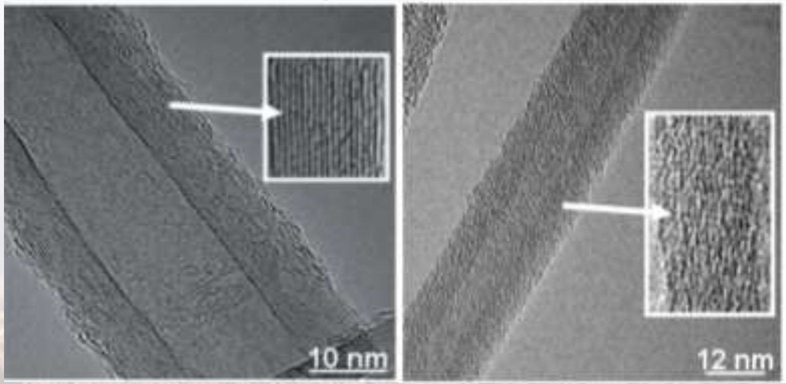
Cross-Linking within MWCNT



Precise Cutting of CNT



Amorphization of CNT



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Charged particle radiation can result in various nanostructures

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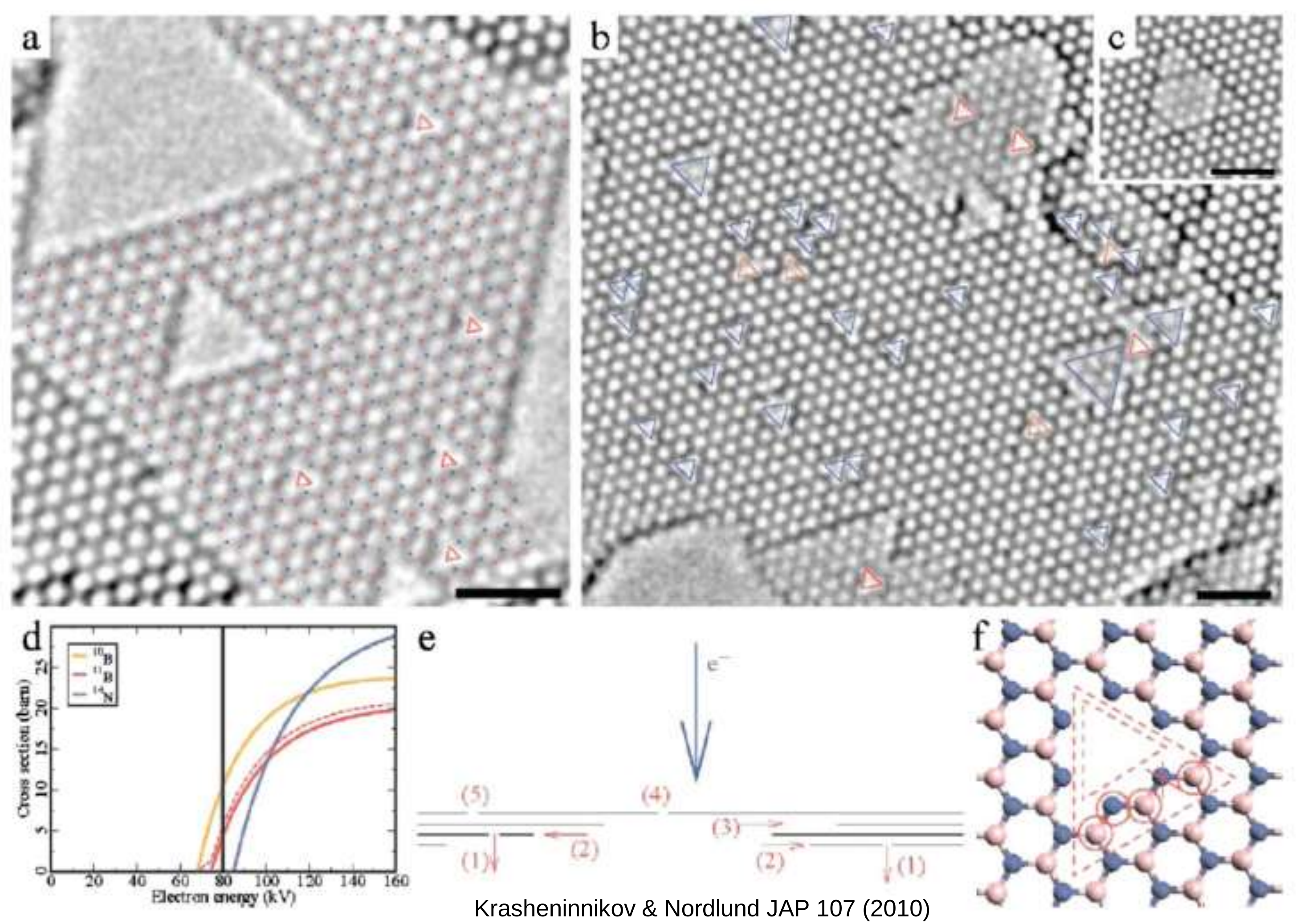
Radiation Damage in BN Layers



Krasheninnikov & Nordlund JAP 107 (2010)

- 80 kV Electron beam irradiation
- Various defect structures can be created
- By tailoring the energy, the preferential removal of certain compositions can be achieved.

Defect structures from charged particles is not limited to carbon structures

Experimental – Photoluminescence & Cathodoluminescence

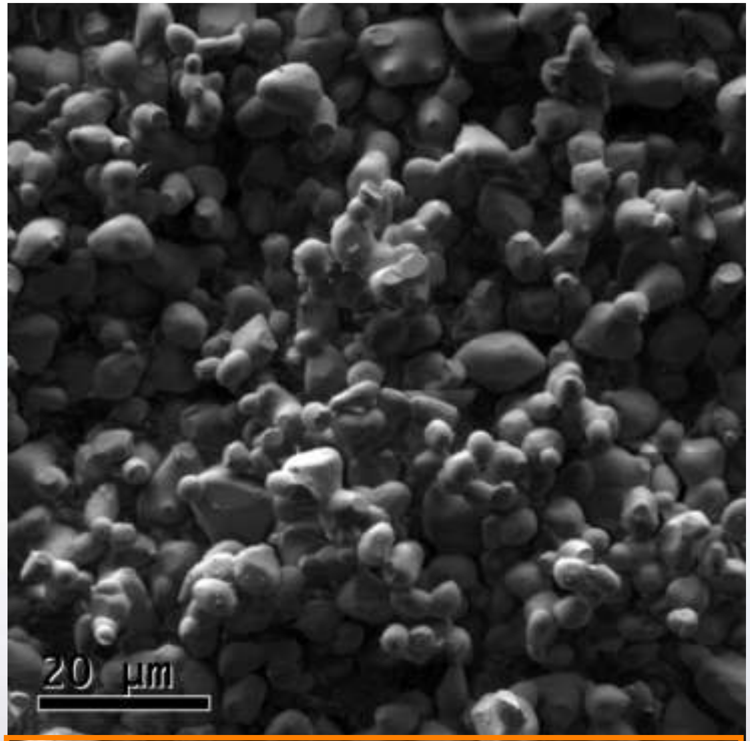
It is critical to study materials with various excitation mechanisms

Photoluminescence

- PL measurements performed with a Horiba Jobin Yvon Fluorolog spectrofluorometer
- Halogen lamp excitation with monochromator to select wavelength
- Samples excited at 337 nm unless observed emission depending on excitation wavelength

Cathodoluminescence

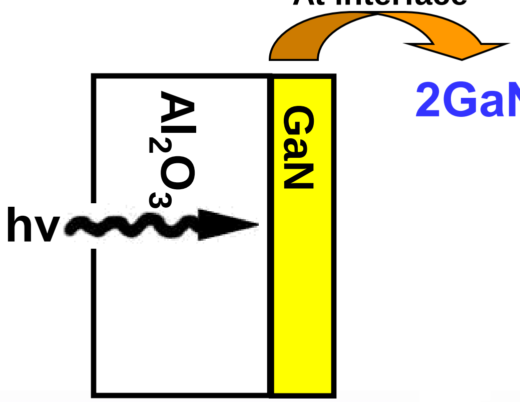
- 3 kV electrons, 2.6 nA current
- PMT operating at -750 V
- Magnification: 1300X or 5000X



1300X SEM image of Y_2O_3:Eu powder – location of CL spectrum

Results – GaN and InGaN/GaN Quantum Wells

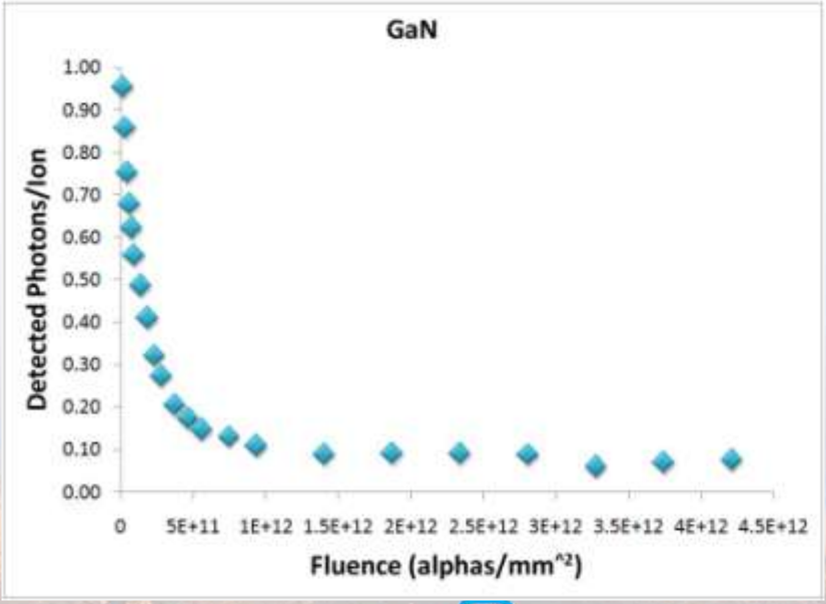
Can make thin films of GaN and radiation hardness acceptable



$$2GaN \xrightarrow{\Delta} 2Ga(s) + N_2(g)\uparrow$$

GaN film on Cu ring

- ***Advantage*: GaN can be removed from substrate as free-standing thin film**
- ***Advantage*: Despite initial sharp drop-off GaN's efficiency remains higher than that of other materials studied**
- ***Disadvantage*: Thin films difficult to handle**
- ***Disadvantage*: Long decay time of yellow light will cause accidental coincidences**



Experimental – Luminescent Decay Times & Radiation Hardness

Decay and radiation hardness are critical parameters for application

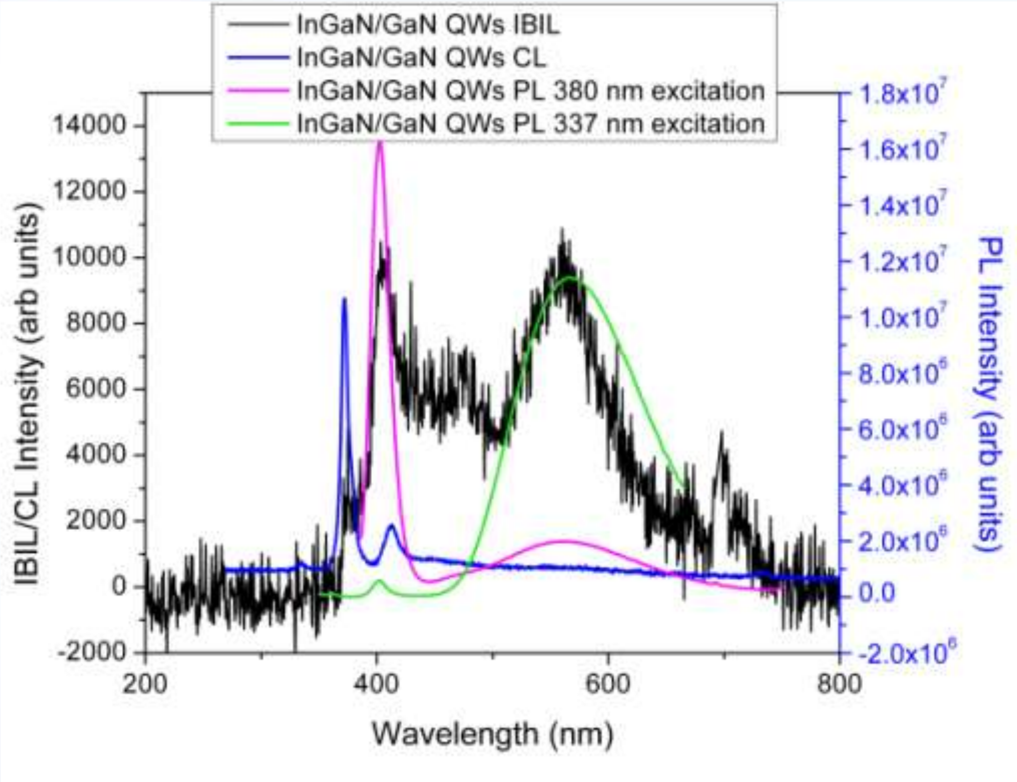
Decay Times

- Photon Technology International (PTI) GL-3300 nitrogen pulsed laser used as excitation method
- Light collected with a ThorLabs 210 or PDA-55 silicon photodiode
- Signal put directly into Tektronix TDS 5104 digital phosphor oscilloscope
- Light intensity measured as a function of time after laser pulse

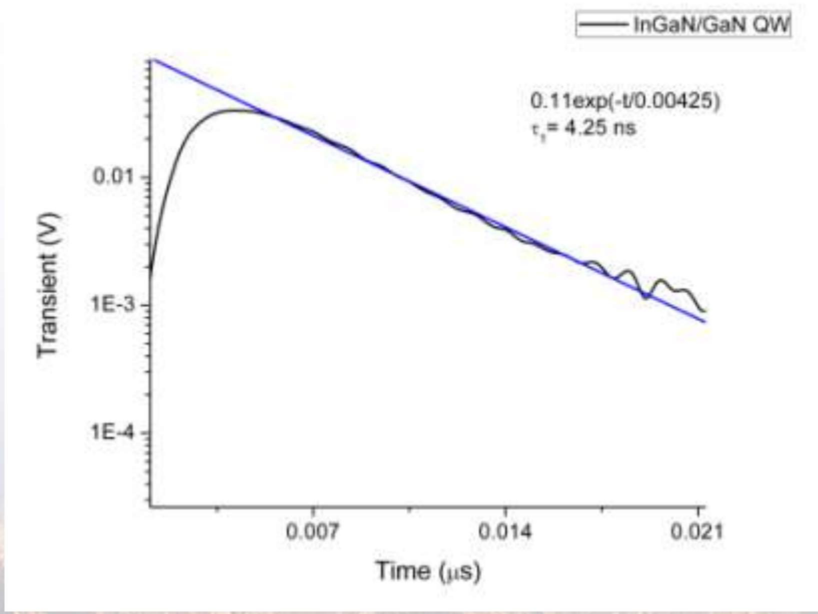
Radiation Hardness

- Radiation hardness experiments performed with 4.5 MeV H^+ beam from tandem accelerator
- Thin films of samples were mounted on PIN diodes
- Hamamatsu PMT was used in single photon counting mode
- Counters measured the number of IBIC signals from PIN diode (# of ions) and number of photons hitting PMT
- Experiment repeated at same position on sample for a period of time

Results – GaN and InGaN/GaN Quantum Wells



- InGaN/GaN quantum wells were designed and grown at SNL to optimize blue, fast bandedge emission
- Relative intensities of emission bands greatly dependent on excitation mechanism and energy



- ***Advantage:*** blue bandedge emission has very fast decay; yellow band had good emission wavelengths
- ***Disadvantage:*** blue emission overlaps with air; yellow band demonstrates very long decay times

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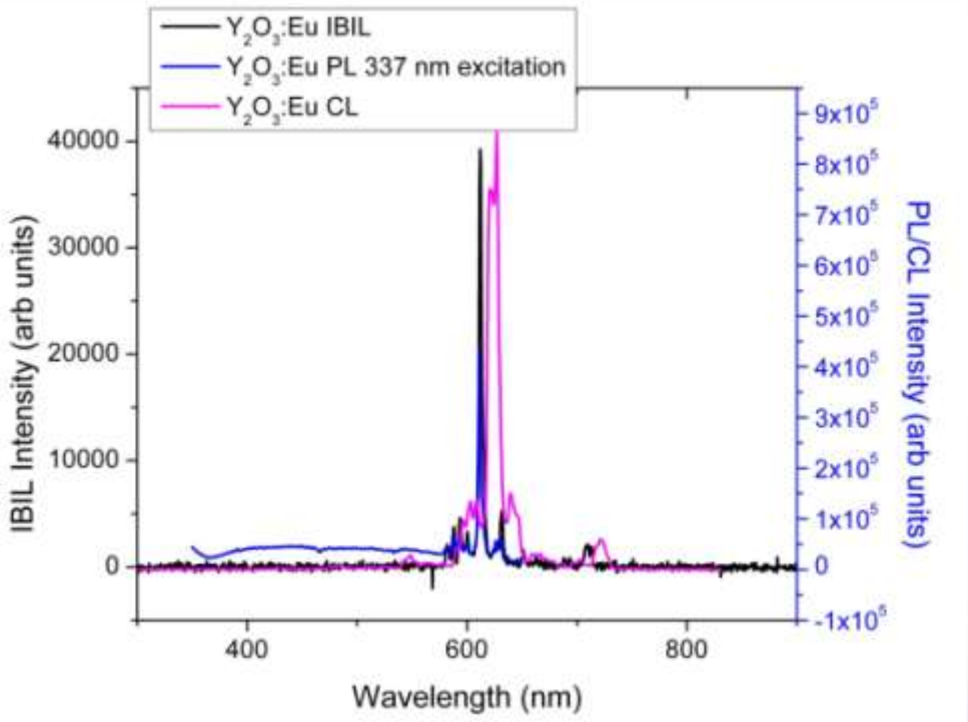
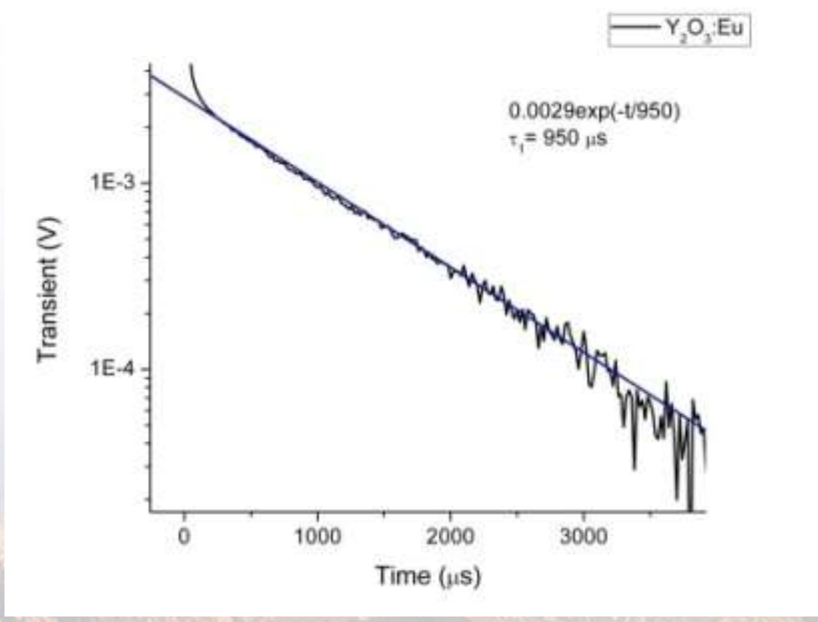
Results – Lanthanide-Doped Ceramics

Europium-doped ceramics have easily engineered emission properties



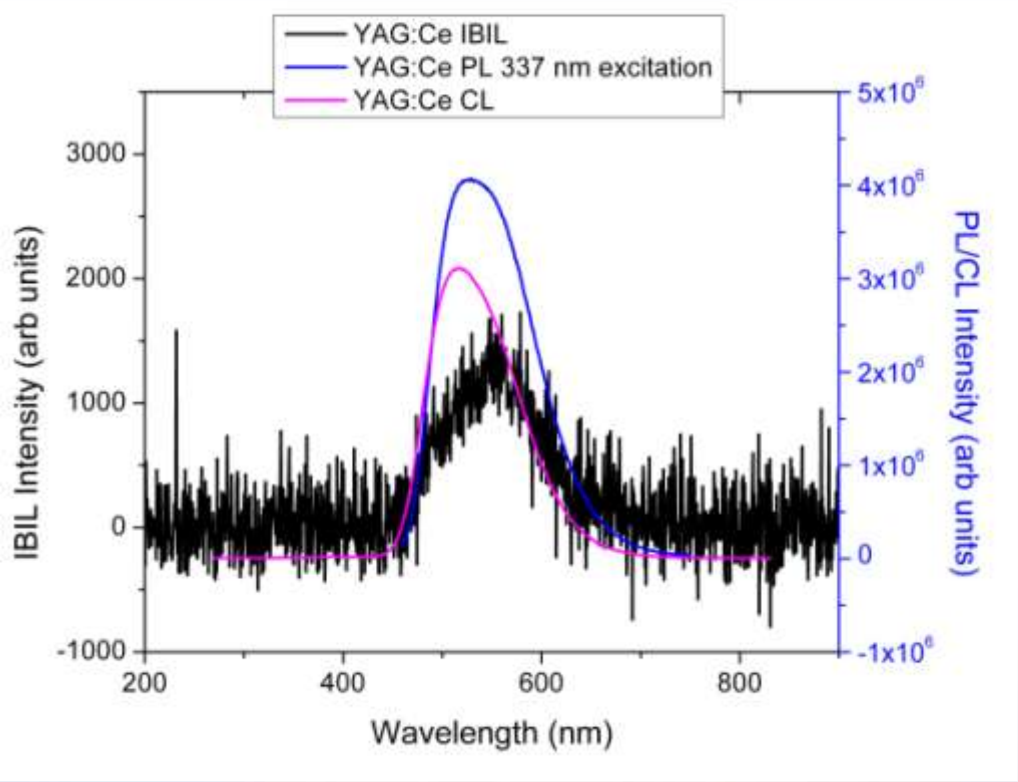
- ***Advantage:*** **Y_2O_3:Eu has a great emission spectrum – intense lines at wavelengths much above that of air**
- ***Advantage:*** **IBIL and PL characteristics very similar**



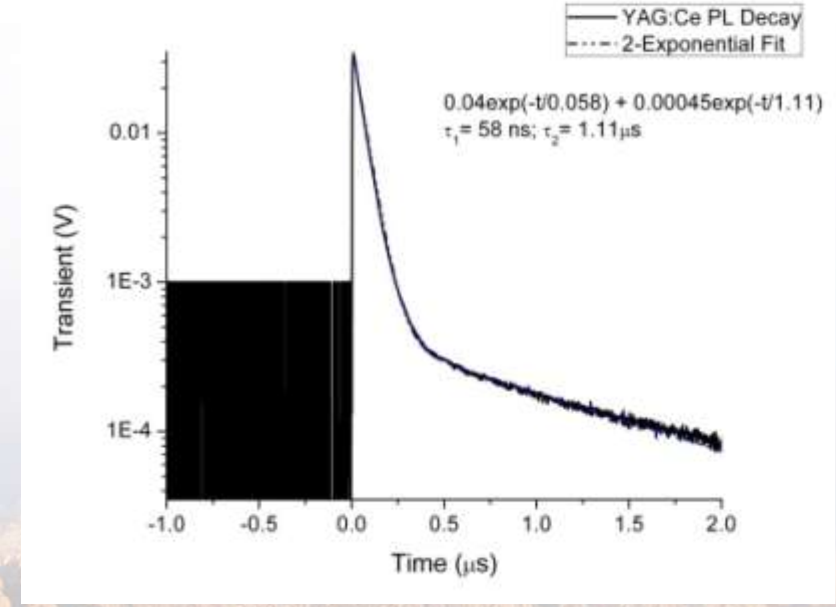
- ***Disadvantage:*** **Decay time of Y_2O_3:Eu is incredibly long**
- **Would lead to accidental coincidences for IPEM application**

Results – Lanthanide-Doped Ceramics

YAG:Ce is most promising IPEM material studied



- ***Advantage:*** **YAG:Ce has broad emission band centered around 520 nm**
- ***Disadvantage*****: Not as intense as Y_2O_3:Eu**

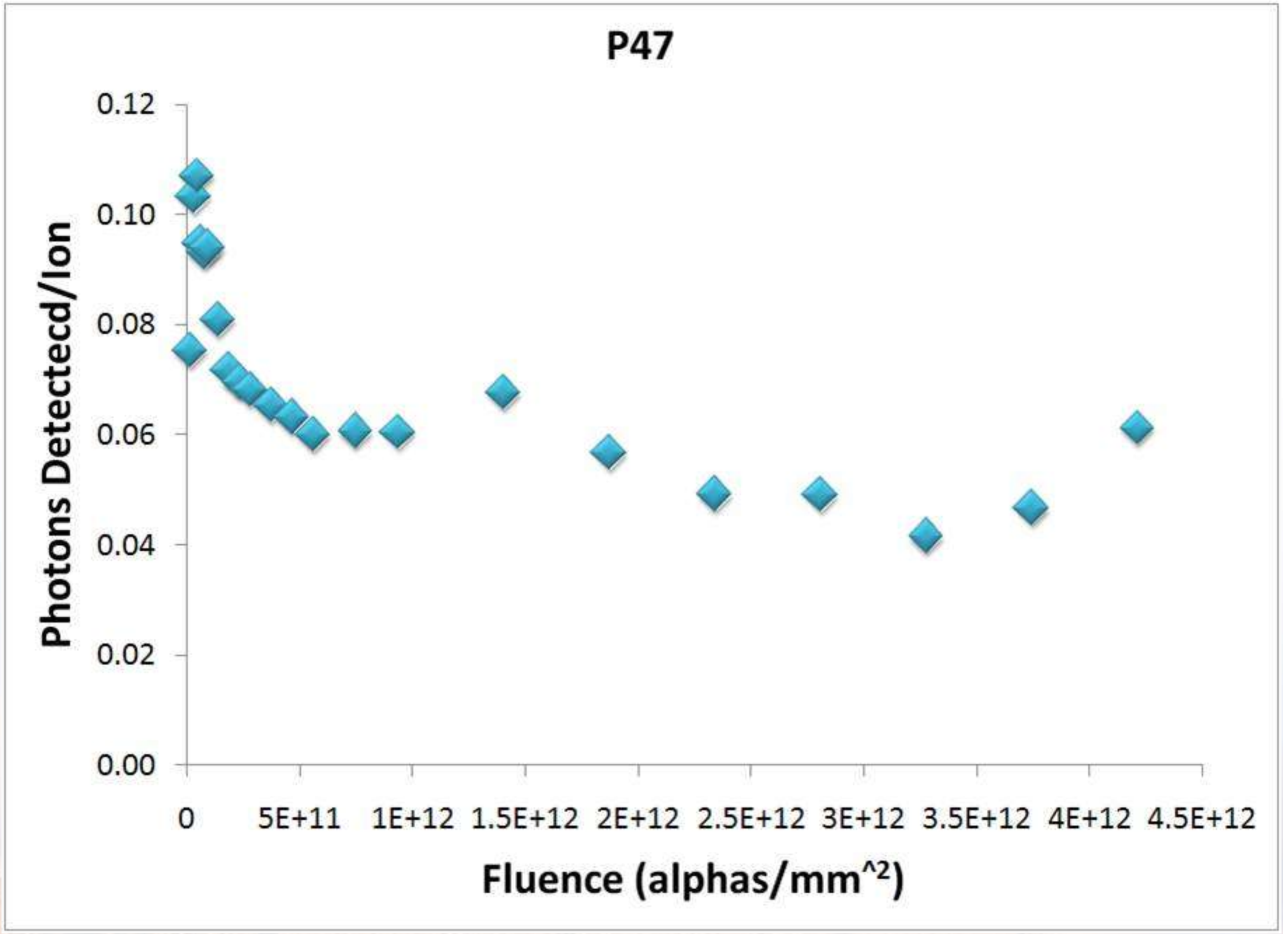


- **YAG:Ce decays with a bi-exponential**
  - ***Advantage:*** **Both decays are sufficiently short to be useful**

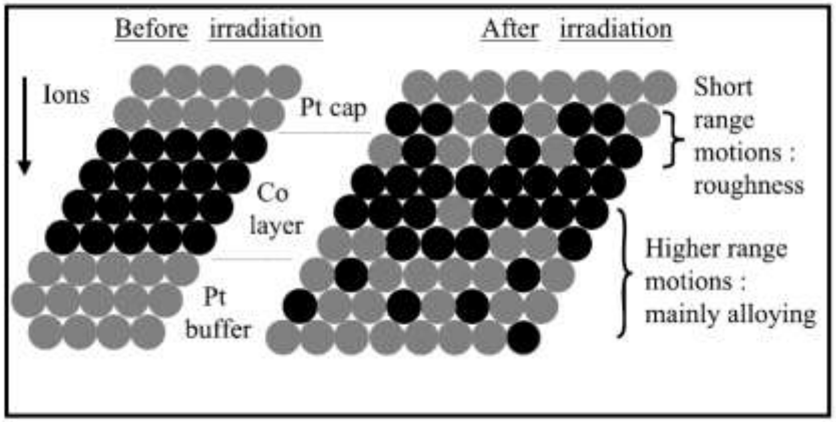
Results – Lanthanide-Doped Ceramics

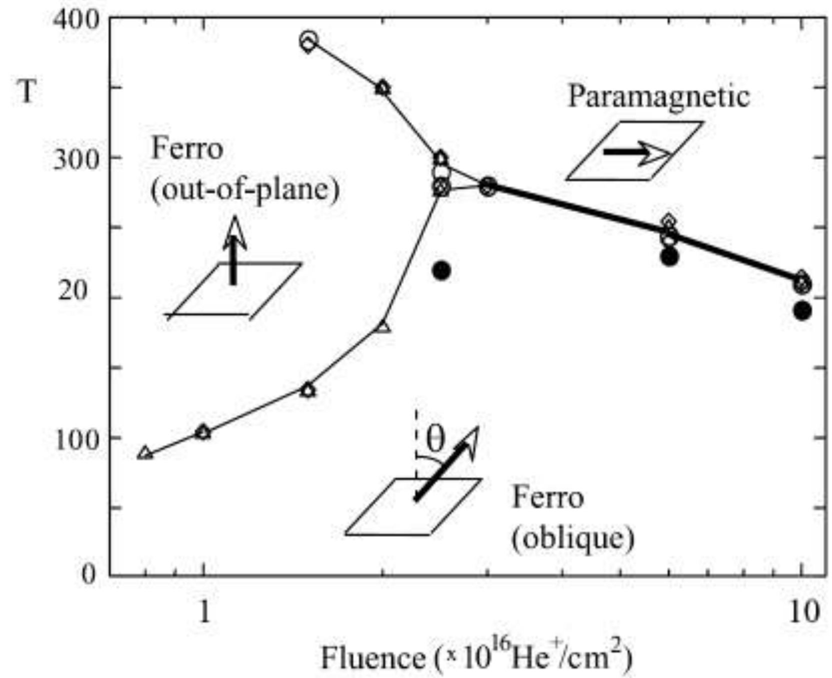
Ceramics demonstrate acceptable radiation hardness

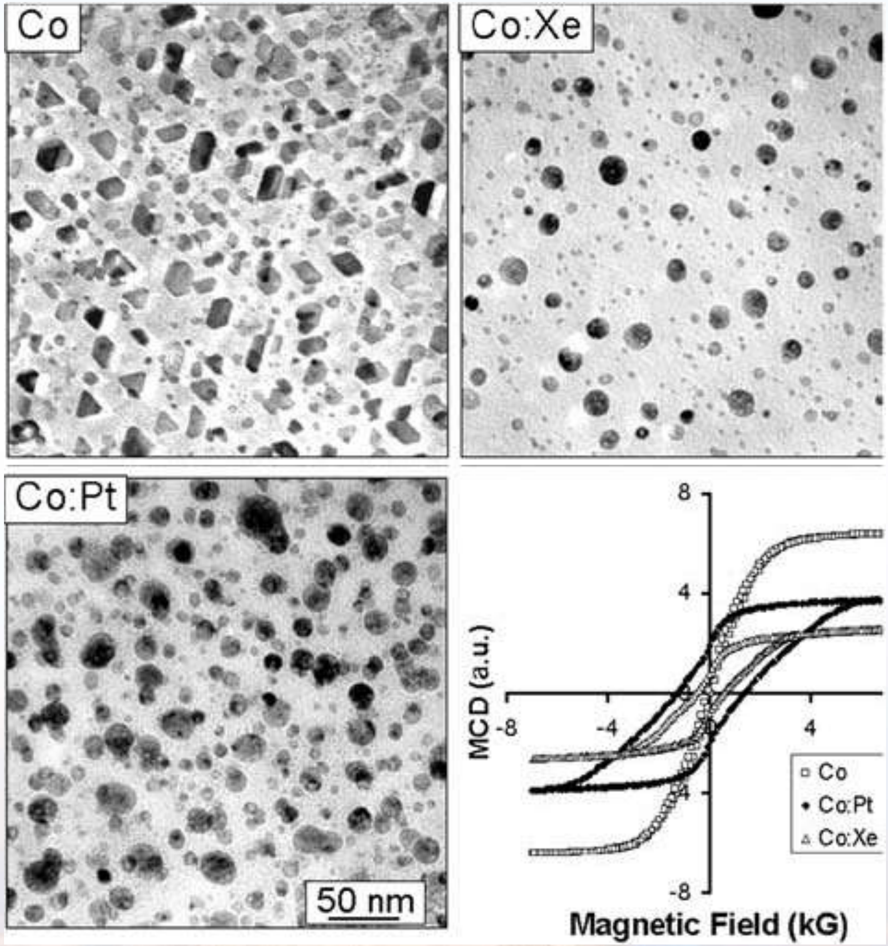
- ***Advantage*: Ceramic-based phosphors have good radiation hardness; small initial drop in efficiency that levels off**
- **Considering good emission, short decay time, and radiation hardness, YAG:Ce is optimal for IPEM**



Ion Beams Altering Magnetic Properties







Magnetic properties, like many other, can be tailored by Temp. and Fluence

H. Bernas "Materials Science with Ion Beams"

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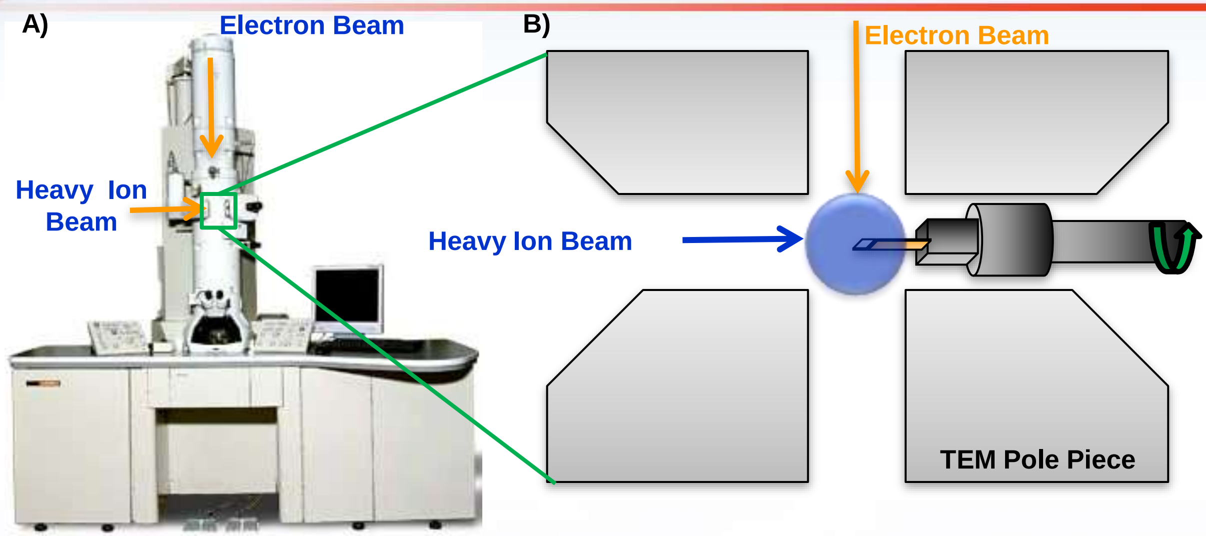
Clustering study with the “Nuclear” TEM

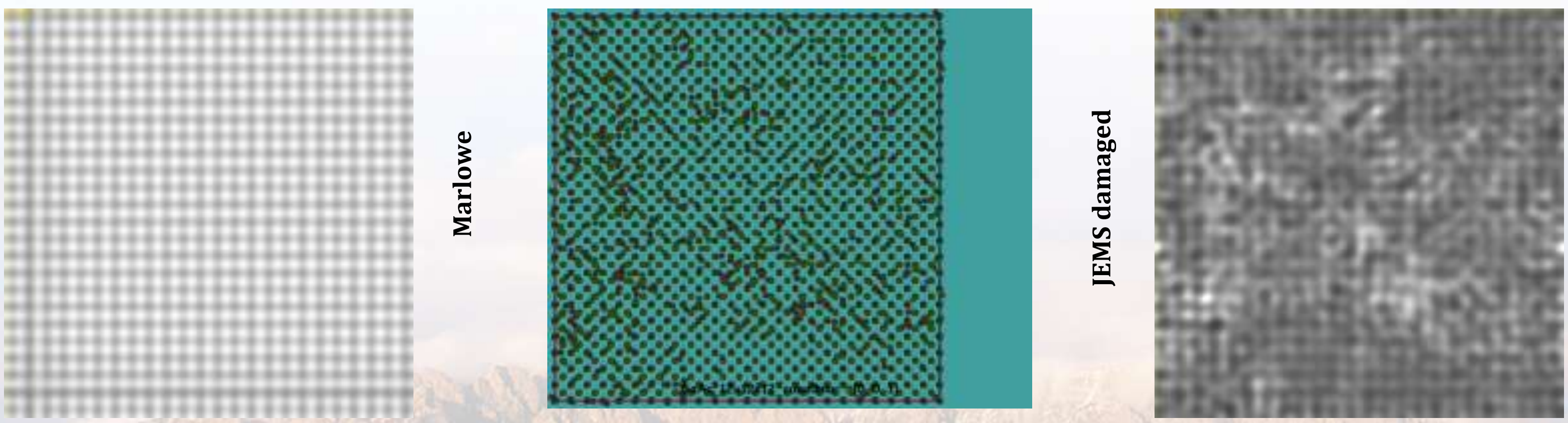


Simulation (Marlowe+JEMS) shows the project is viable (30 MeV Cu -> GaAs)

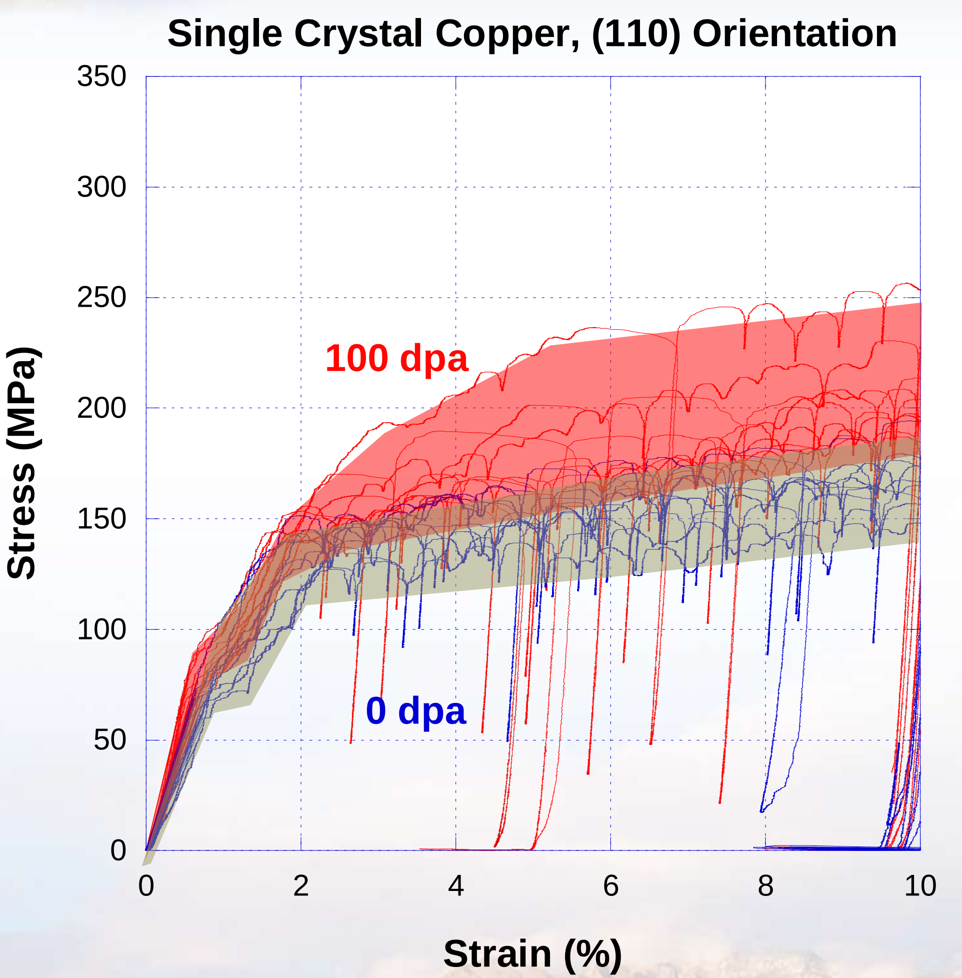
JEMS undamaged

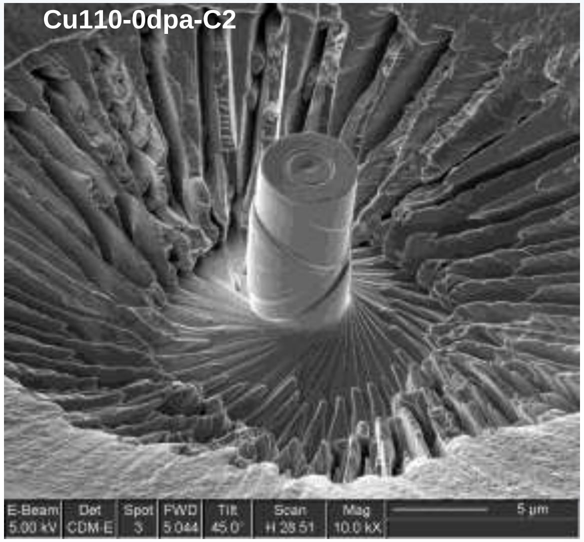
Marlowe

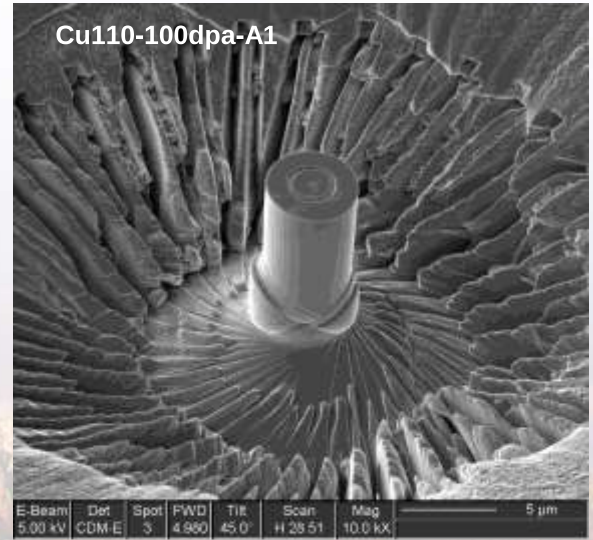
JEMS damaged



Large Micropillar Compression







Minimal difference between the control and irradiated 10 μm-tall pillars. Slip occurred in the bottom fraction of the pillars.

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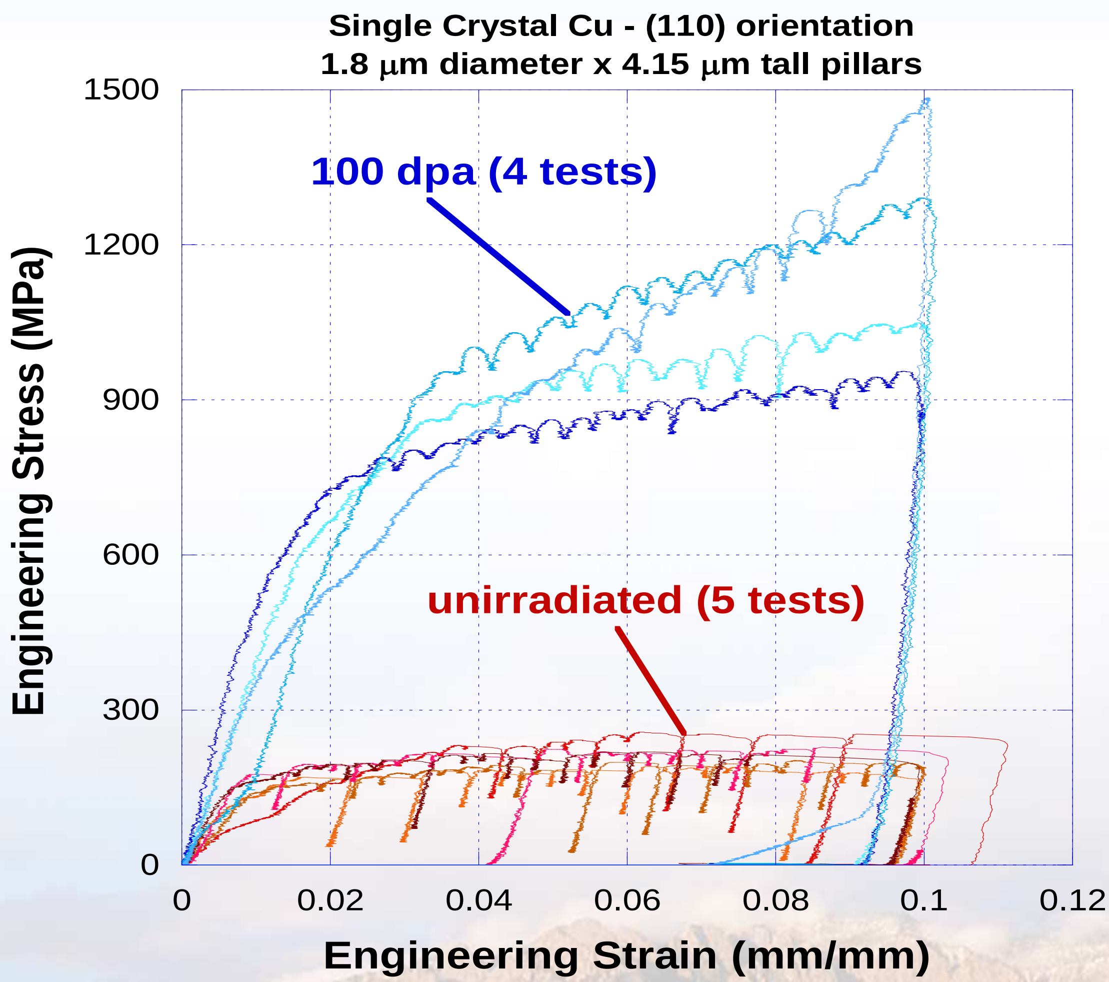
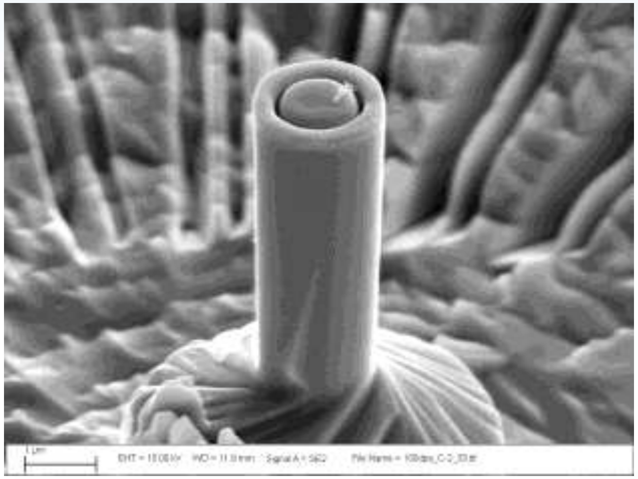
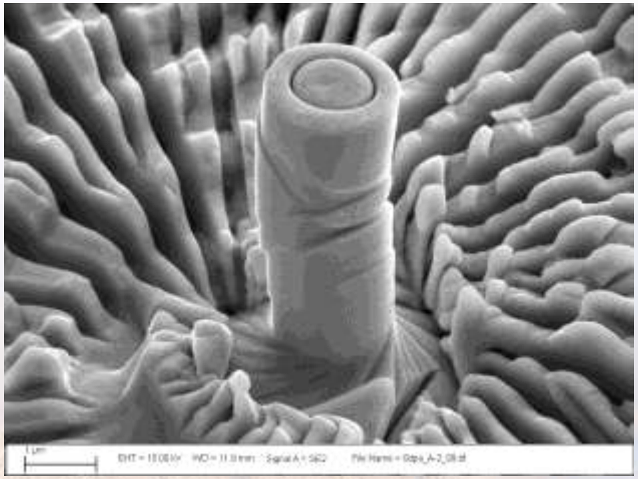
Small Micropillar Compression



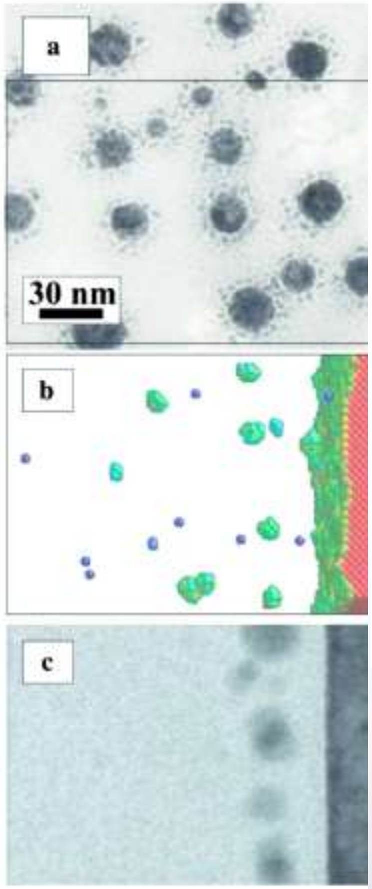




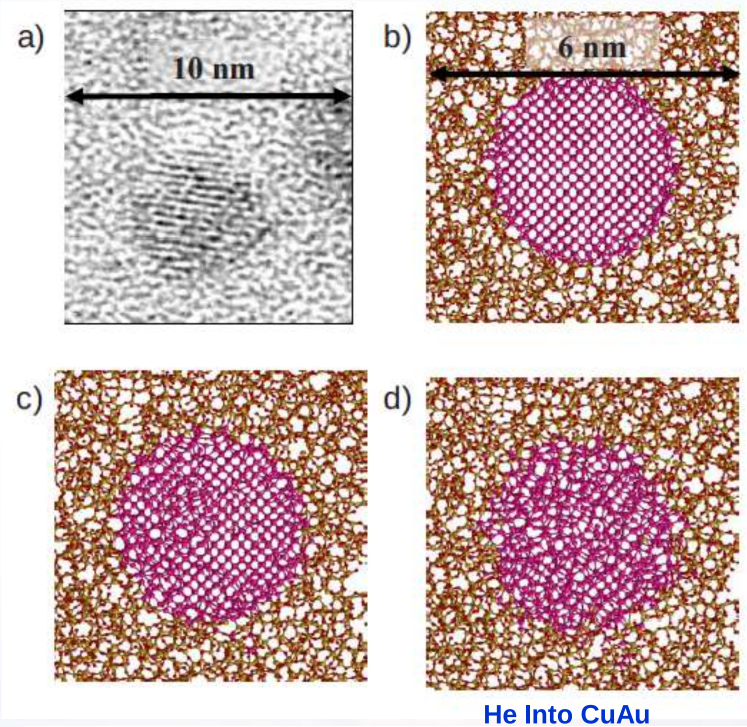
Initial tests indicate that the 4 μm-tall pillars are 5 times stronger and show no signs of slip band formation

Radiation Modification to Nanocrystals

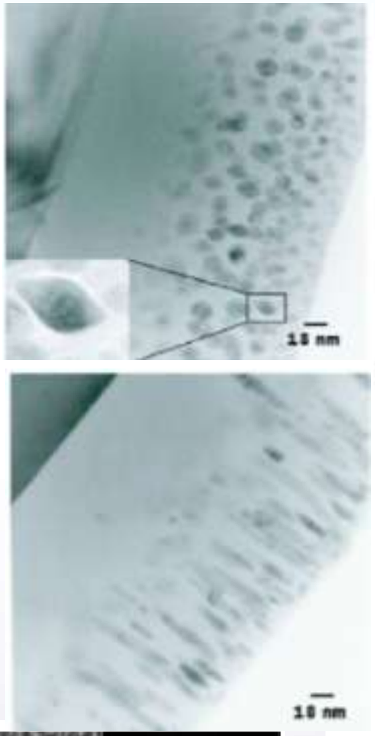
4 MeV Au into Au/SiO2



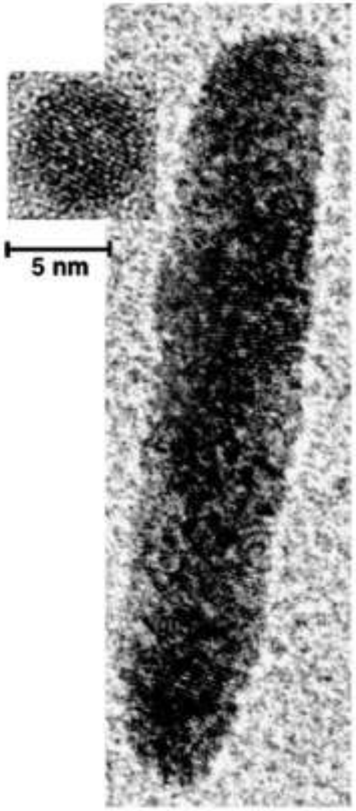
MD simulation of 4eV/atom Ge into Si



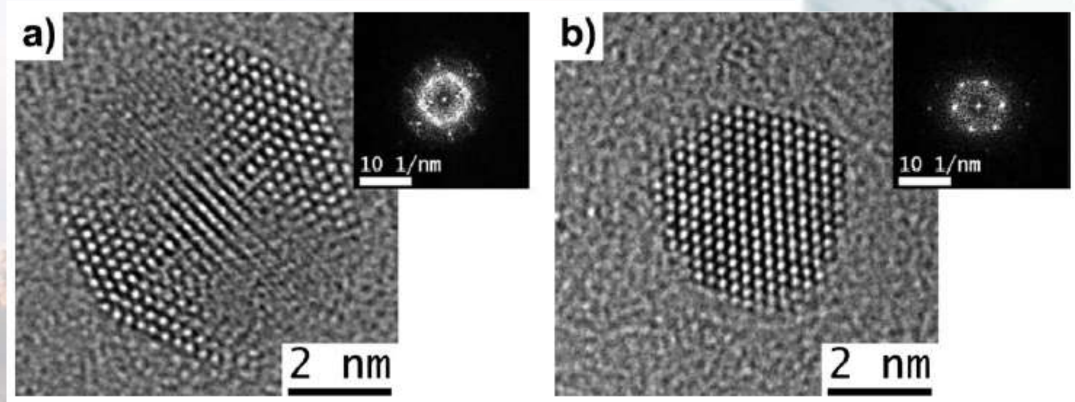
200 MeV into Co/SiO2



185 MeV Au into Pt



He Into CuAu



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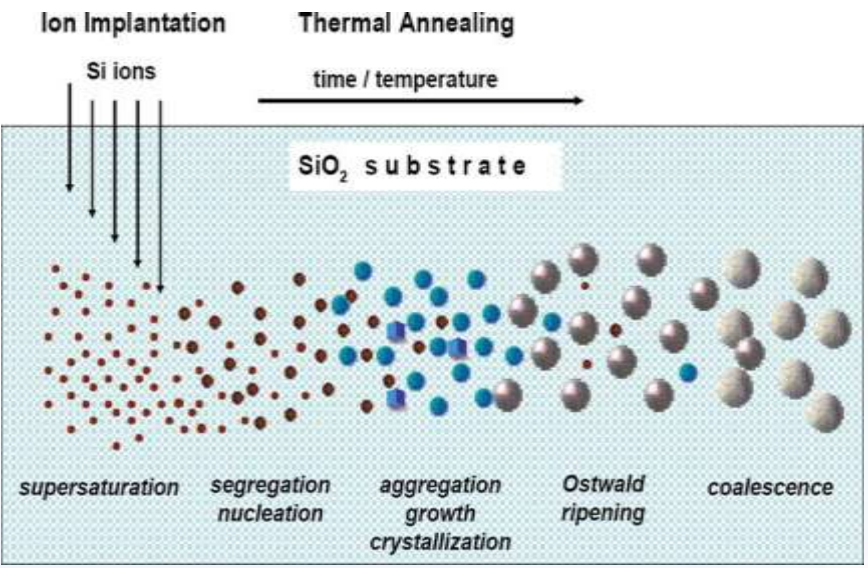
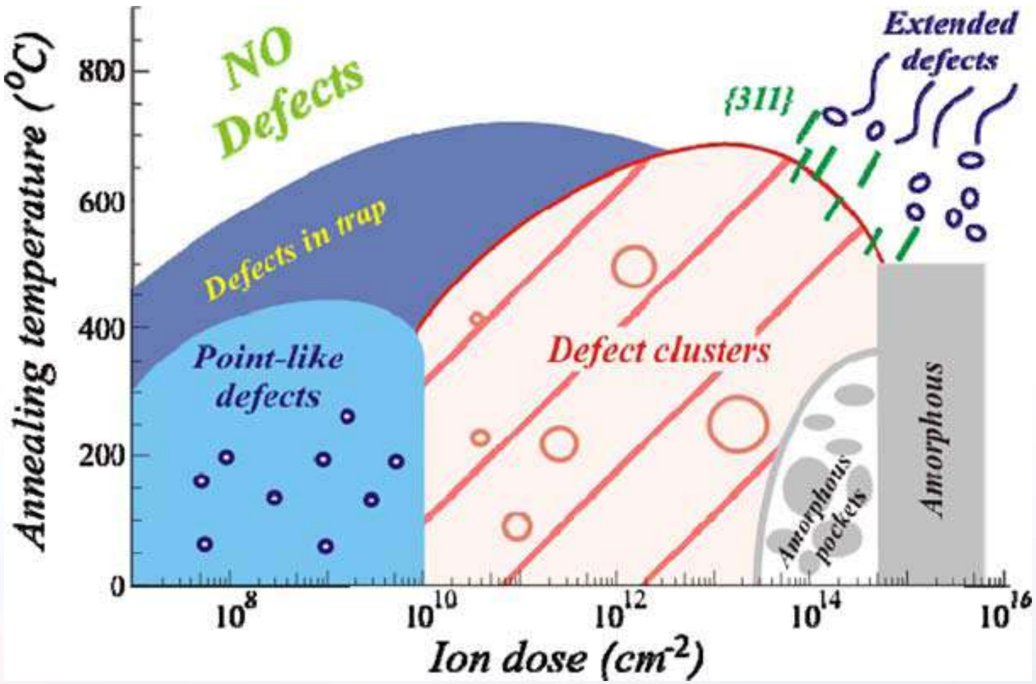
Potential Defect Structures





Combining detailed control of local dose and thermal history permits a wide range of microstructures that govern the resulting properties

H. Bernas "Materials Science with Ion Beams"

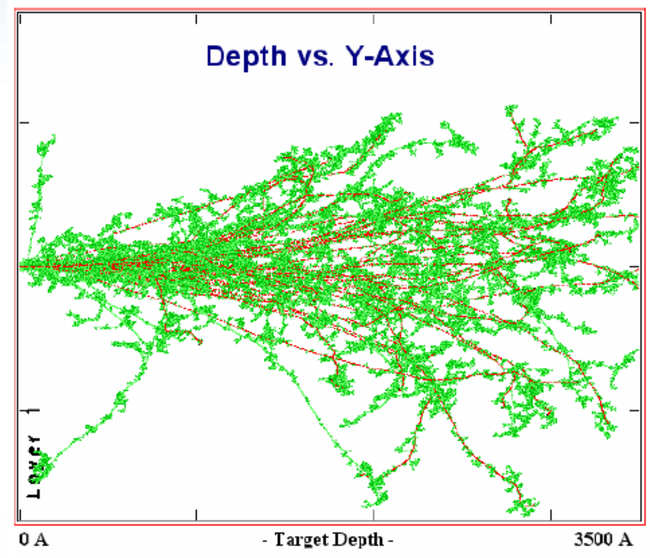
Length Scale Limitations due to Ion Irradiation

Advantages

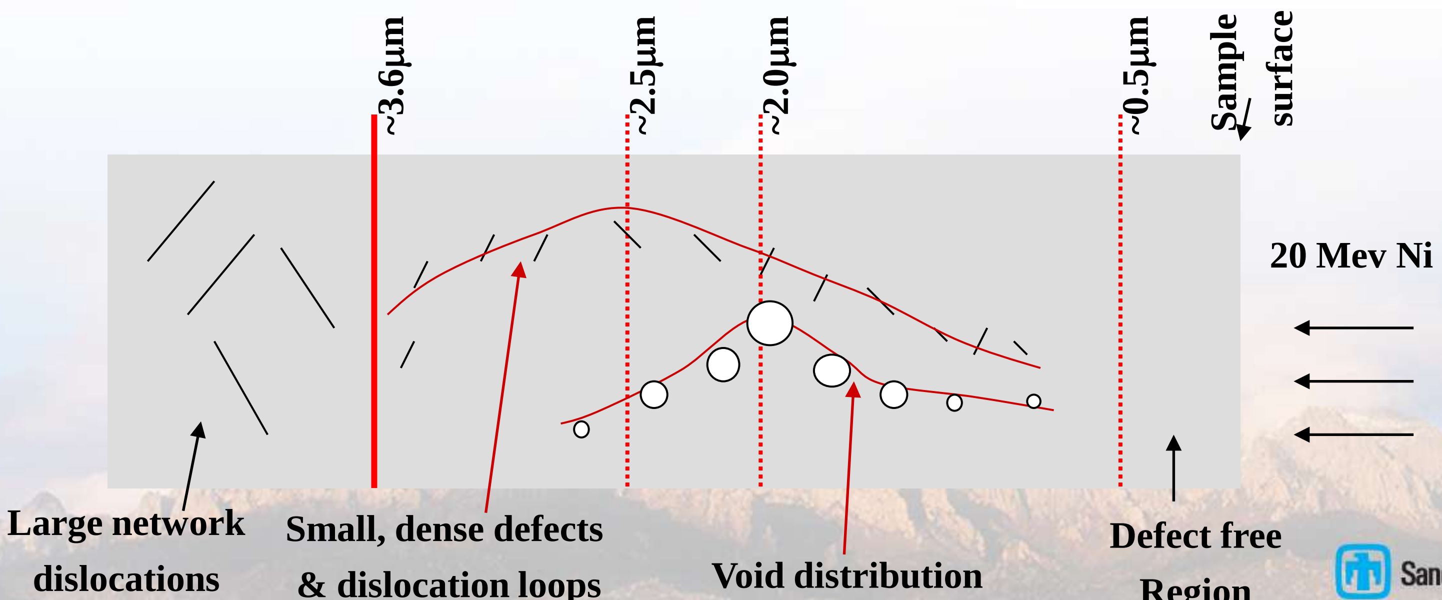
- High total damage in short periods of time
- Relatively accessible

Disadvantages

- Unknown effect of damage rate
- Limited to small volumes
- Heterogeneous microstructure



TRIM



Micropillar Compression Experiments

Sample Preparation:

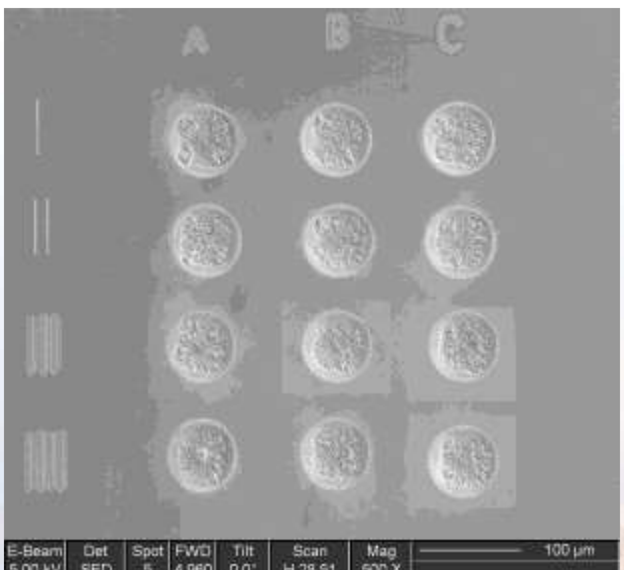
- Copper single crystals (FCC)
- Different crystallographic orientations: (100), (110), and (111)
- Self-ion Implants at 30 MeV to
- •0 (control), 50 dpa, and 100 dpa.

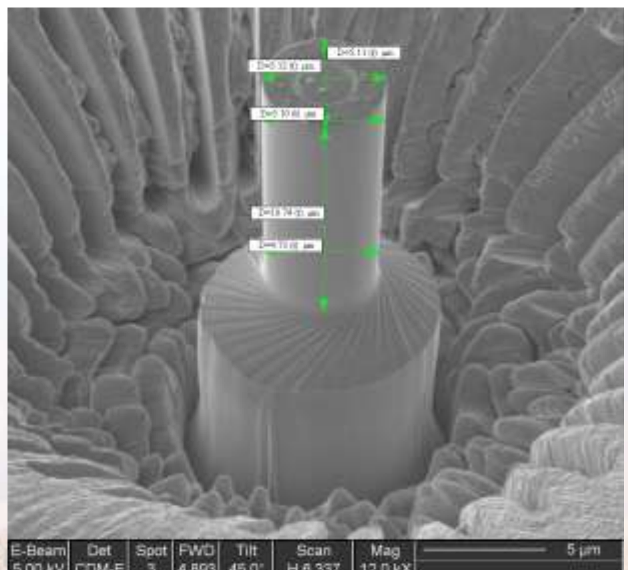
Pillar Manufacturing:

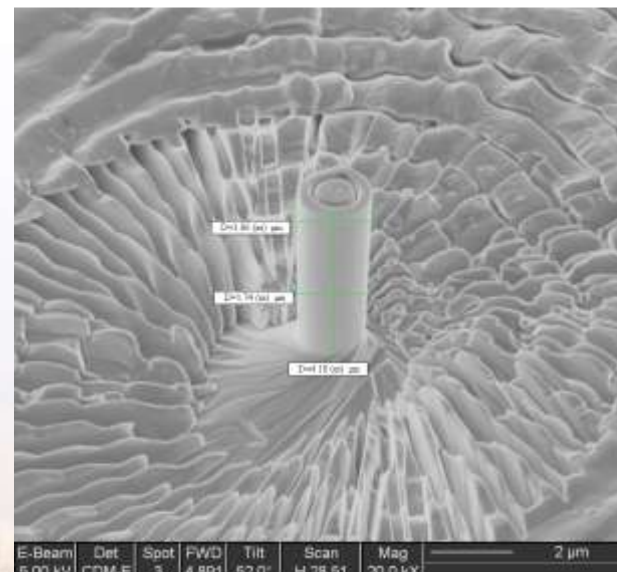
- We employ Uchic's FIB lathe machining process for straight-walled cylinders.
- Array of at least 9 nominally identical pillars tested per condition to assess statistical variability.
- •Height varies from 4 μm to 10 μm

Compression Testing:

- •Hysitron Performech Nanoindenter permits <1 nm and <1 μN resolution.
- •25 μm flat ended cone indenter in feedback displacement control, rather than typical force control.
- •Pillars compressed 10% strain at a strain rate of $0.025\ s^{-1}$.







Testing of Irradiated Stainless Steels

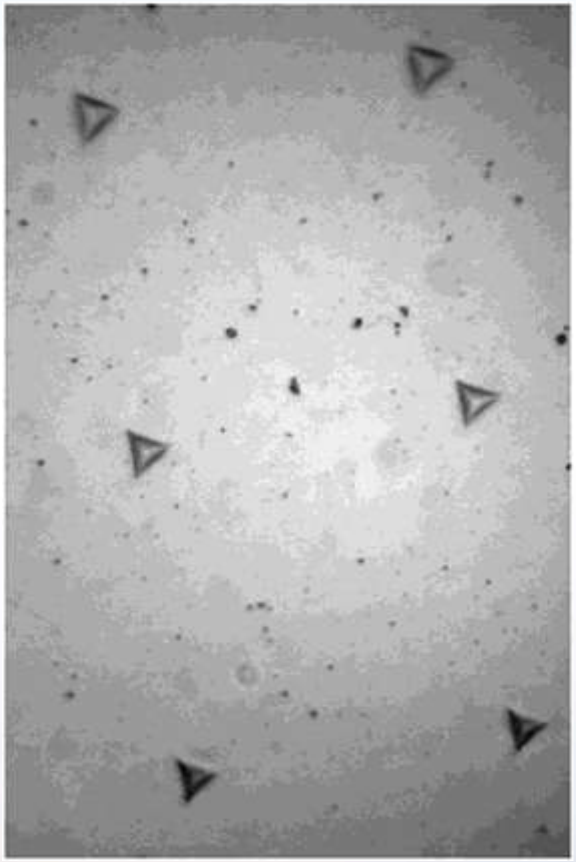
- Micropillar is difficult for many polycrystalline materials
  - Due to the dependence of FIB milling rate on orientation

To validate the approach:

1. Metals previously tested by Neutron Irradiation must be tested
2. The effect of temperature and various ion characteristics must be considered

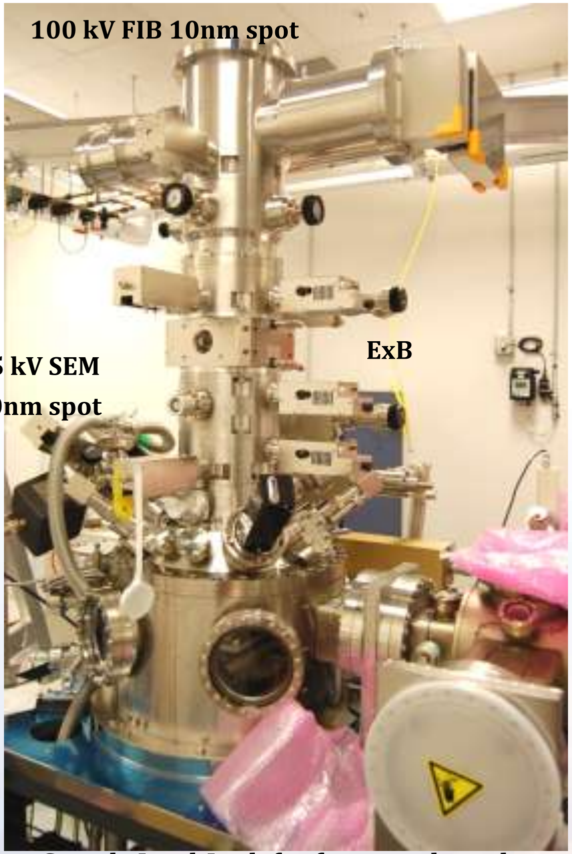
Thus, we irradiated

- 420, 409, and 316L SS
- Approximately 10 dpa, 40 dpa, and 100 dpa
- Temperatures of 400 ºC, 500 ºC, and 600 ºC



Three steel compositions were irradiated under various conditions. Nanoindentation was selected as the optimal small scale testing method.

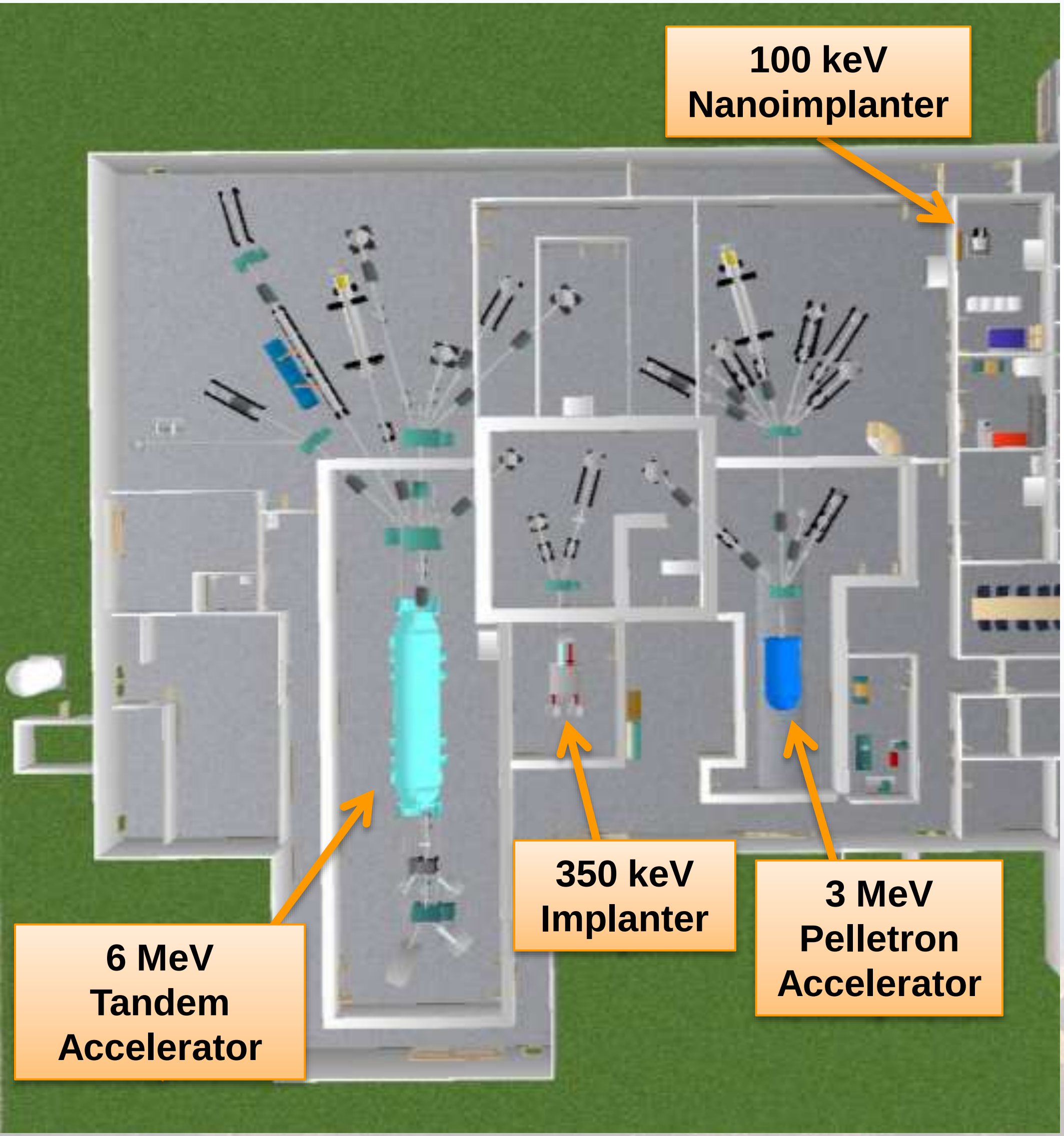
Nanoimplanter Specifications



Sample Load-Lock for fast sample exchanges

- **Combined Focused Ion Beam (FIB) and Scanning Electron Microscope (SEM)**
- **Acceleration Voltages up to 100 kV – higher energies allow for implantation and sub-surface modifications**
- **Ion Probe diameter less than 10 nm at 1 pA at 100 keV for Ga+**
- **Multiple Ion Species to include Ga, Si, Be, Au, etc... using LMIS - allows for wide range of ion species to be available for applications**
- **ExB Filter – allows for multiple charge states and ions to be resolved for example AuSi – Au+, Au++, Si+, Si++**
- **Internal sample stage 100 mm of travel with 2.5 nm resolution**
- **Focused ion beam implantation and lithography using Raith ELPHY, gas assisted etching/deposition**
- **In-house LMIS Preparation Unit**

Incorporation into Ion Beam Lab User Facility



Potential Capabilities:

- Leveraging a Sandia User Facility
- Multiple Ion Beam Capabilities
- Outside Limited Area

Benefits to NA-22 Users:

- Dedicated beamline
  - Reduced time/cost for experimental set-up, permitting rapid feedback
- Direct correlation of PL, CL, and IBIL data
- Simulation of energy range associated with nuclear materials by:
  - Tunable excitation energies of laser, electrons, and ion beams
  - Tunable gamma source
- Complete and systematic characterization of advanced materials
- Unified characterization technique for the scintillator field

IBIL Application to Various Scintillators

Application Requirements

1. **Emission wavelength that matches detector optimal wavelength**
2. **High efficiency (at least one photon per event)**
3. **Tailored luminescence decay time**
4. **Easy to manufacture**
5. **Controllable dimensions**
6. **Tolerant to ambient and extreme enviroments**
7. **Tolerant to various radiation dosages**
8. **Predictable and homogenous response to radiation exposures**

Availiable Scintillators

1. **Organic Scintillators**
   - Bicron, etc.
2. **Doped Cermaic Scintillators**
   - P46, P47, etc.
3. **Semiconductor Scintillators**
   - GaN, etc.
4. **Research Scintillators**
   - MOFs
   - Nanoparticles

Little is reported in the literature on the luminescence properties of any scintillators during ion or neutron irradiation