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Title: Irradiation response and stability of nanoporous materials

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Irradiation Response and Stability of Nanoporous Materials

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Outline

Motivation

Theoretical Prediction

Experimental Observation

MD Confirmation

Conclusion and Future Work

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What are Nanoporous Materials?

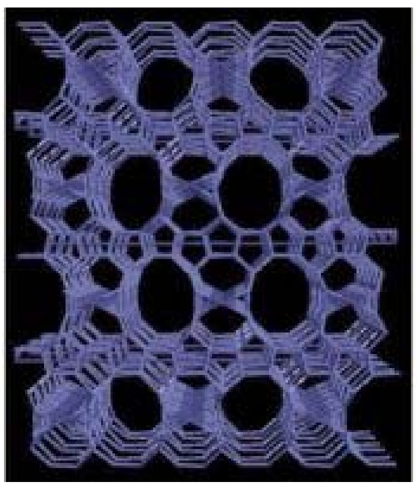
Wikipedia: Nanoporous materials consist of a regular organic or inorganic framework supporting a regular, porous structure. Pores are by definition roughly in the nanometre range, that is between 0.2 nm and 100 nm.

Subdivisions: Nanoporous materials can be subdivided into 3 categories (IUPAC):

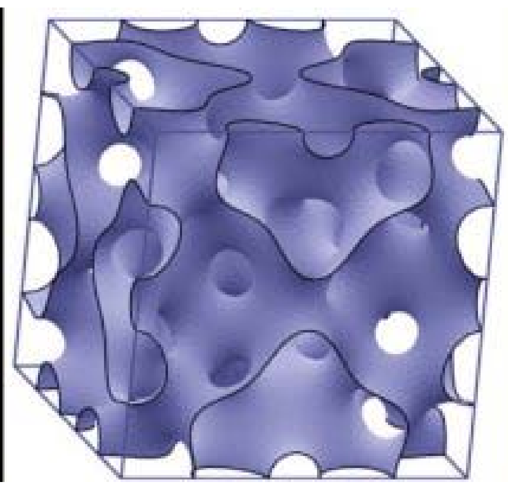
Microporous materials: 0.2–2 nm

Mesoporous materials: 2–50 nm

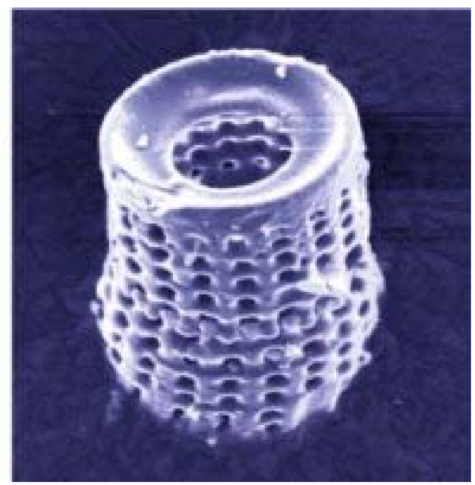
Macroporous materials: 50–1000 nm



Microporous titanosilicate ETS-10



Mesoporous SBA-1



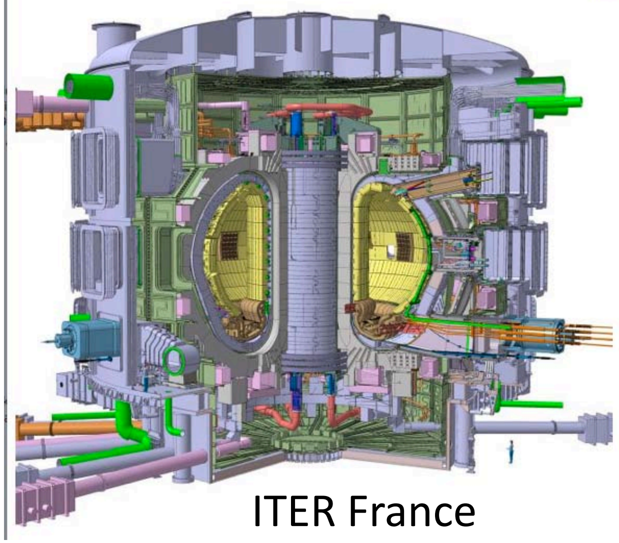
Macroporous diatomaceous earth

(Courtesy of *The University of Manchester, UK)*

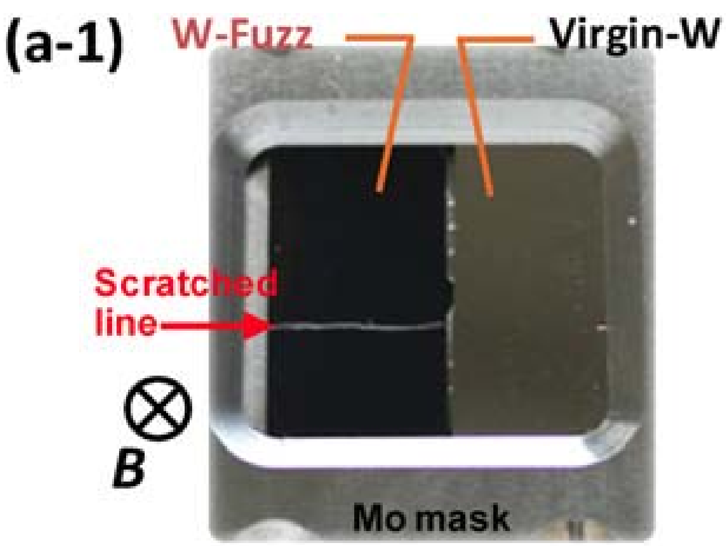
Radiation Damage Effects in Nanoporous Materials: Magnetic Fusion Design - ITER

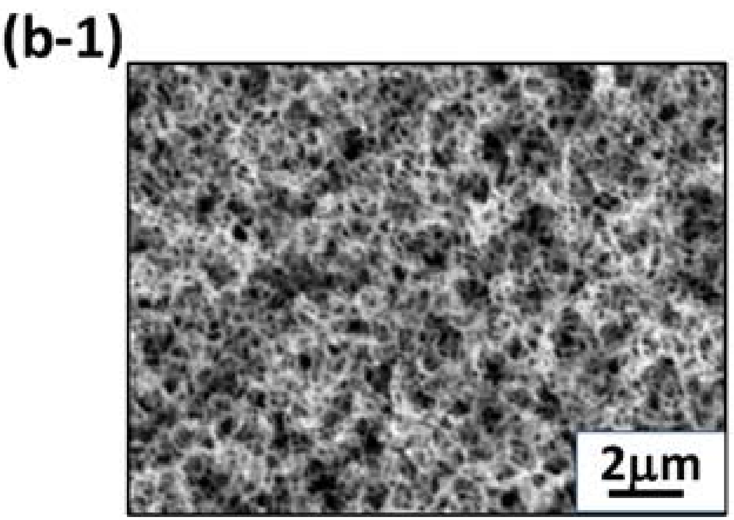
Radiation damage induce porous structure in tungsten in ITER

- **Nanoporous tungsten created in the linear divertor simulator**
- **Growth of nanometer-sized fiberform structure (W-fuzz) observed in PIECES**



ITER France





Temp. 1000-2000 K

Helium ion E > 20 eV

Tokitani, et al. Nucl. Fusion 51 (2011) 102001

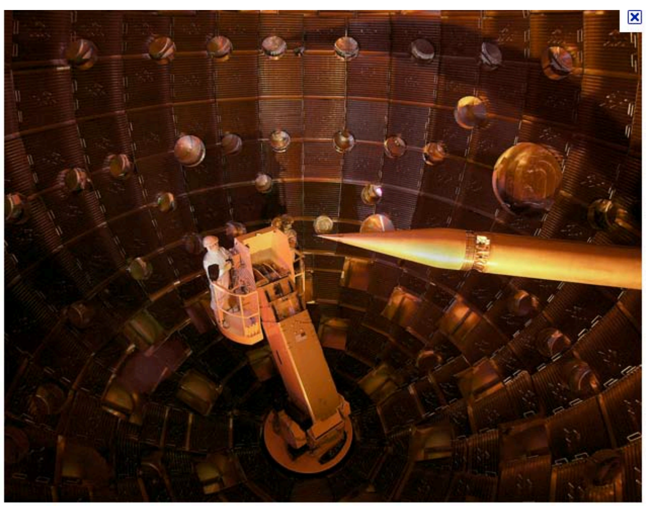
Radiation Damage Effects in Nanoporous Materials: Inertial Confinement Fusion Design - NIF

Nanoporous materials for hydrodynamic stability in NIF targets

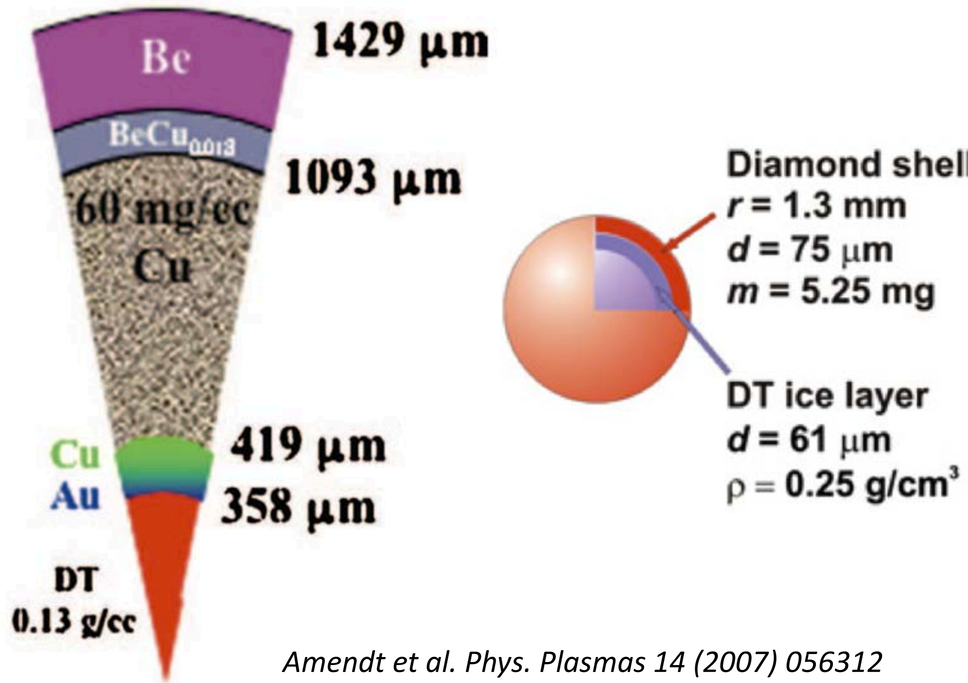
- Foam shells in DT capsule in inertial confinement fusion design
- Low-density nanoporous Cu
  - <100 mg/cc; cell size ~100 nm

Non-cryogenic NIF ignition target

- DT at RT
- Radiation effects might affect Cu foams performance during laser ablation and shell collision in NIF target



National Ignition Facility at LLNL

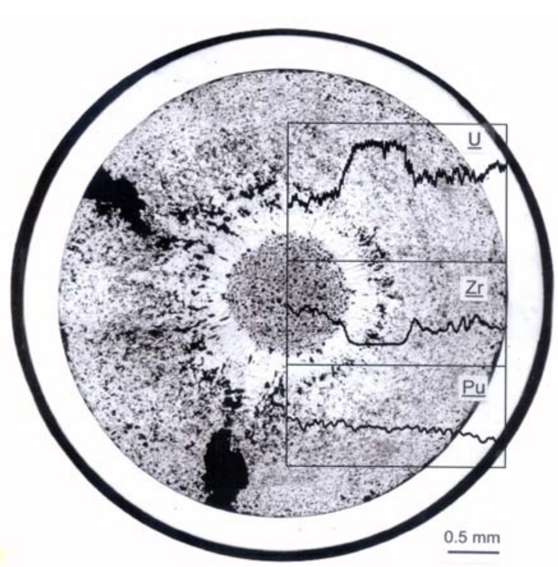


Amendt et al. Phys. Plasmas 14 (2007) 056312

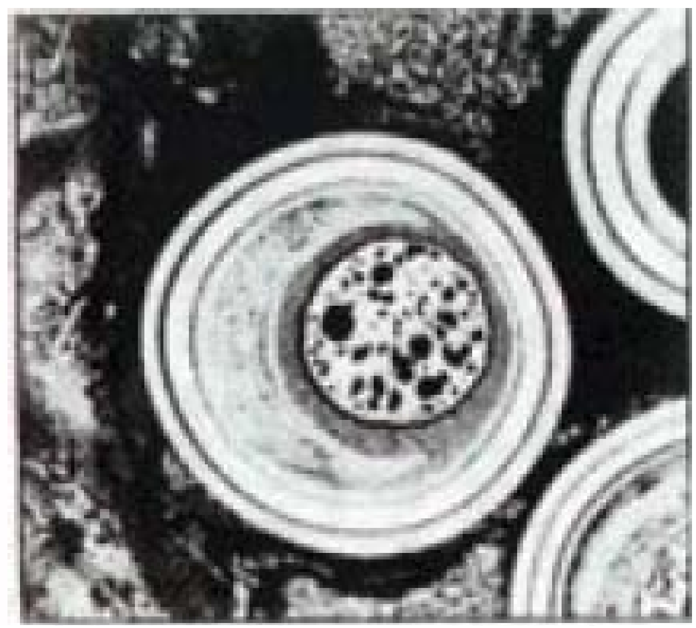
Radiation Damage Effects in Nanoporous Materials: Fuel in Fission Reactors & Nuclear Space Propulsion

- **Refractory Open-Cell Foam Fuel for High Energy Nuclear Space Propulsion**
- **Nuclear fuel foam patent for fission reactor fuel assembly**
- **Radiation damage in nuclear fuels produce foam-like structure**

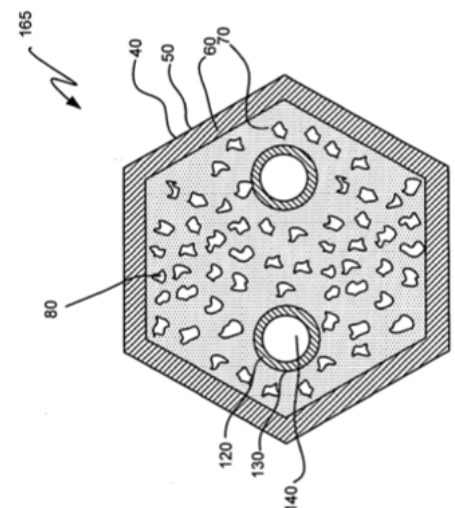
Fuel Pin in a Fast Reactor



TRISO Particle in Pebble Bed Reactors



US. Patent on Foam based Fission reactor fuel assembly



Nuclear fuel foam: Foam expands due to heat generation and fission gas release

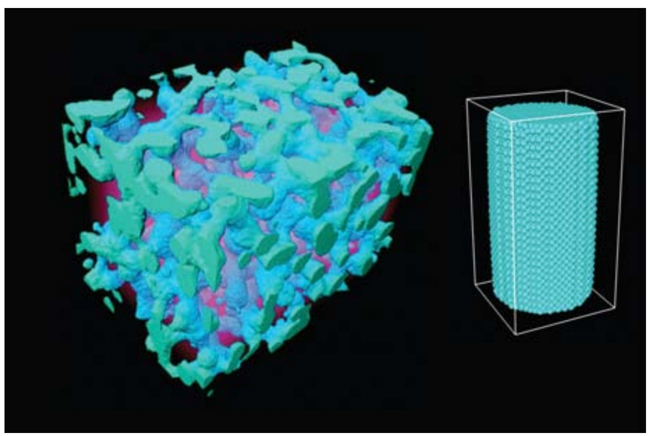
Radiation damage effects on nanoscale metallic foams: Theoretical Prediction

<u>Objective:</u> Explore the physics of surface-driven bulk physical behavior, such as radiation tolerance

<u>Opportunity</u>: Nanoporous materials could become a new class of extremely radiation tolerant materials

- **Nanoporous materials offer a large amount of free surfaces**
- **Free surfaces act as sinks providing opportunity for irradiation induced defects to annihilate through diffusion**

MD Computer simulation of np-Au foams and Au ligament



L. Zepeda-Ruiz in reference: Biener et al. NMAT 8 (2009) 47

Cover page Nano Letters July 2012

Atomic displacements larger than a_0 are shown
Red indicates more than 4 a_0

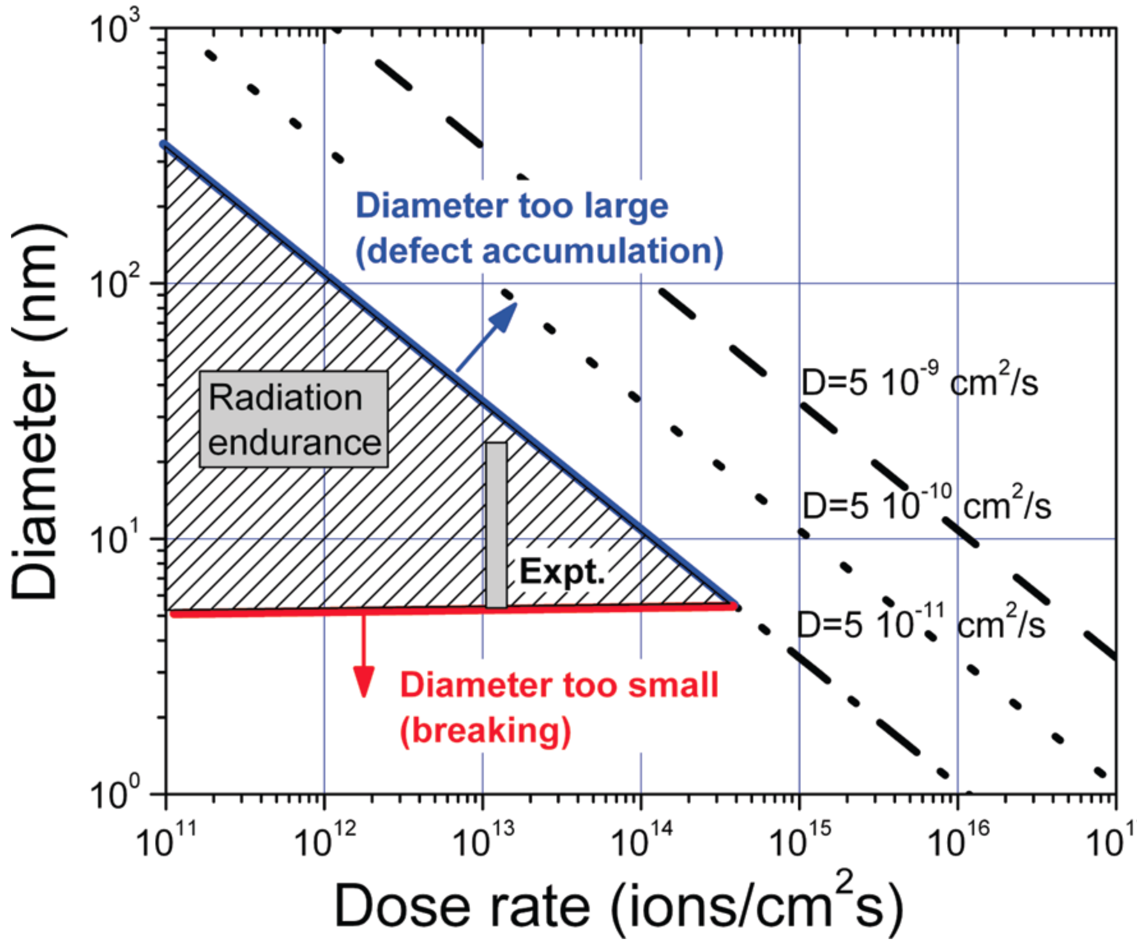
E. M. Bringa et al. Nano Letters, 12 (2012) 3351-3355

The model: Window of Radiation Endurance

There exists a window in the parameter space where nanoporous material shows radiation resistance

- **There exists an optimum ligament size at which radiation resistance occurs**

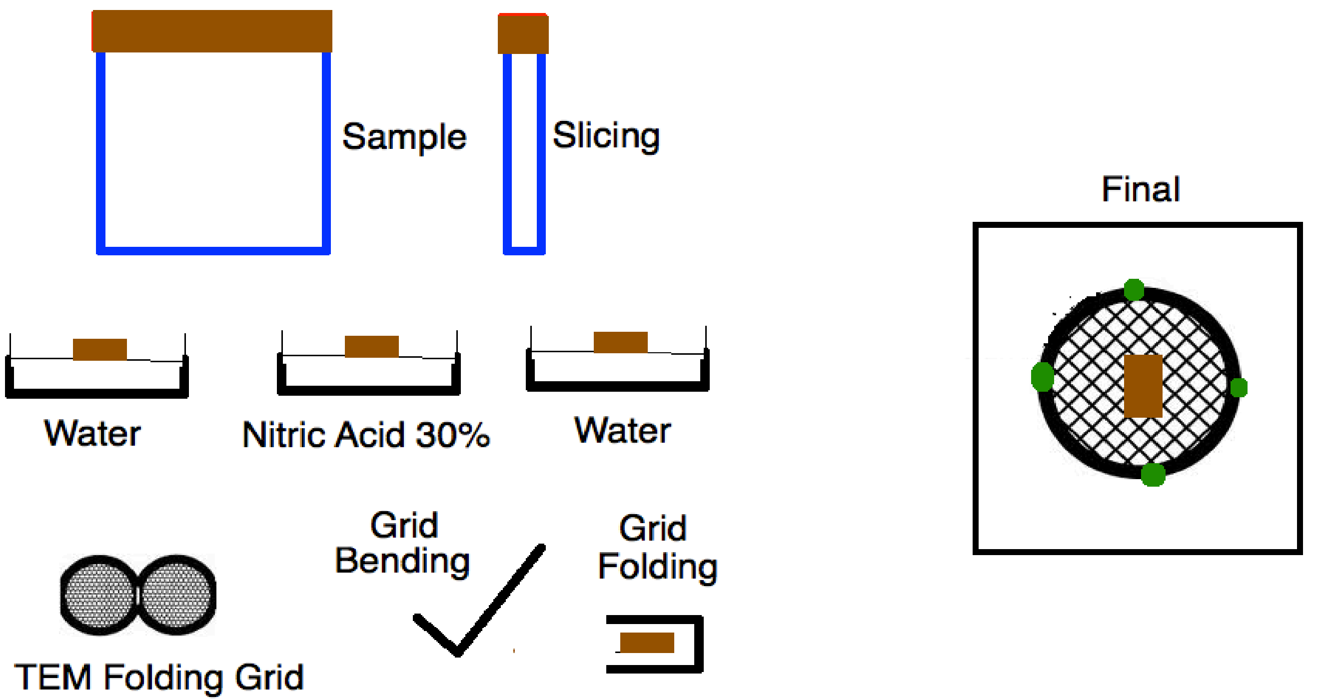
- **Defect migration to the ligament surface happens faster than the time between cascades, ensuring radiation resistance for a given dose rate**



E. M. Bringa et al. Nano Letters, 12 (2012) 3351-3355

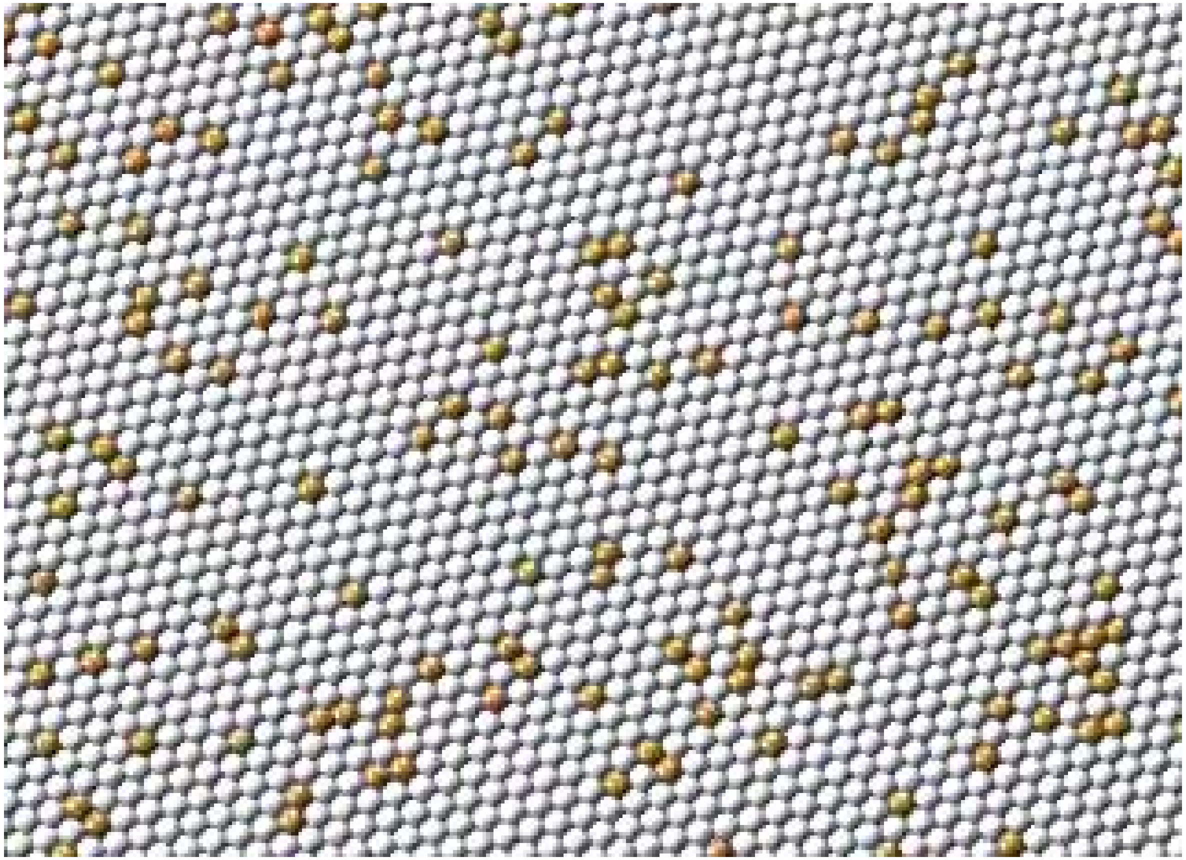
Experimental procedures: Schematics of np-Au foam specimen preparation

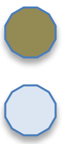
- **Synthesis of Au-Ag films:** E-beam evaporation (RT) on NaCl substrates
- **Synthesis of np-Au foams:** Dealloying Au-Ag films in diluted (40%) or concentrated (70%) nitric acid (HNO_3) with varying dealloying time (1h to 18h)



Dealloying process in Au-Ag thin films

Ag atoms dissolve layer by layer and Au atoms clump together and form "clusters"





Surface diffusion and dissolution events as simulated by the code MESOSIM

J. Erlebacher, Professor, Materials Science and Engineering Chemical and Biomolecular Engineering
http://p0217.projects.make-things.com/index.php/research/detail/fundamentals-of-dealloying

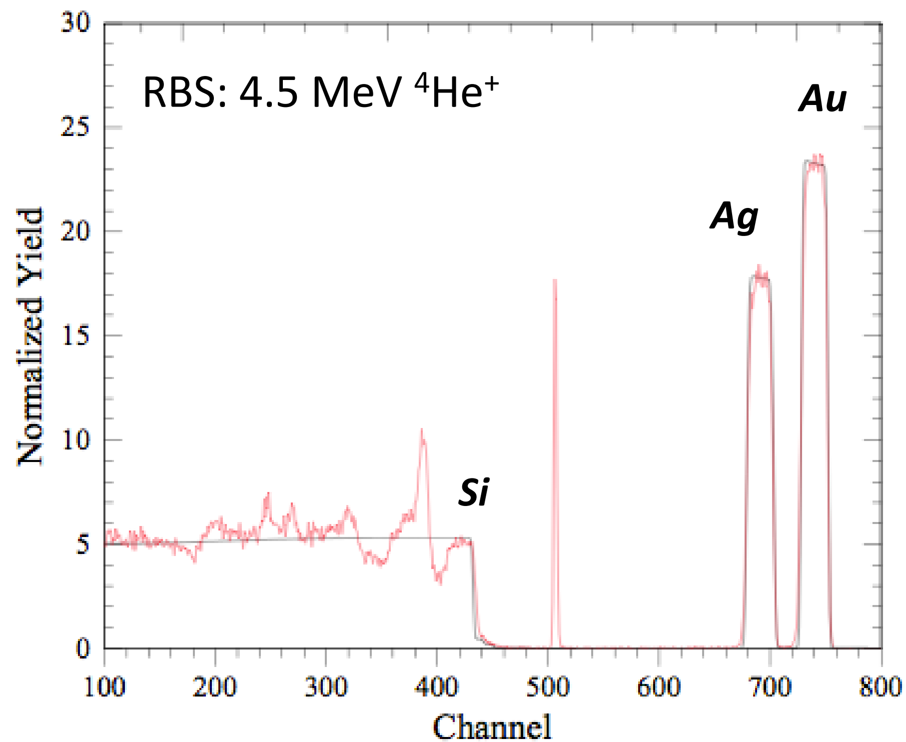
Optimizing Au-Ag Thin Film Thickness and Composition

Thin Film Fabrication

- Electron beam evaporation
  - Ag/Au co-deposition on single crystal NaCl (001) substrates
- Evaporation Conditions
  - Deposition Rate:
  - Ag 0.35 nm/s, Au 0.15 nm/s
  - RT, high vacuum < 5 x 10^{-8} torr
  - High purity Ag and Au > 99.9 %
- Variable thickness and Au%
  - 90 – 230 nm; 17 – 33 %Au
  - RBS with 4.5 MeV ^{4}He ions (red line)
  - Spectrum analysis (RUMP software) – black line

Au is uniformly distributed in thin film

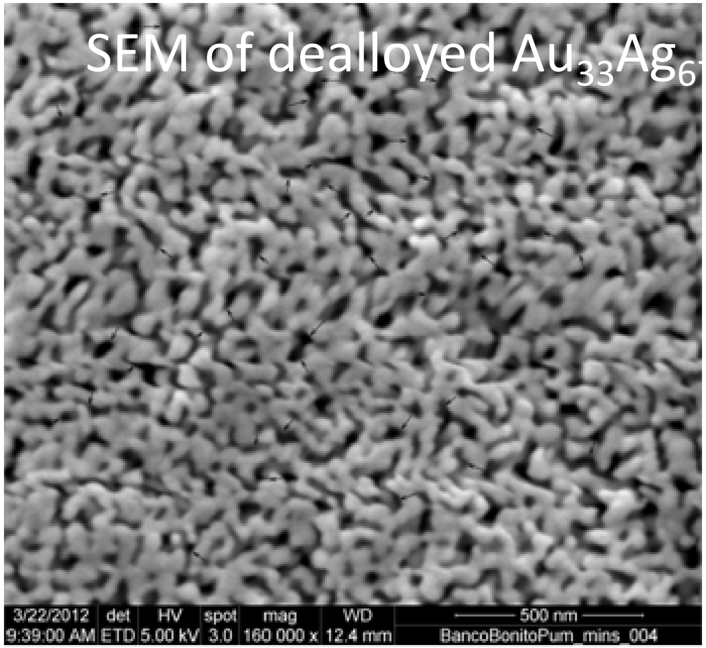
- RBS Example
- Thin Film Thickness ~ 160 nm
- Ag/Au Ratio ~ 7/3



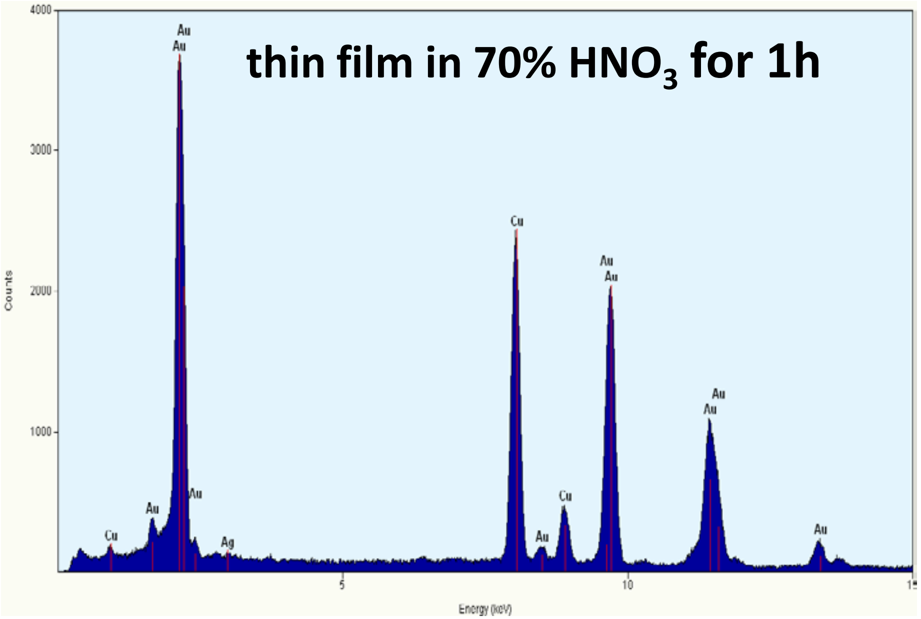
Characterization of non-irradiated np-Au foams

- SEM image shows uniform ligament network
- Open porosity; Ligament size ~ 26 – 42 nm

- Ag dissolution occurs early in the dealloying process
- EDS shows no Ag left after dealloying



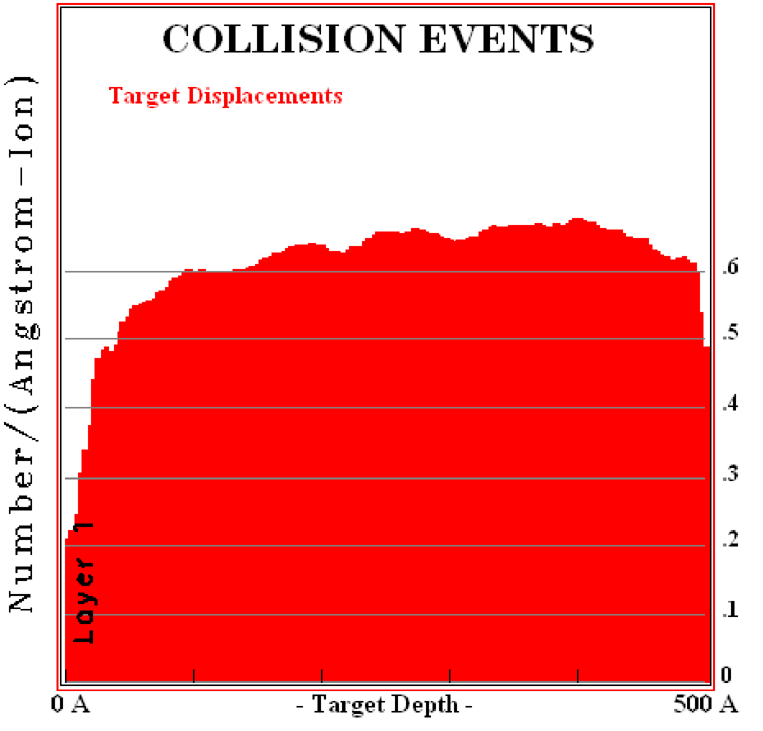
Thin film thickness ~ 230 nm
Etched for ~ 15 h in 40% diluted nitric acid



TEM Micrographs : FEI Tecnai 30, 300 kV
Oxford EDS system
SEM Micrographs: FEI Inspect F

Damage simulation by SRIM

- **400 keV Ne^{++} ions in ~ 50 nm thickness of Au**
- **High ratio dpa/Ne concentration:**
  Introduction of enough damage without forming Ne bubbles
- **Damage:** 0.65 number/(A-ion) corresponds to ~1 dpa in the range between 0 and 50 nm for a fluence of ~8.6×10^{14} ions/cm^2
- **Total damage accumulation:** 1 dpa
- **Ne Concentration:** < 0.03 at%

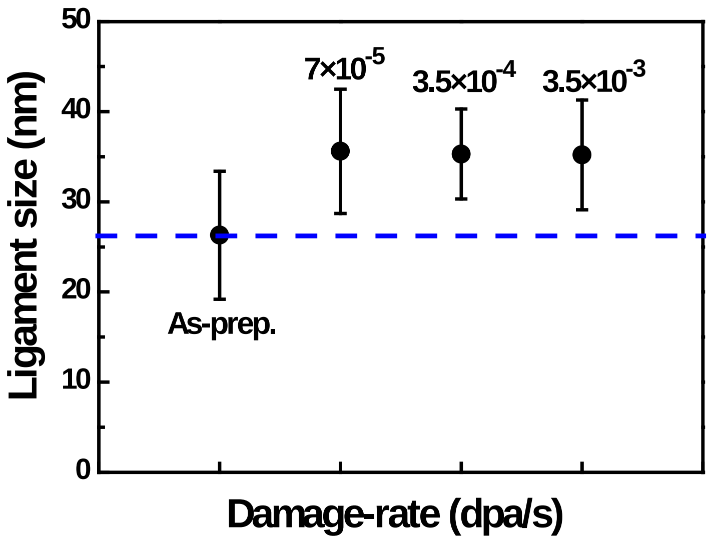


Studies on radiation response of np-Au

- **Irradiation parameters**
  - 400 keV Ne^{++} ions;
  - Total fluence: 8.6×10^{14} ion/cm^2
  - Total damage: 1 dpa
- **Temperature dependent study**

  Liquid nitrogen temperature (LNT) and Room temperature (RT)
- **Damage rate dependent study**

  3.5×10^{-3}, 3.5×10^{-4}, and 7×10^{-5} dpa/s



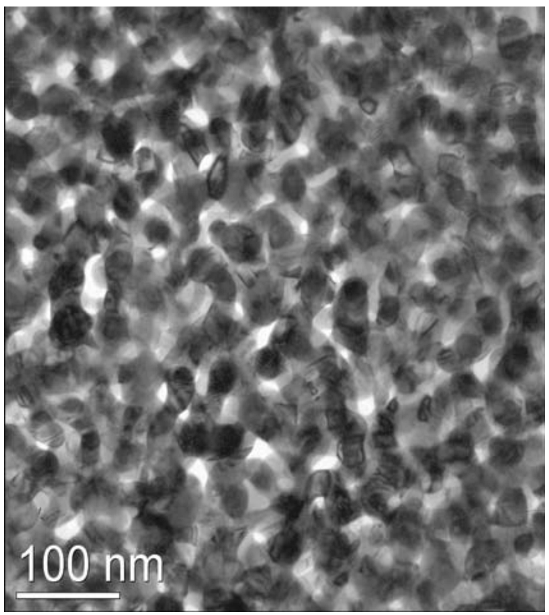
- **TEM studies on irradiated np-Au show the ligament sizes increases after irradiation (coarsening) but no apparent temperature dependence**

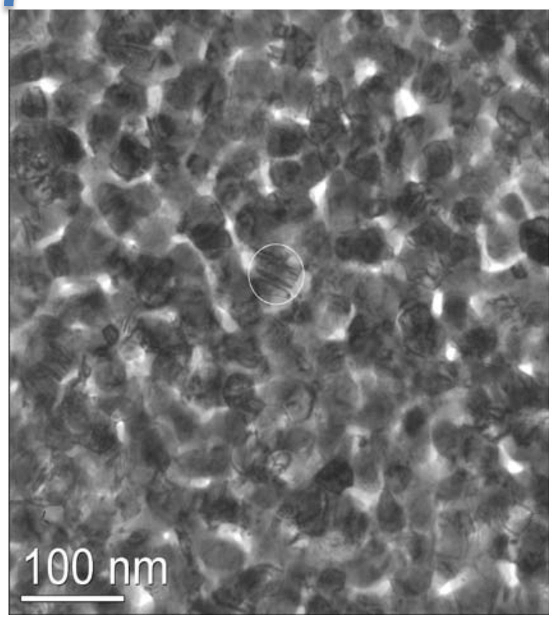
TEM before and after irradiation at LNT and RT

- The ligament network is still present after irradiation with 400 Ne^{++} ions
- Dose: ~ 1 dpa
- Highest dpa-rate: 3.5 x 10^{-3} dpa/s

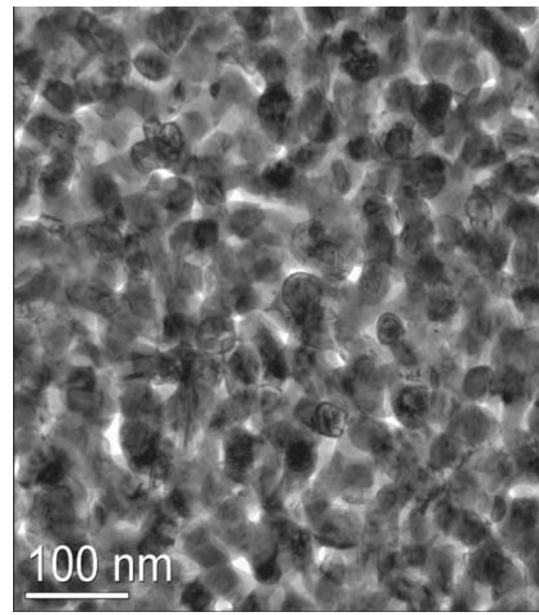
Irradiated np-Au foams

As-prepared np-Au





Liquid Nitrogen Temperature (LNT)

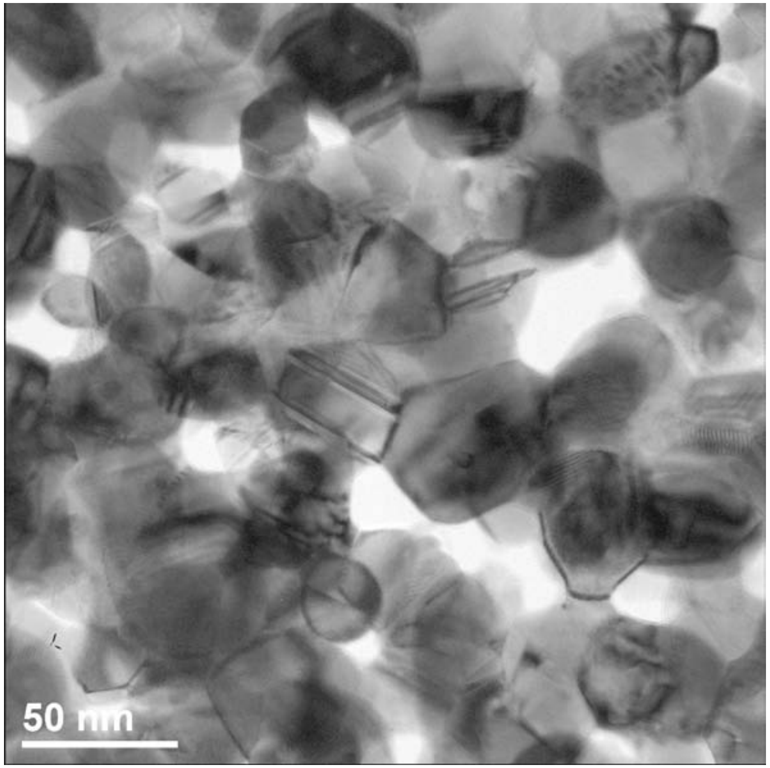


Room Temperature (RT)

Radiation effects on defect formation: TEM images of np-Au irradiated at RT to 1 dpa

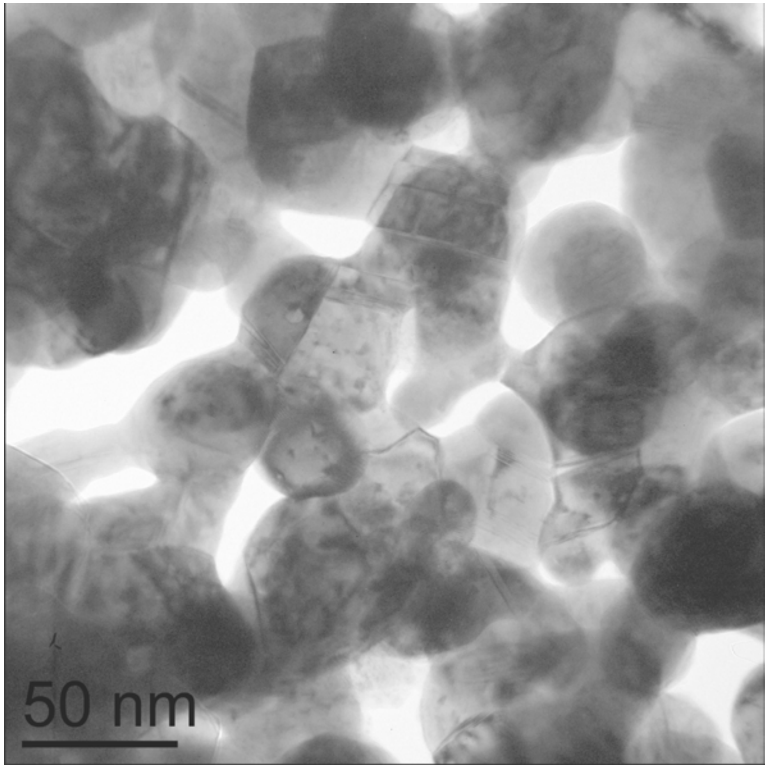
Non-irradiated Condition

- Pre-existing twins and stacking faults before irradiation

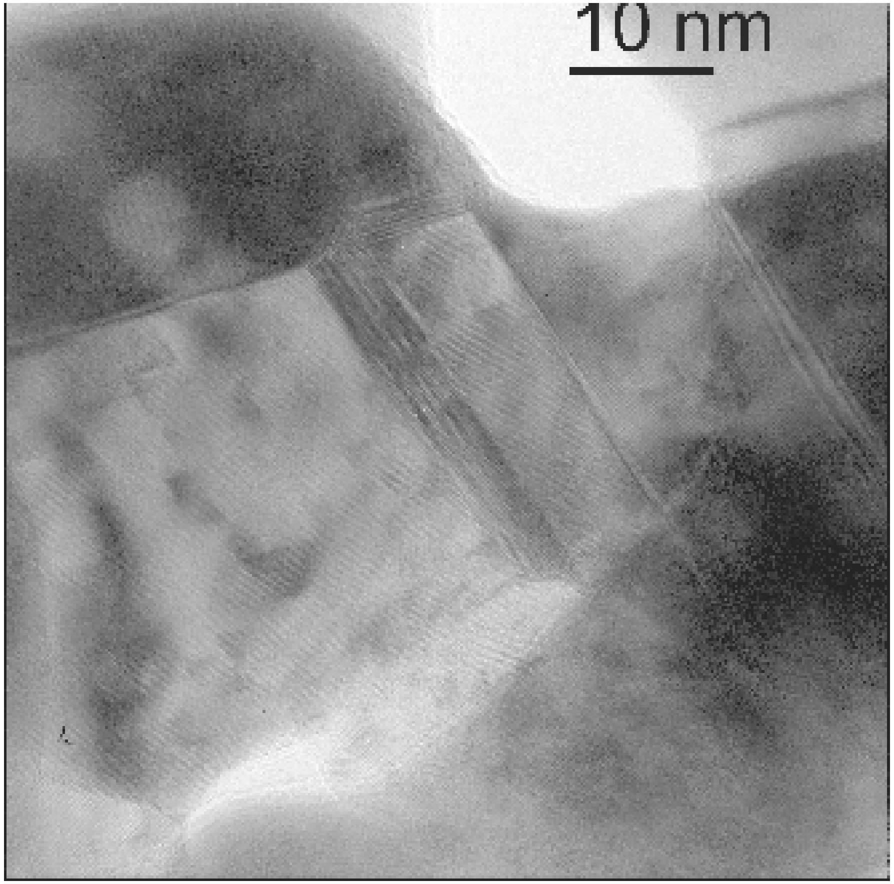


Irradiated Condition

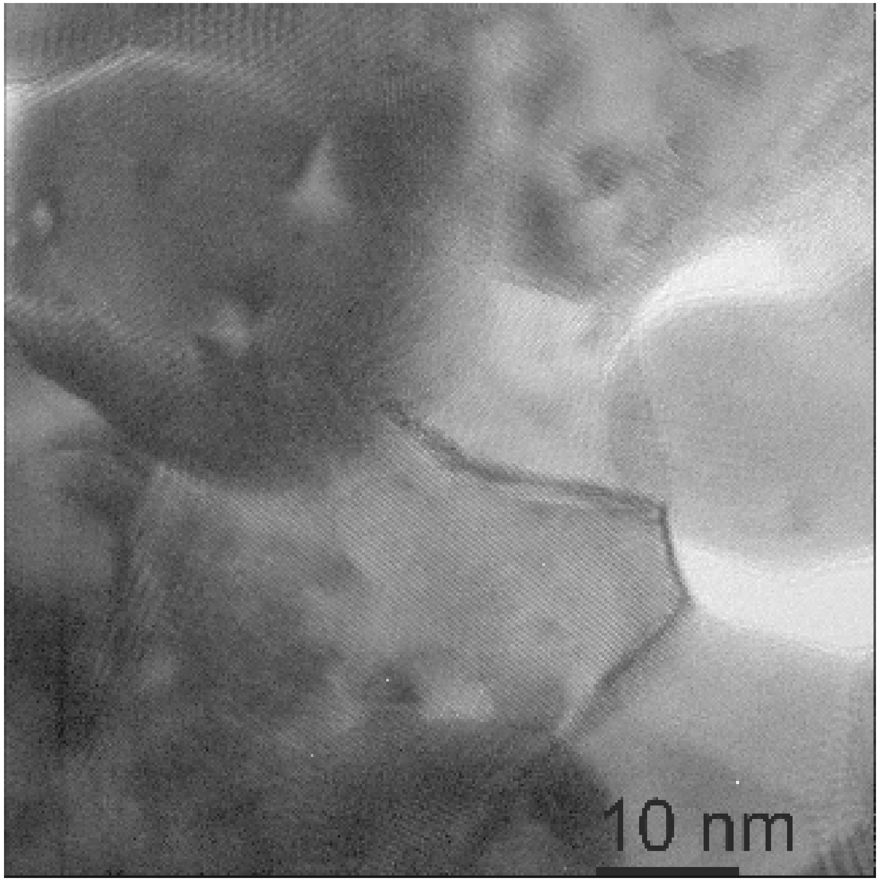
- Dark dots appear inside the ligament in the irradiated sample



HRTEM images of defect formation:
At RT: the formation of Stacking Fault Tetrahedra (SFTs)

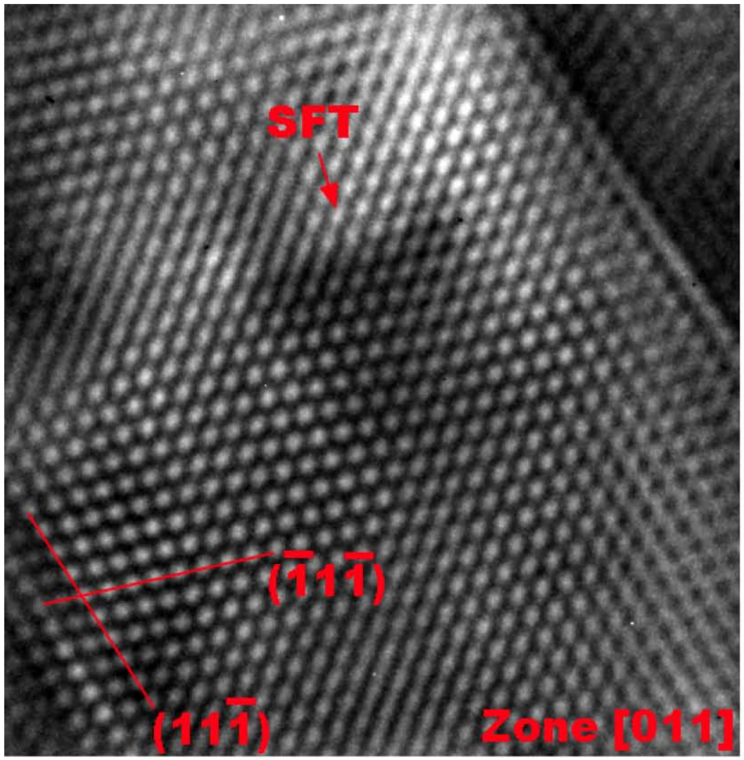


Twin Structure

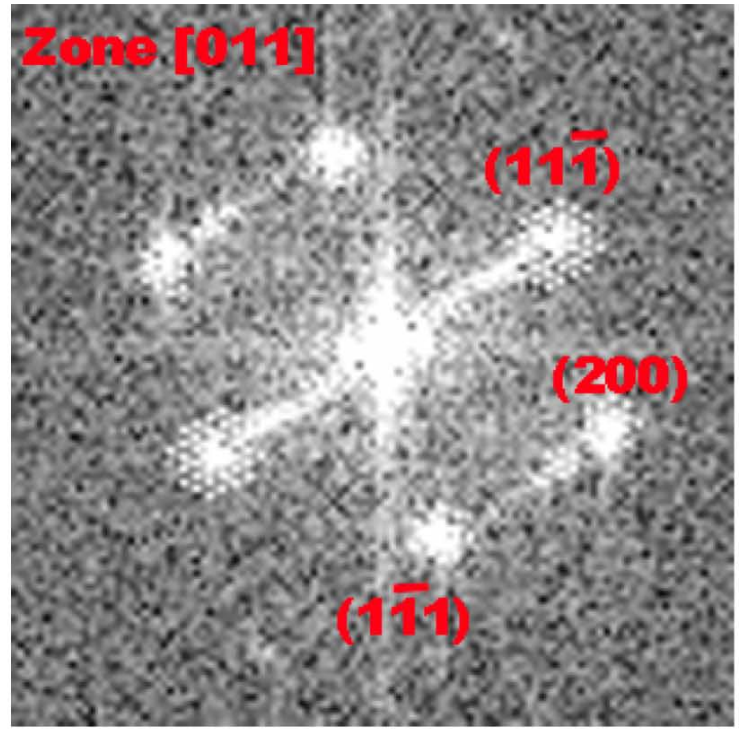


Grain Boundaries

HRTEM shows SFTs are formed in RT irradiated np-Au



(a)



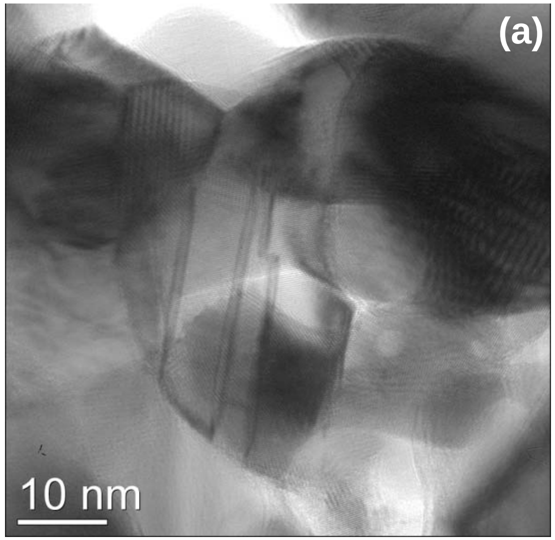
(b)

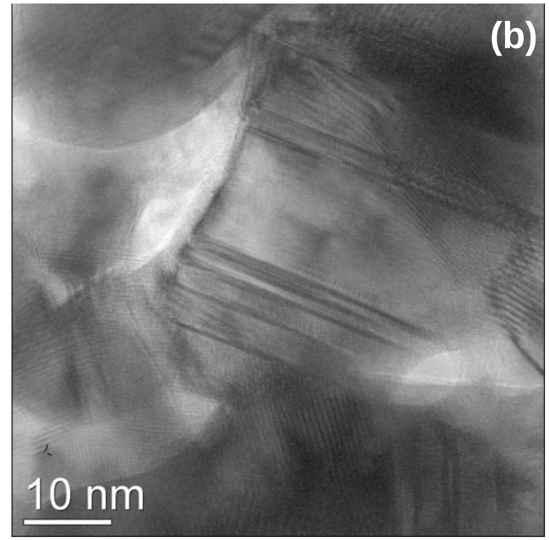
(Left) 5 nm large SFT along (110) projection and (Right) corresponding diffraction pattern with zone axis [011] for the highest dose rate of : 3.5×10^{-3} dpa/s.

HRTEM images of defect formation at different dose-rates

At RT: formation of SFTs under intermediate and highest dose rates

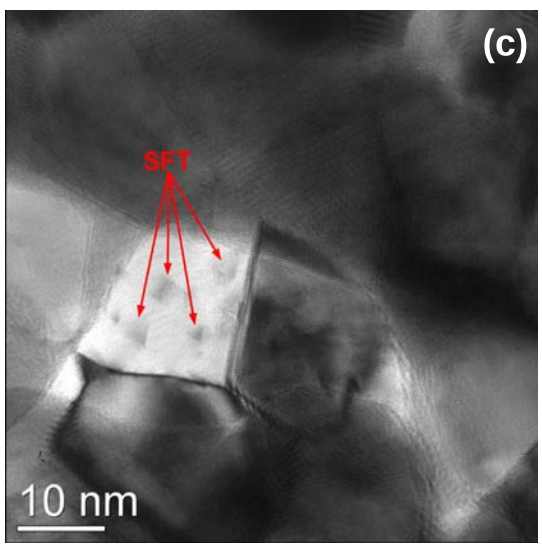
As-prepared

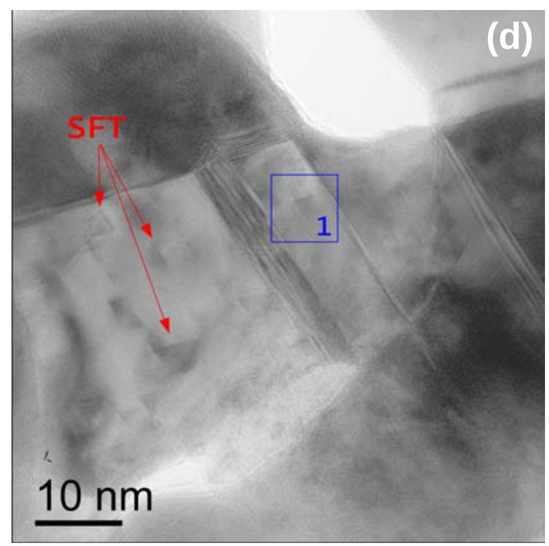




$7x10^{-5}$ dpa/s

$3.5x10^{-4}$ dpa/s

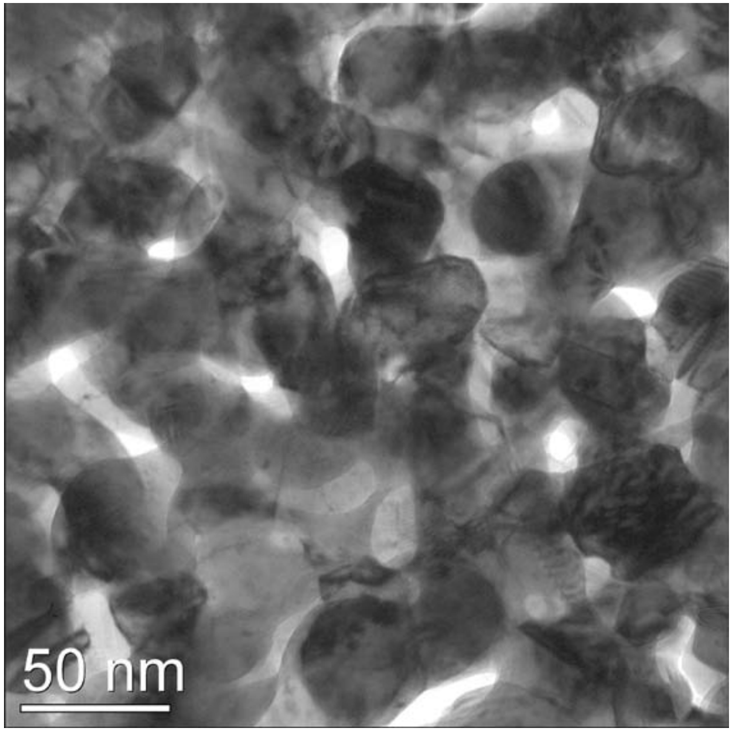




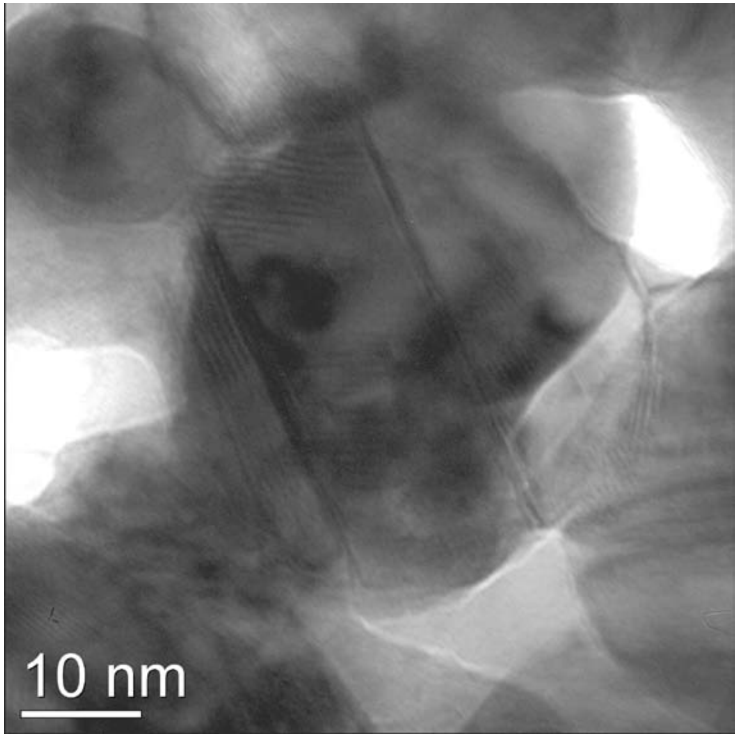
$3.5x10^{-3}$ dpa/s

TEM and HRTEM image of defect formation:
At LNT: No formation of SFTs at the highest dose rate

TEM



HRTEM

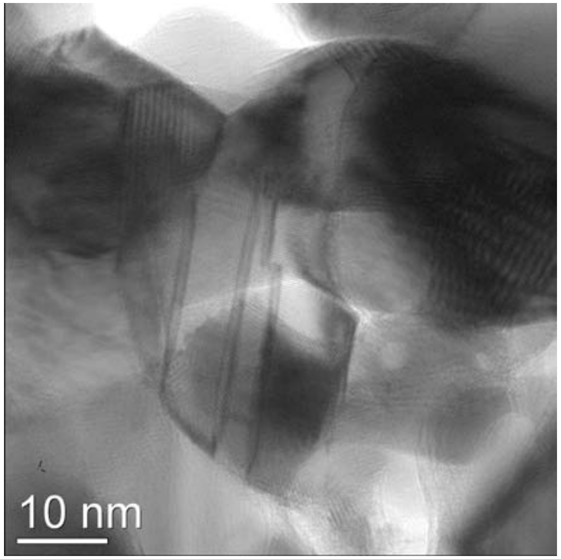


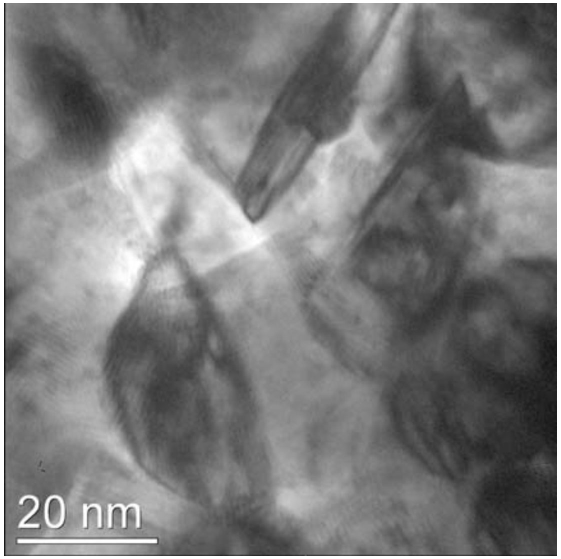
No SFTs are formed in np-Au after irradiation at LNT temperature

HRTEM image of defect formation at different dose-rates

At LNT: no formation of SFTs under different dose rates

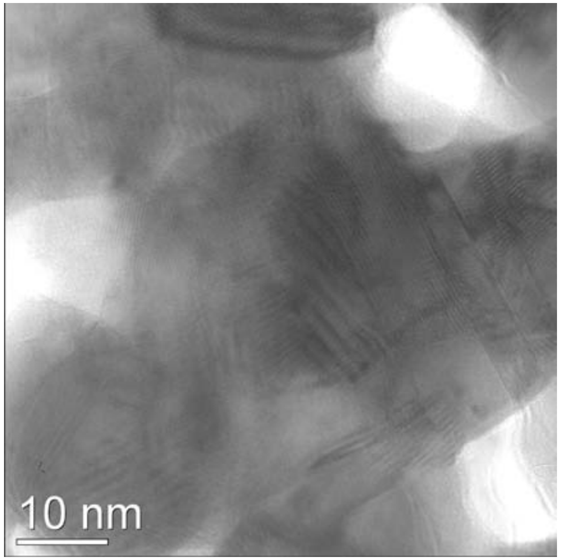
As-prepared

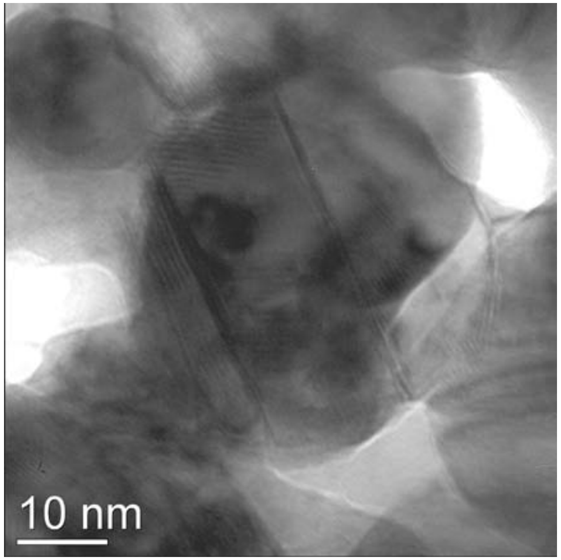




7x10^{-5} dpa/s

3.5x10^{-4} dpa/s





3.5x10^{-3} dpa/s

Discussions on experimental observations

Temperature effect:

- **RT allows vacancies to form SFTs at high dose rate**
  - **At RT vacancies easily diffuse, accumulate and form SFTs**
- **Vacancies were frozen at LNT**
  - **Vacancies cannot diffuse to agglomerate and collapse to form SFTs**

Dose rate effect:

- **Low dose rate offers enough time interval for SIAs and vacancies to diffuse to the surface or to recombine**
- **High dose rate allows vacancies to form SFTs before diffusing to the surface or recombining with SIAs since the rate of defect creation is high**

Estimates based on rate theory and diffusion rate

- The time between cascades depends on the dose-rate (R) and represent cascade volume (L^3), where L is the ligament diameter. MD simulations for Au cascades in Au ligaments suggest that each cascade produces ~10 displacements. Thus the time between cascades can be defined as:

  t = 10/(dose-rate * number of atoms)

- Vacancy migration distance can be estimated from Einstein relation:

  $$\langle r^2 \rangle = 6Dt$$

  where $\langle r^2 \rangle$ represents the mean-square distance traversed by the diffusing vacancies.

- For a given system, vacancy diffusion coefficient in pure gold at RT: D = 5 x 10^{-9} cm^2/s, and ligament diameter L = 25 nm, corresponding to a total number of atoms in the cascade volume: 9.2 x 10^5 atoms.

Dose-rate (dpa/s)	7.0×10^{-5}	3.5×10^{-4}	3.5×10^{-3}
Time between cascades (sec.)	0.095	0.019	0.002
Vacancy migration distance (nm)	76 (> L)	34 (~ L)	11 (< L)
SFT formation at RT	No	Yes	Yes

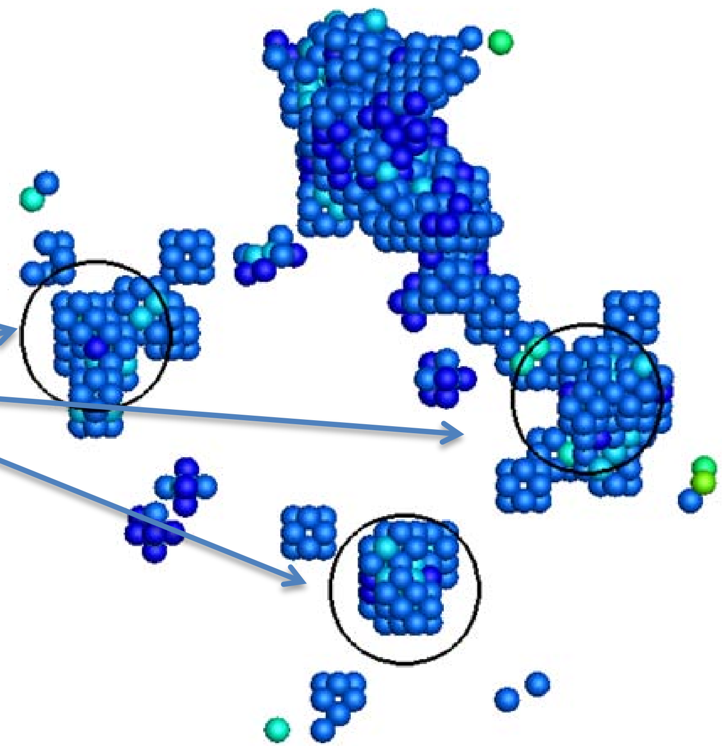
Molecular Dynamics simulations confirm damage accumulation and formation of several SFTs in Au ligaments

MD simulations of defect formation in Au ligaments under irradiation

- Steps in the simulation
  - RT equilibration (~ 2000 steps)
  - Followed by collision cascades
- Several 1.5 keV PKAs initiated at the ligament surface in the radial direction
  - Method: MD LAMMPS
  - Au cylinder 10 nm : 20 nm
    - [001]-oriented ligaments
    - 10^5 atoms

LAMMPS http://lamps.sandia.gov
EAM: Embedded atom method Foiles, Baskes, Daw PRB 33 (1986) 7983

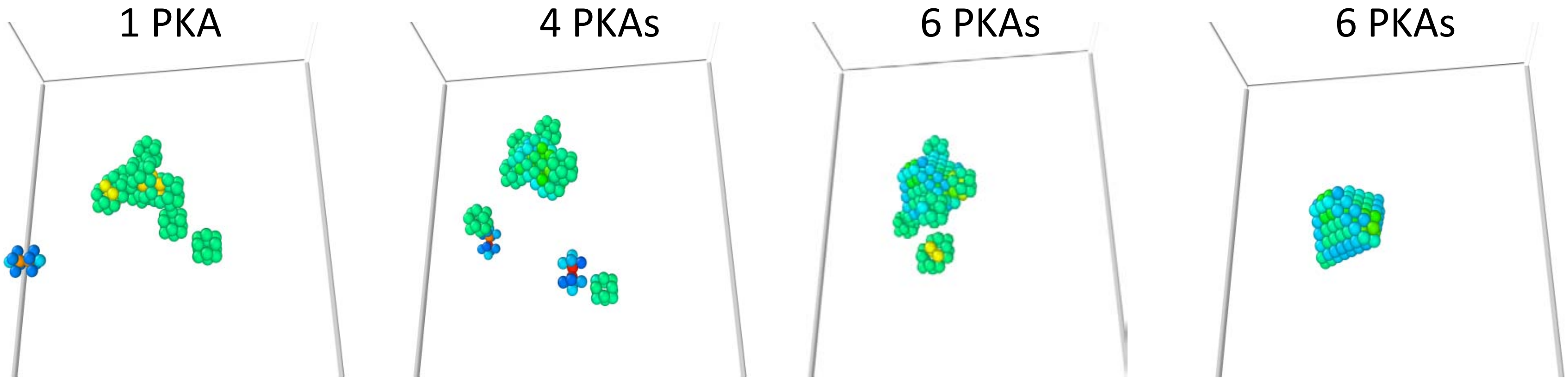
SFTs formed after 8 cascades



Defective atoms at the end of several collision cascades

Au ligament response after accumulation of several 1.5 keV PKA induced cascades

- At the end of each collision cascade the ligament gets decorated by in dividual vacancies and very few self-interstitial atoms appear (SIA: indicated by blue atoms)
- As the ligament cools down SIAs migrate to the surface or recombine with other vacancies; Example: SIA is present in 1-4 PKAs, but is not present in 6 PKAs.



Resultant configuration of a Au ligament with D:L 10:20 nm after insertion of 1.5 keV PKA. Only defective atoms are shown. All perfect FCC atoms are removed for clarity.

Conclusions

- np-Au foams were successfully synthesized by de-alloying process
- np-Au foams remain porous structure after Ne ion irradiation to 1 dpa
- SFTs were observed in RT irradiated np-Au foams under the highest and intermediate fluxes, but not under the lowest flux
- SFTs were **not** observed in LNT irradiated np-Au foams under all fluxes
- The vacancy diffusivity in Au at RT is high enough so that the vacancies have enough time to agglomerate and then collapse to form SFTs.
- The high ion flux creates more damage per unit time; vacancies don't have enough time to diffuse or recombine. As a result, SFTs were formed at high ion fluxes.

Future Work

- Determine the role of surface-to-volume ratio on the irradiation response of nanoscale foams, i.e. different ligament/pore size in np-Au
- Irradiation response under irradiation with different projectiles (He, Xe)
- Dose dependence of defect evolution in np-Au
- Irradiation at elevated temperatures
- Other np-metals (Ni-Pt alloy foams)

Acknowledgement

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on
Radiation Resistant Nanoporous Materials