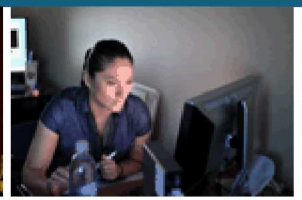
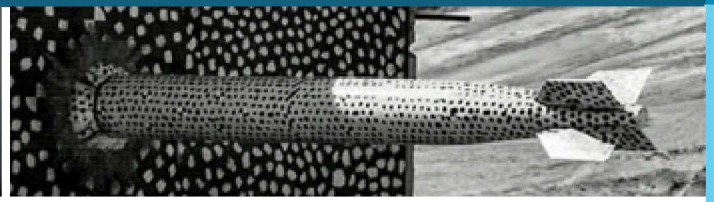
SAND2019-10190C

Investigation of Helium Behavior in Multilayered Hydride Structures Through In-situ TEM Ion Implantation





PRESENTED BY

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Khalid Hattar, Paul Kotula, Dale Zschiesche, Ron Goeke (SNL-NM)
Bruce Arey, Bethany Matthews (PNNL)

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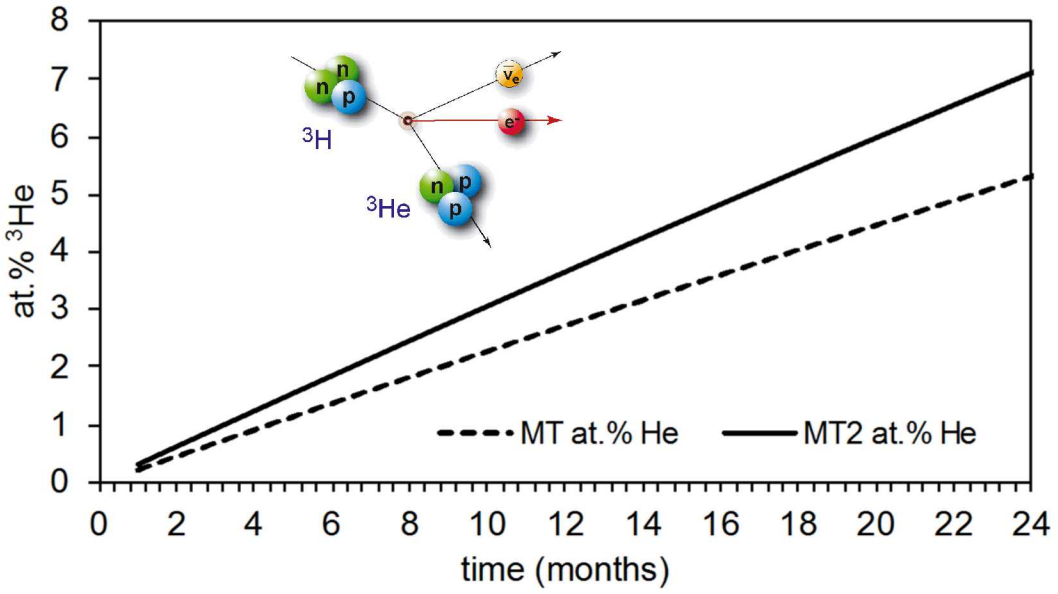
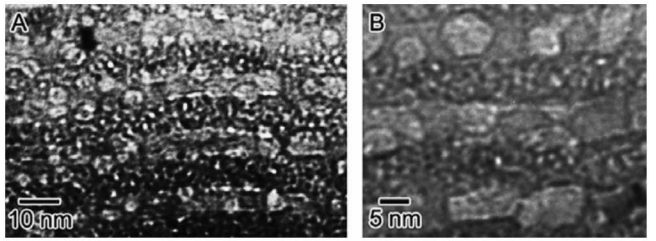
Background

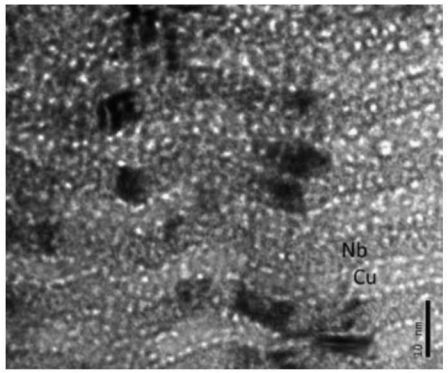
Tritium Storage & Processing



Multilayered Nanocomposites Trap Helium

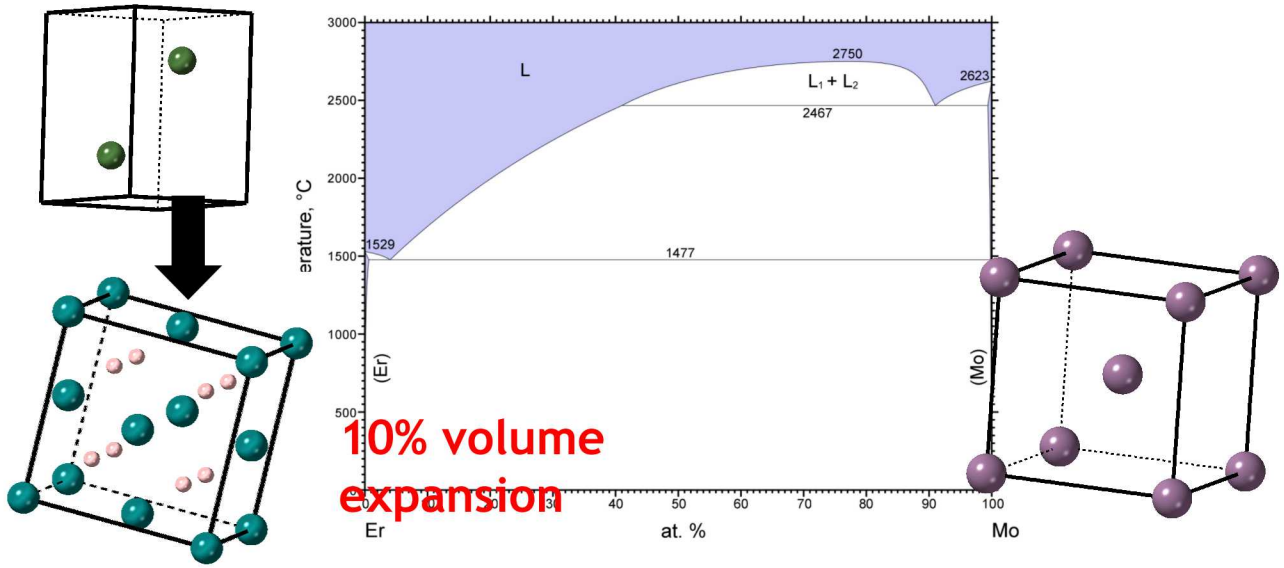


Hattar *et al*. Scripta Materialia 58 (2008) 541-544



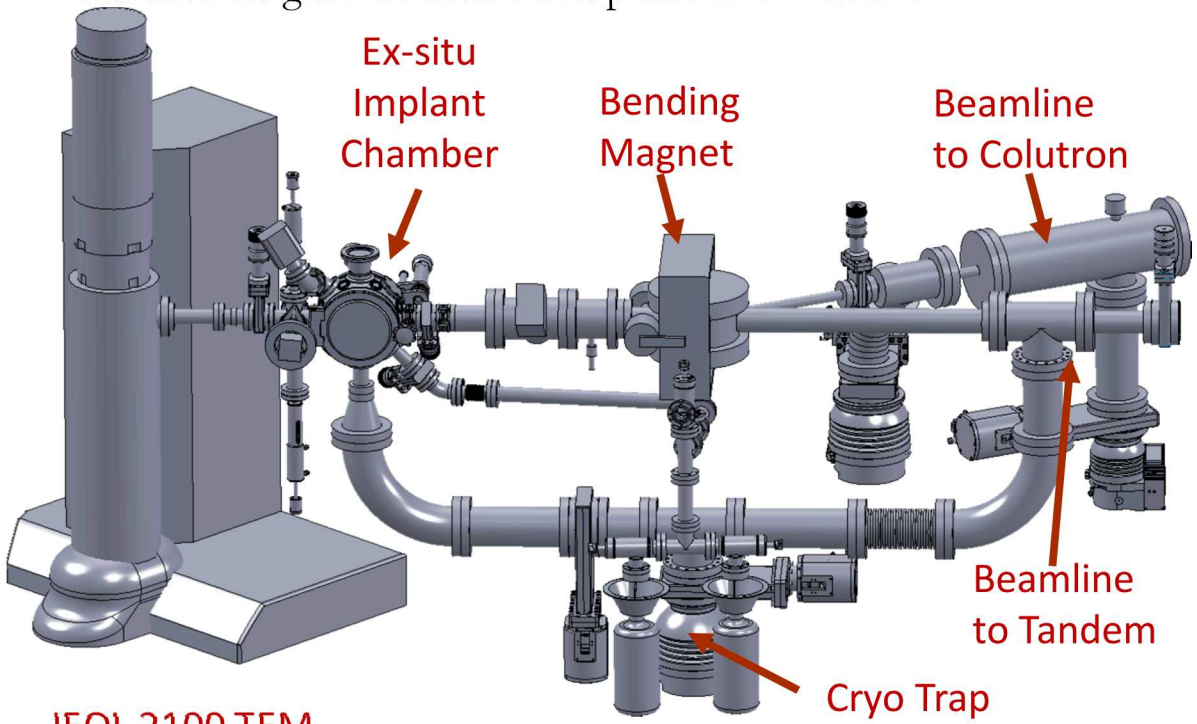
Demkowicz et al Curent Opinion in Solid State and Materials Science 16 (2012) 102-108

This Work Uses ErD_2 and Mo Nanocomposites

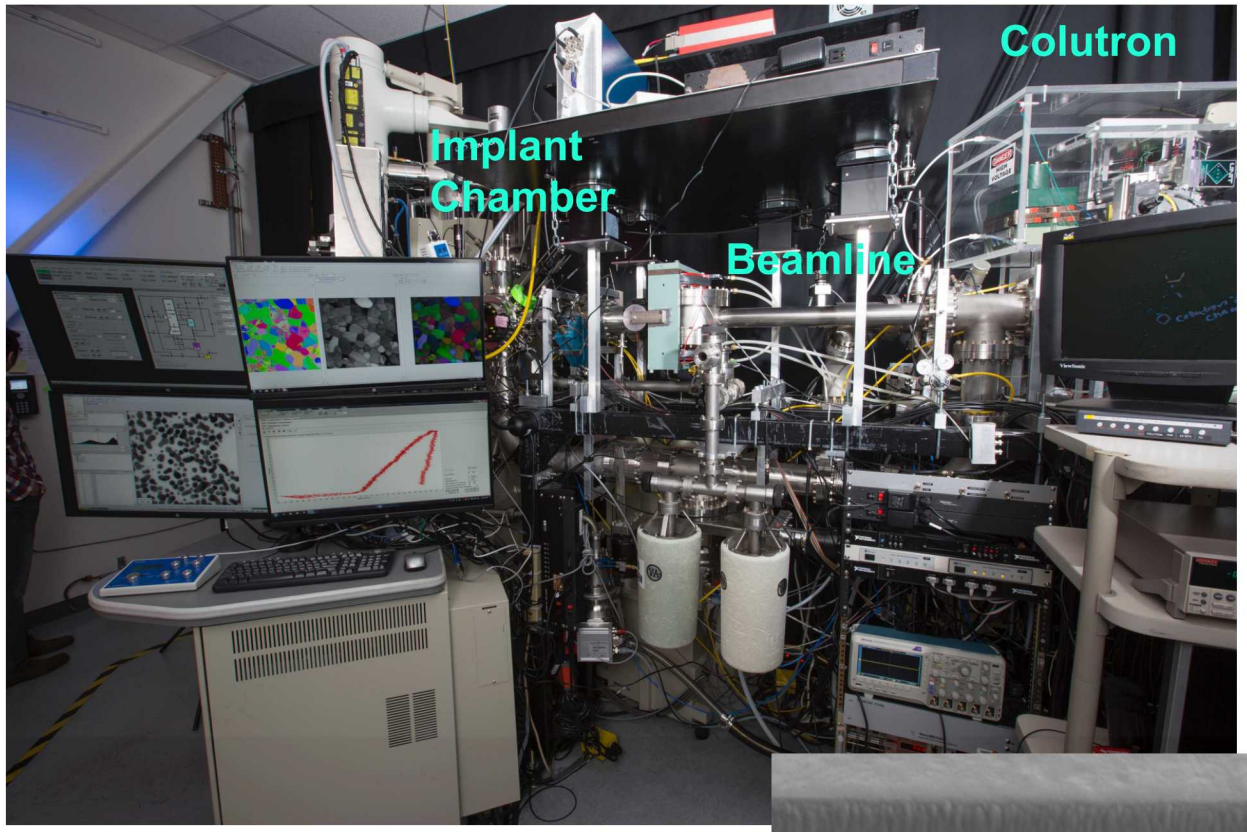


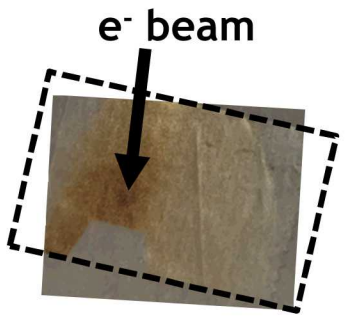
Rapid Evaluation of New Multilayered Structures using Sandia's I³TEM

- Bubble evolution can be quantified in a TEM sample in the same location as a function of He concentration.
- **In-situ implantation** only takes a few hours – tritium aging takes several months and rad work.
- **In-situ annealing** with the Gatan DT stage is used to quickly assess the stability of bubbles and multilayers.
- **Nanomegas** Precession Electron Diffraction (PED) is used to characterize grain structure and phase information.

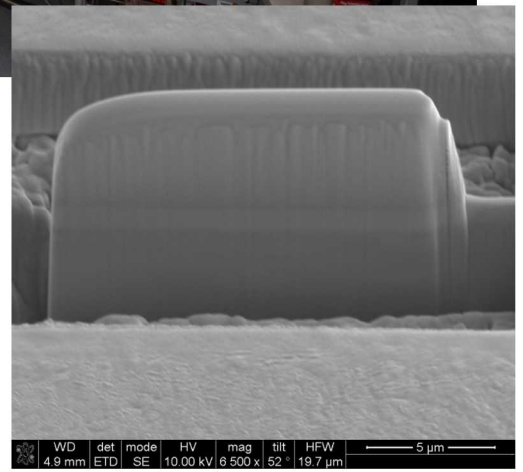


JEOL 2100 TEM





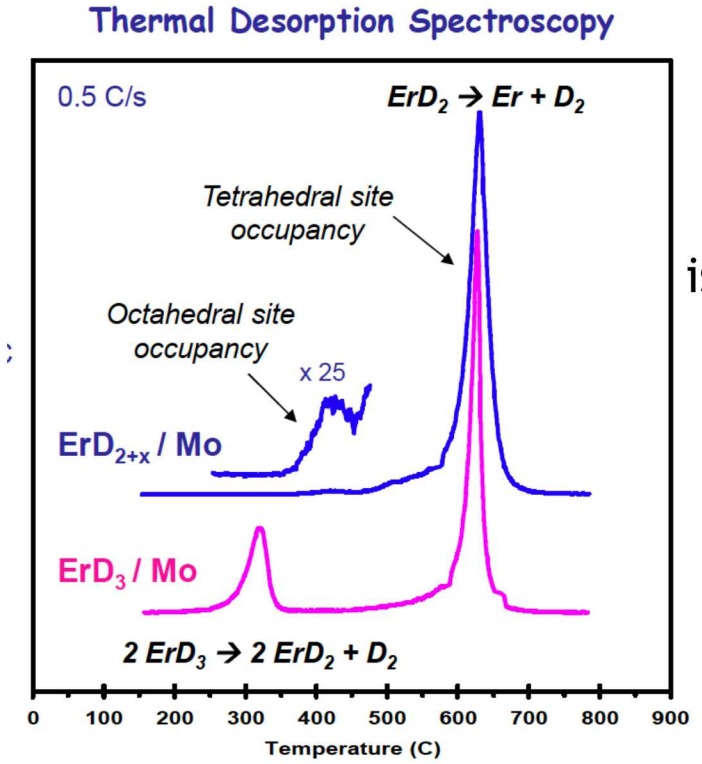
10 keV He Beam Spot in Low Mag, +30° tilt in x



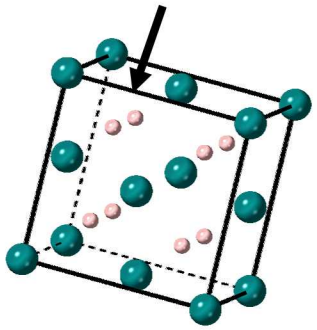
Multilayer Stability and Bubble Growth were Explored with In-situ Annealing

Hydride Phase Stability

- In perfectly stoichiometric ErD_2, deuterium begins to desorb above 500ºC
- Desorption occurs from the octahedral sites of super-stoichiometric ErD_{2+x} above 250ºC

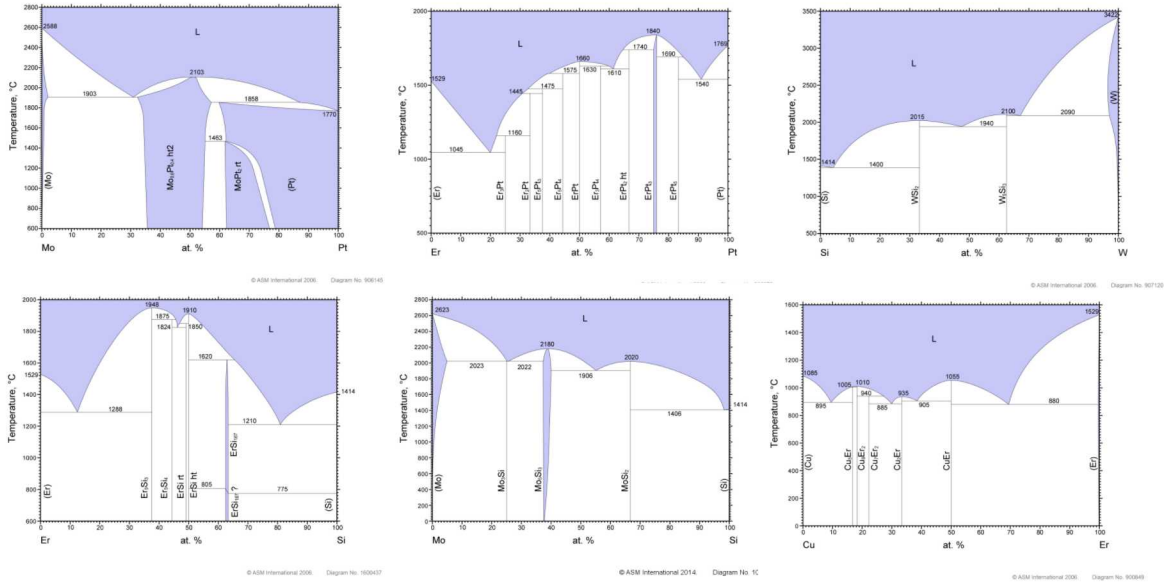


Most hydrogen is in tetrahedral sites

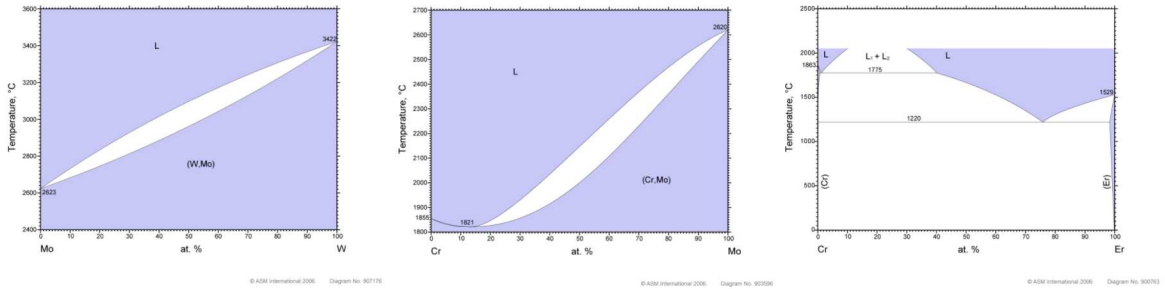


Potential Intermetallic Formation

- Er and Mo remain immiscible up to 1477ºC
- Er, Mo, and W react with Si, Pt, and Cu.

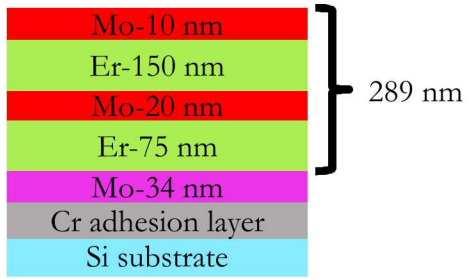


- Mo forms bcc intermetallics with W (50%) and Cr (30%), but is immiscible with Cu. Er is immiscible with Cr.



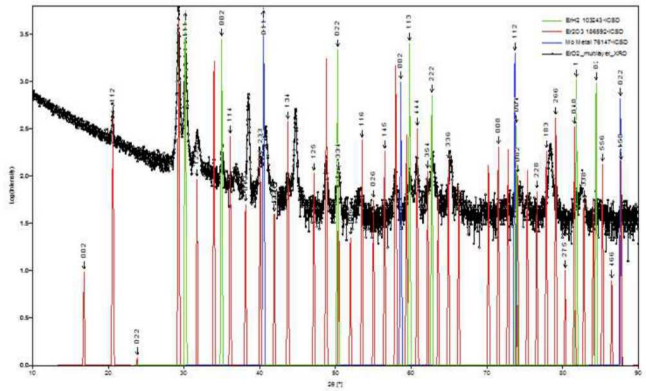
Multilayer Film Deposition – Structure 1

Deposition parameters



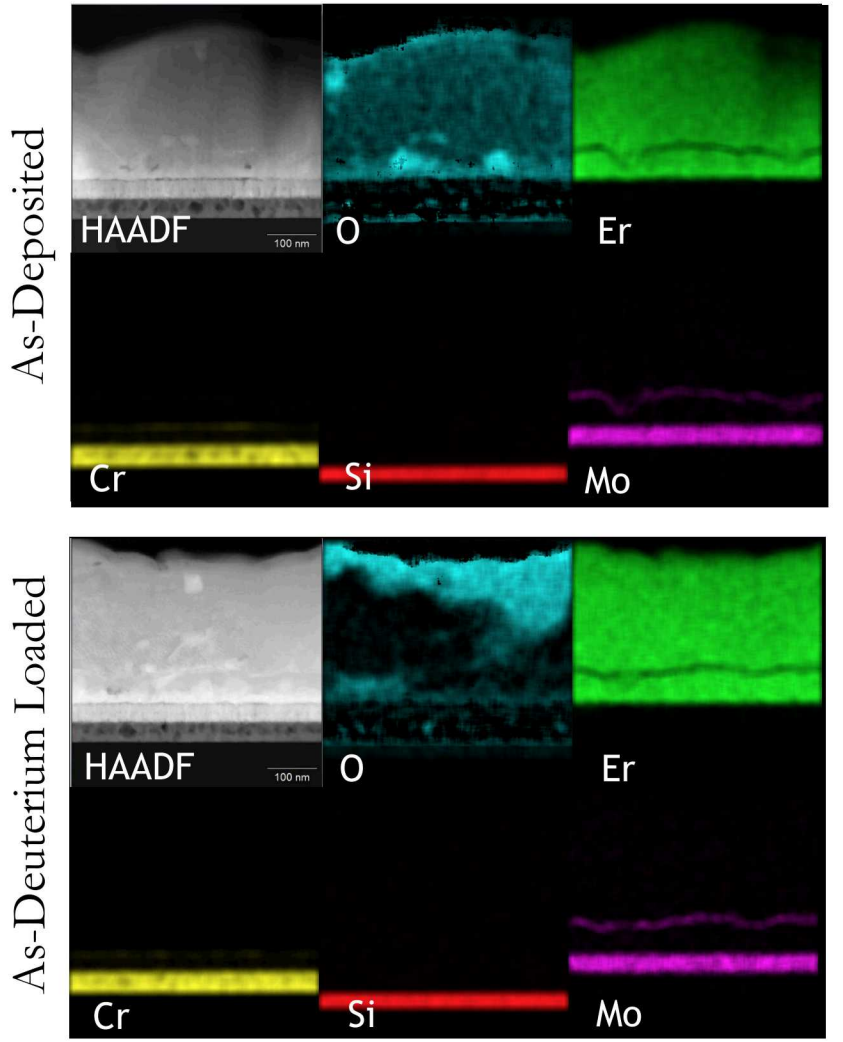
- Cr/Mo layers were sputter deposited at room temperature onto a Si substrate.
- 4 Er/Mo layers were electron beam evaporated at 400°C.
- Samples were diced into 1 x 1 cm squares, then loaded with deuterium by first heating to 450°C for 5 min, then reduced to 400°C and held for 20 min at a D_2 pressure of 10 Torr. This formed ErD_2/Mo layers.
- Chamber pressure was 5×10^{-7} Torr prior to deposition and loading.

XRD Confirmation of ErD_2 Formation



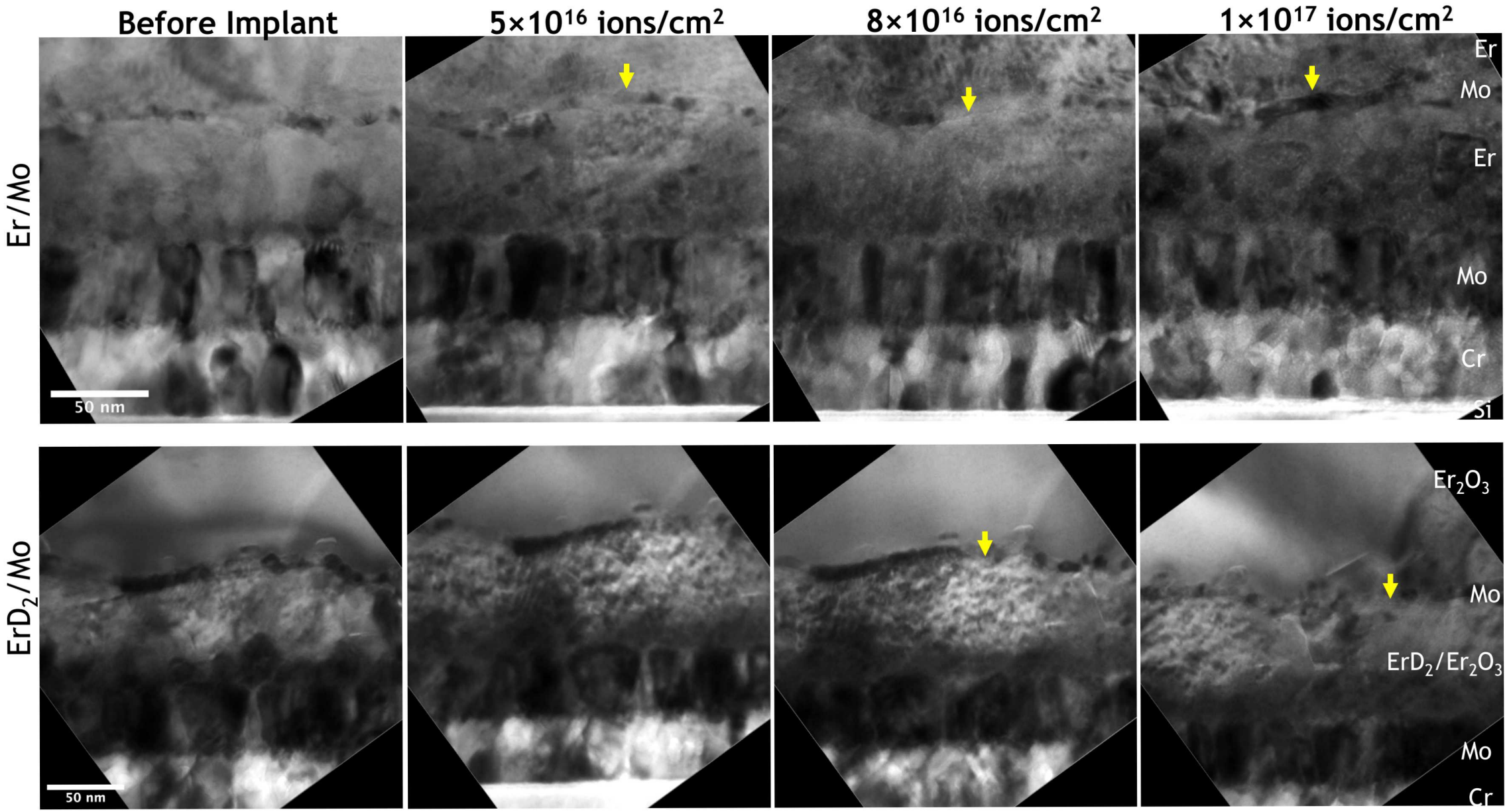
STEM/EDS Characterization

- EDS maps of as-deposited structure showed Cr diffusion through the sputtered Mo layer and some Er_2O_3 grains.



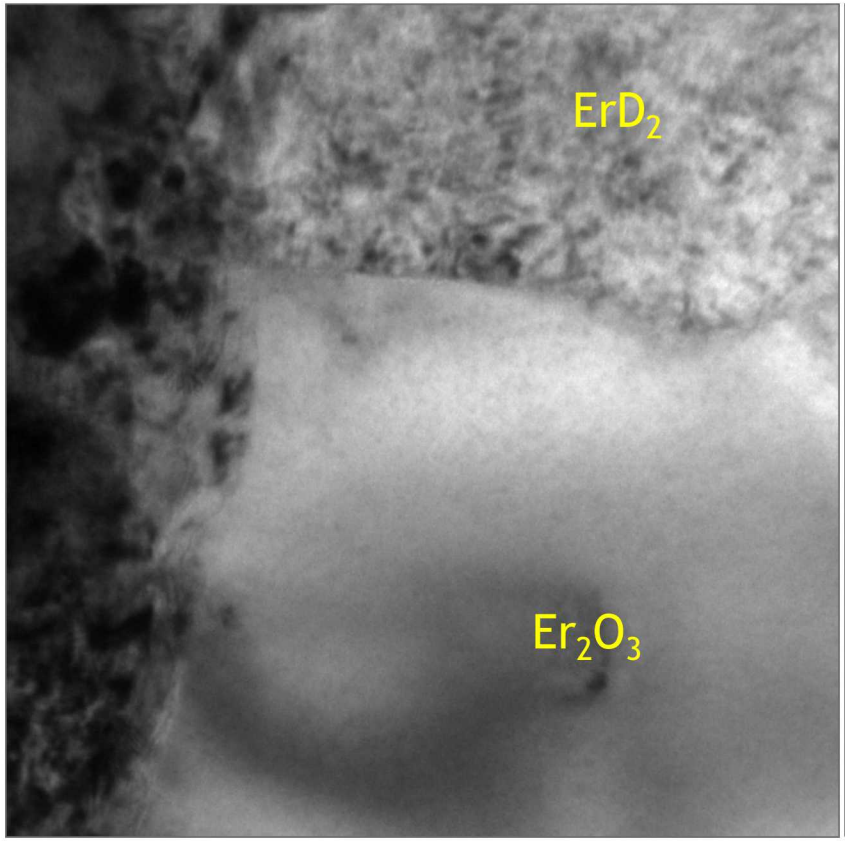
EDS performed by Bethany Matthews & Bruce Arey at PNNL

In-situ Helium Implantation into Er/Mo and ErD_2/Mo Multilayers - Structure I

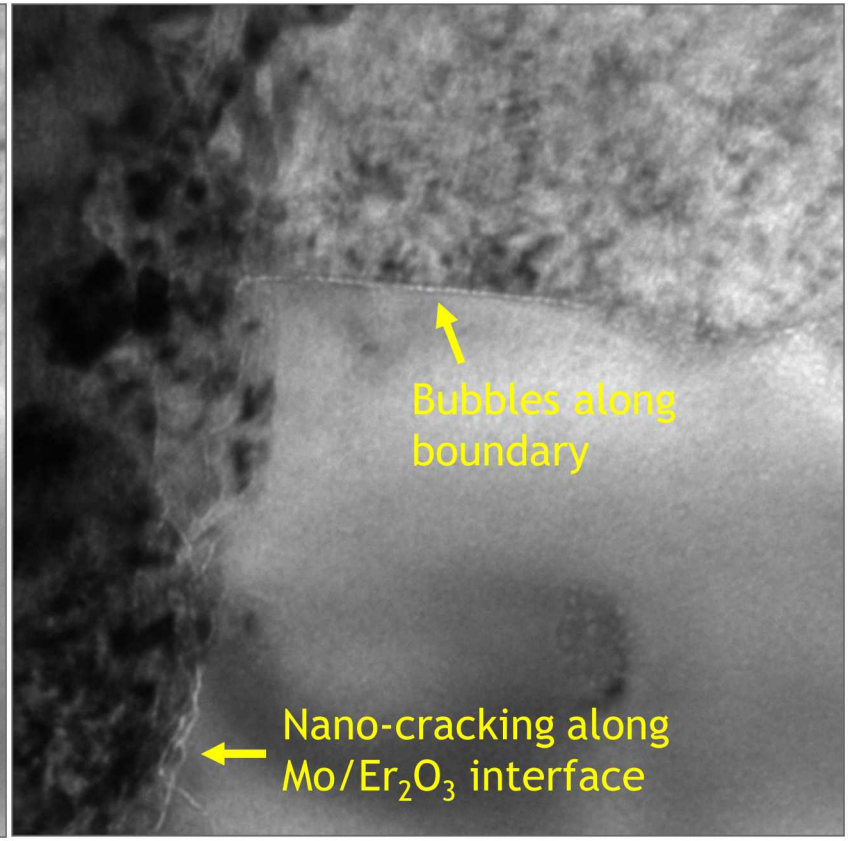


In-situ Helium Implantation into Er/Mo and ErD_2/Mo Multilayers - Structure I

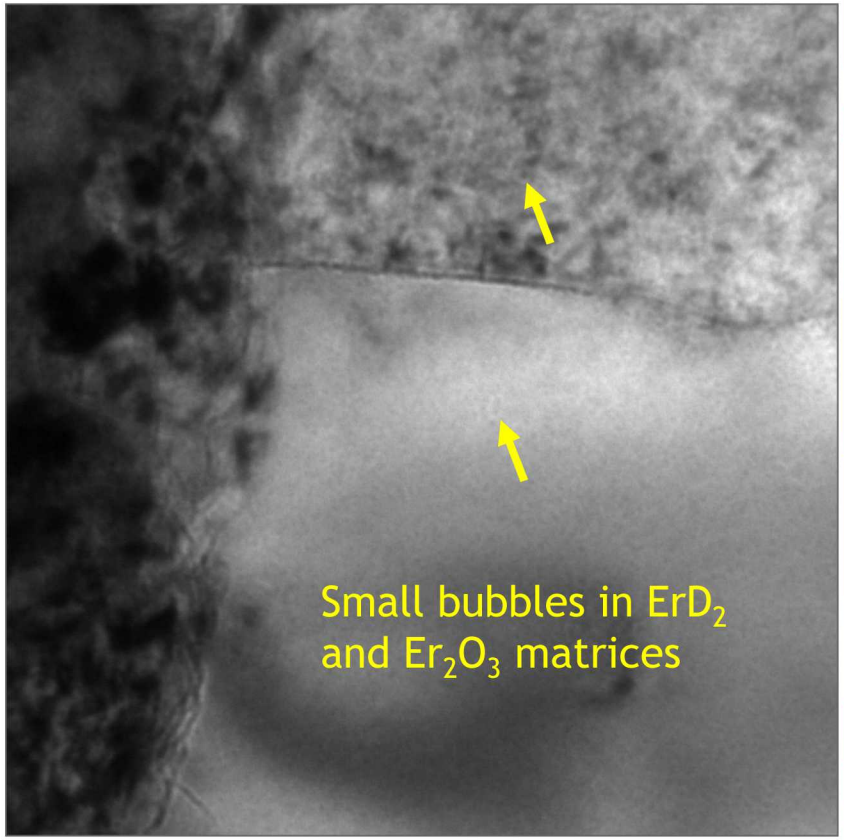
Higher magnifications of He implanted ErD_2/Mo layers taken after tilting to remove some contrast



Focus



-1 µm Defocus

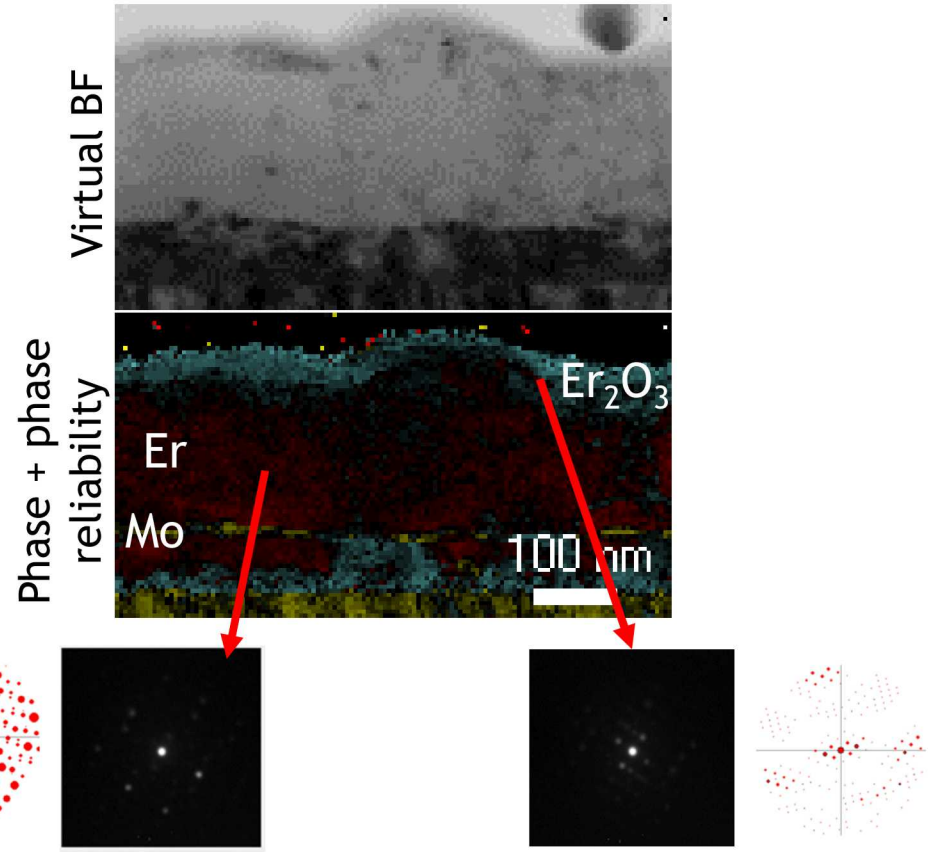


+1 µm Defocus

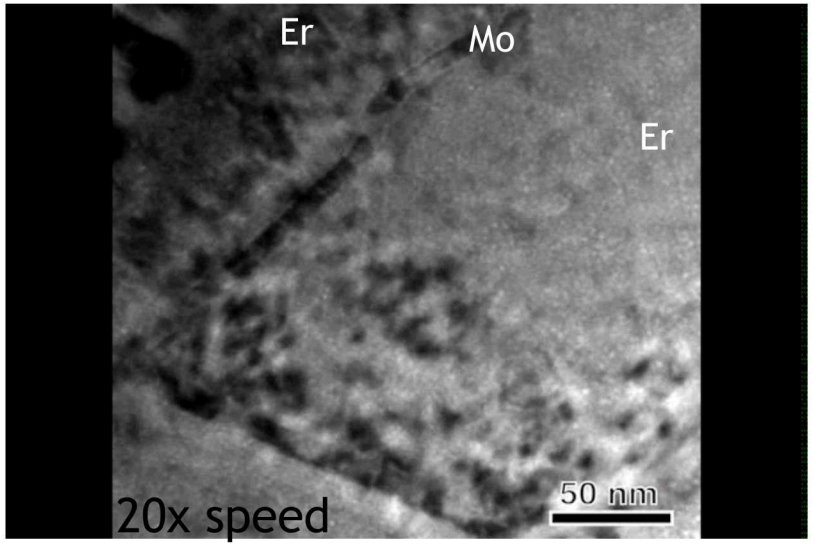
In-situ Annealing of As-Deposited Multilayers - Structure 1

Determining which Grains are Er or Er_2O_3

- EDS showed a high concentration of oxide grains. To make sure in-situ annealing imaging was done on Er or ErD_2 grains, PED was done before the in-situ annealing.
- 5 nm step, 0.4° precession angle

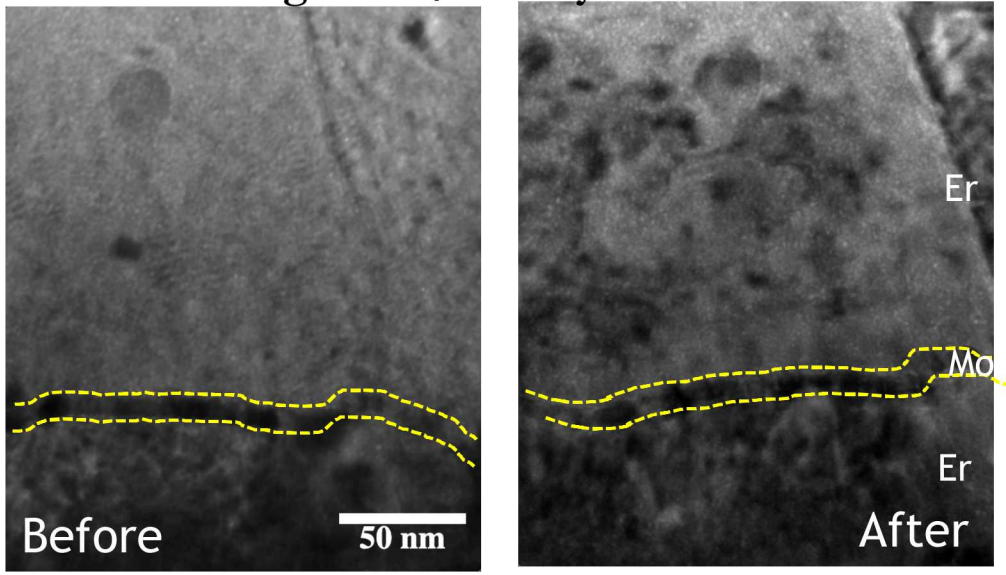


In-situ Annealing of Er/Mo layers at 500°C



Cu grid

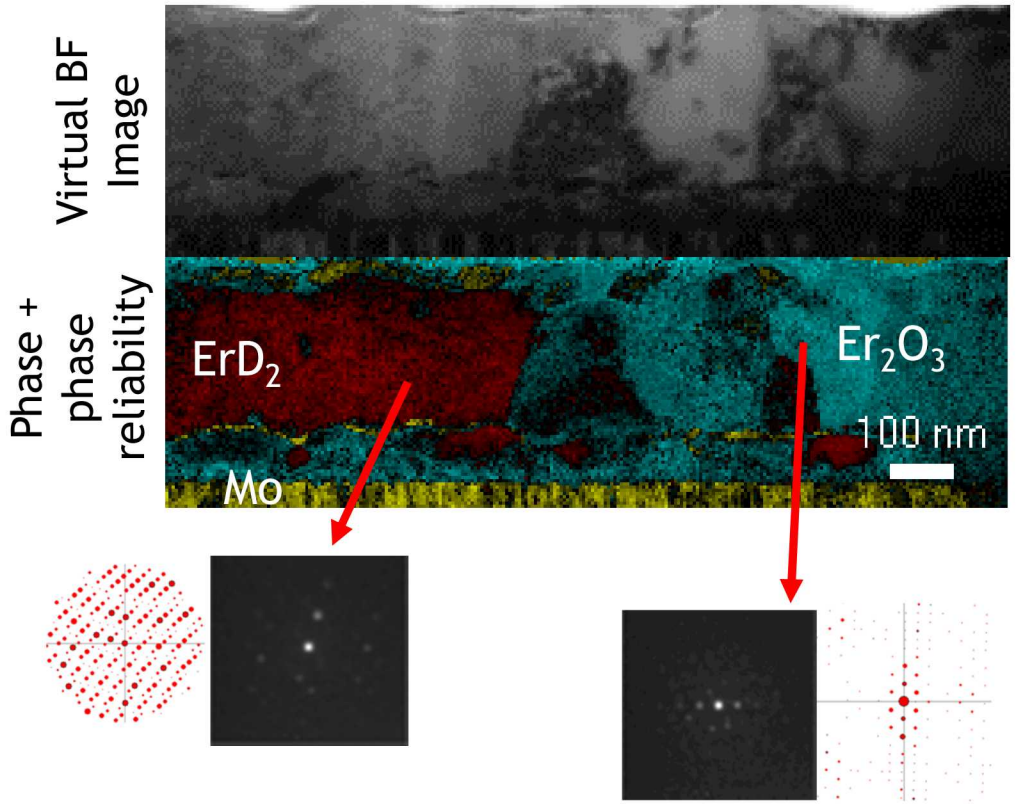
In-situ Annealing of Er/Mo layers at Before and After



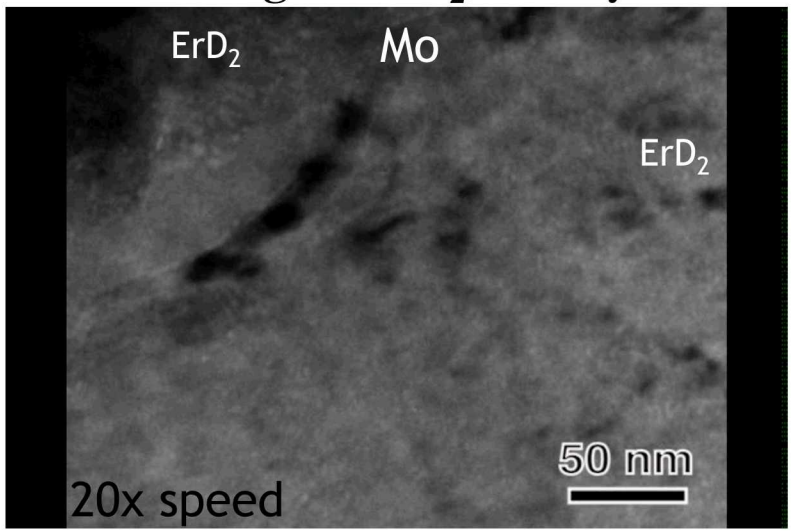
In-situ Annealing of As-Loaded Multilayers - Structure 1

Determining which Grains are ErD_2 or Er_2O_3

- EDS showed a high concentration of oxide grains. To make sure in-situ annealing imaging was done on Er or ErD_2 grains, PED was done before the in-situ annealing.
- 5 nm step, 0.4° precession angle

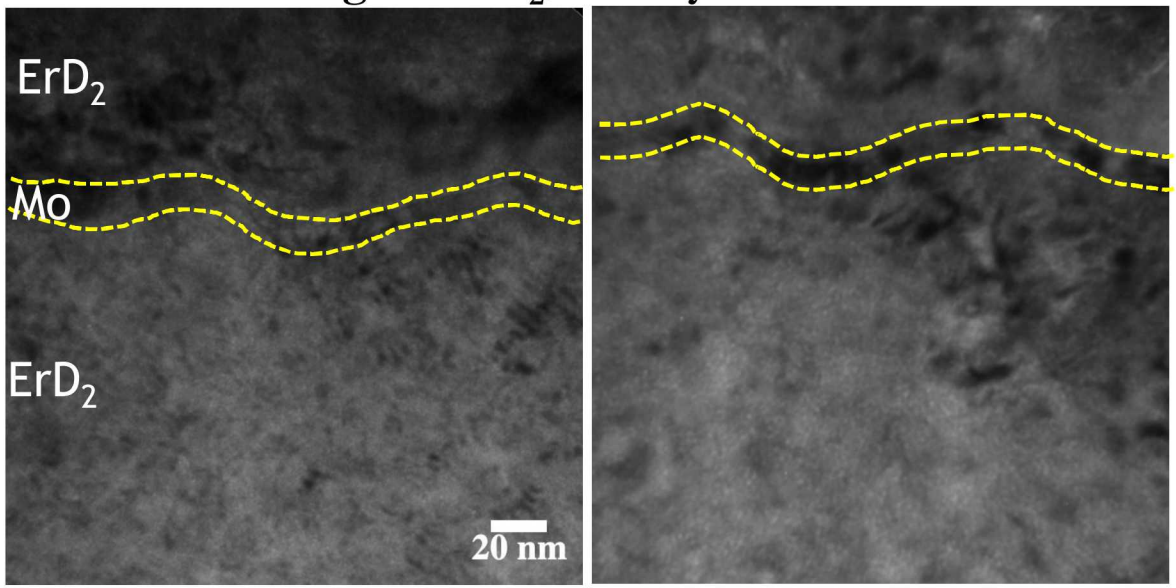


In-situ Annealing of ErD_2/Mo layers at 500°C



Cu grid

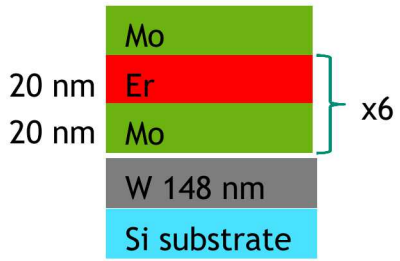
In-situ Annealing of ErD_2/Mo layers at Before and After



Multilayer Film Deposition – Structure 2

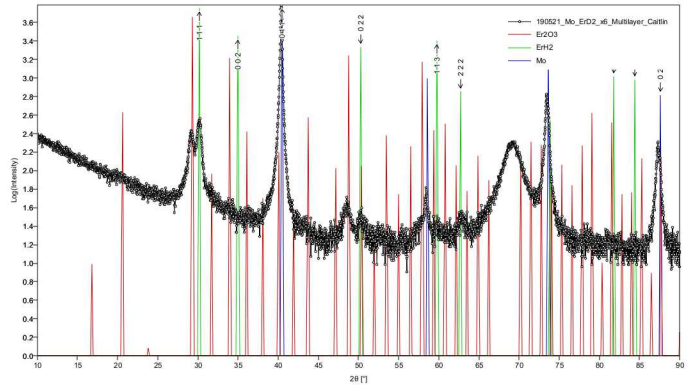
Deposition parameters

- W adhesion layer was sputter deposited onto a Si substrate.



- 13 Er/Mo layers were electron beam evaporated at 400°C.
- Samples were diced into 1 x 1 cm squares, then loaded with deuterium by first heating to 450°C for 5 min, then reduced to 400°C and held for 20 min at a D_2 pressure of 10 Torr. This formed ErD_2/Mo layers.
- Chamber pressure was 5×10^{-7} Torr prior to deposition and loading.

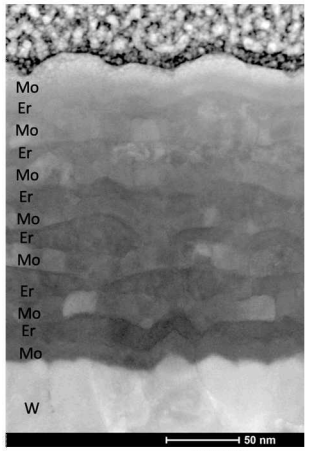
XRD Confirmation of ErD_2 Formation

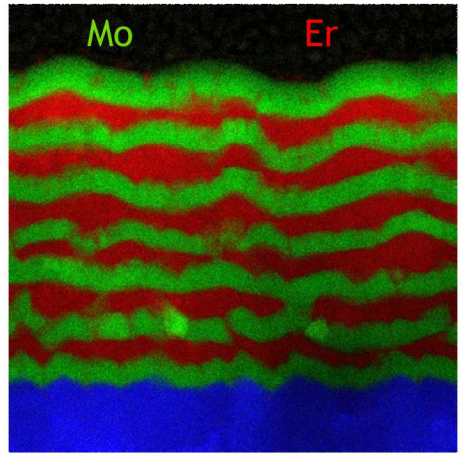


STEM/EDS Characterization

- Oxygen is evenly distributed inside the Er layers in the as-deposited structure

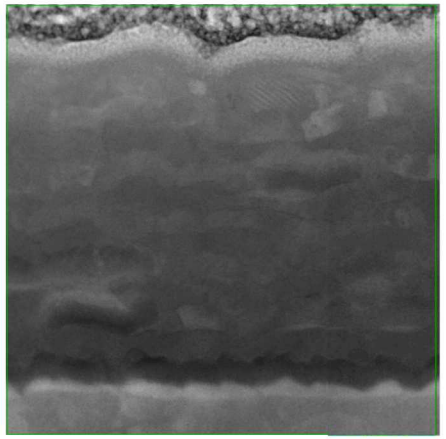
As-Deposited

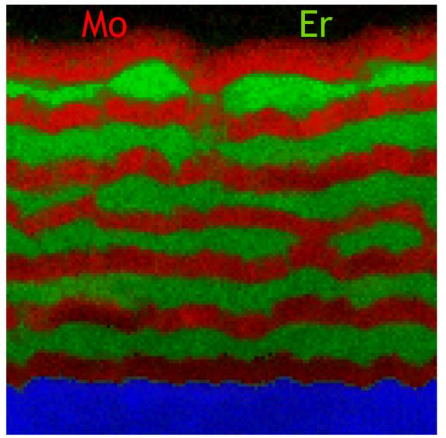




250 nm field of view

As-Deuterium Loaded



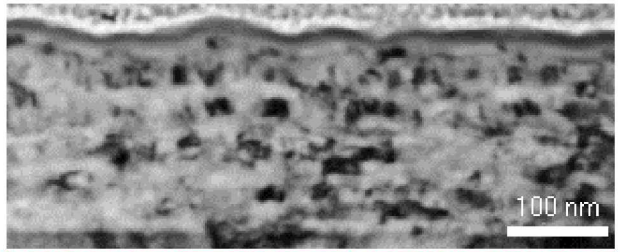


250 nm field of view

EDS performed by Pa

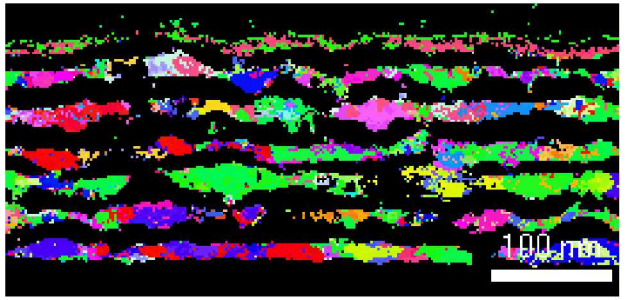
Grain Structure in As-Deposited and As-Loaded Multilayers – Structure 2

Er/Mo (as-deposited) Multilayers

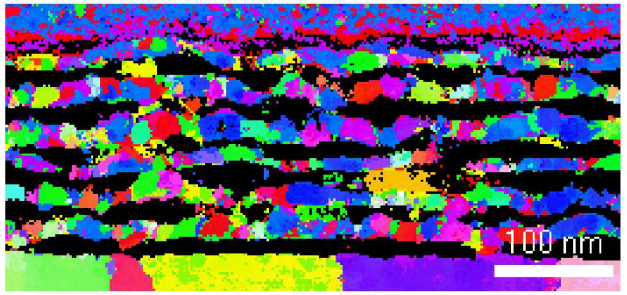


Max Er grain size: 31 nm
Max Mo grain size: **33 nm**

Er z orientation



Mo z-orientation

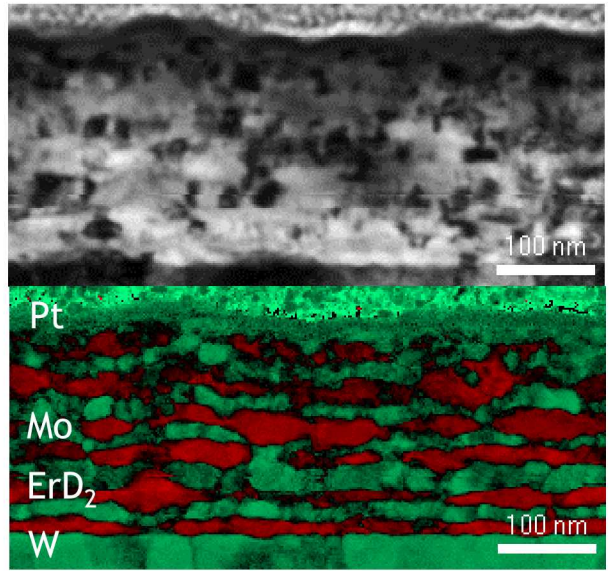


PED parameters
2 nm step size
Smallest condenser,
Spot 5, α = 3
0.1° precession angle

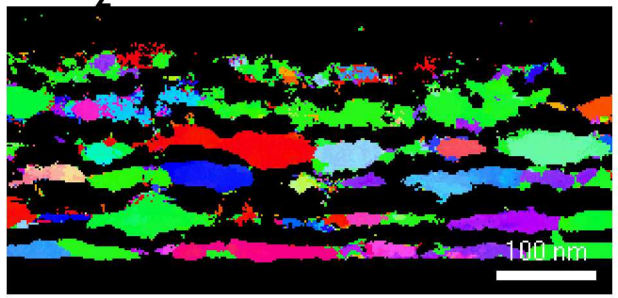
*images were cropped for grain size analysis

ErD_2/Mo (as-loaded) Multilayers

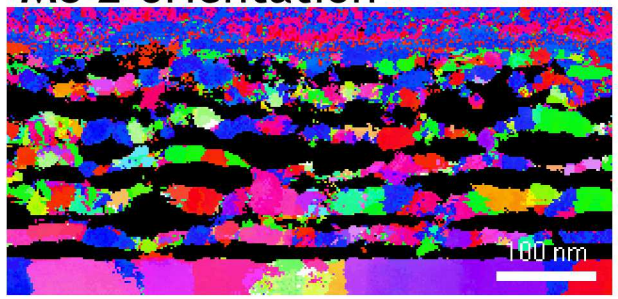
Max ErD_2 grain size: 62 nm
Max Mo grain size: **37 nm**

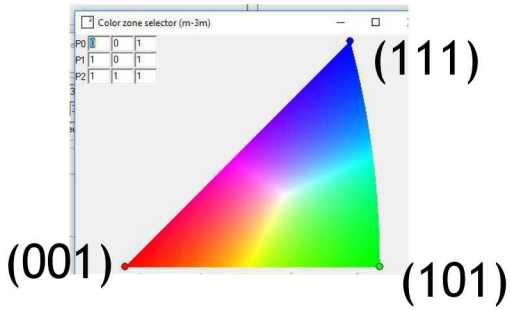


ErD_2 z orientation

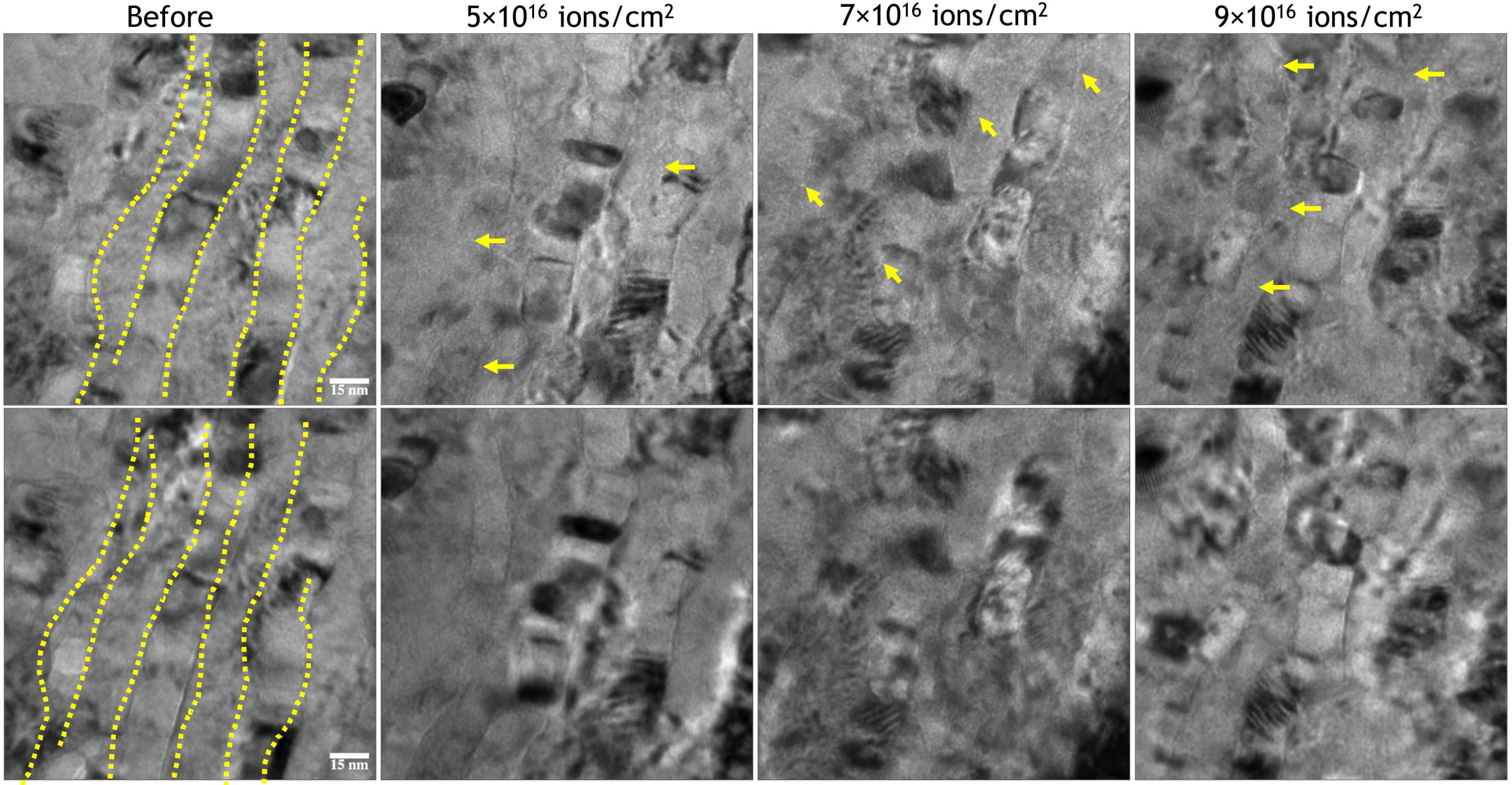


Mo z-orientation



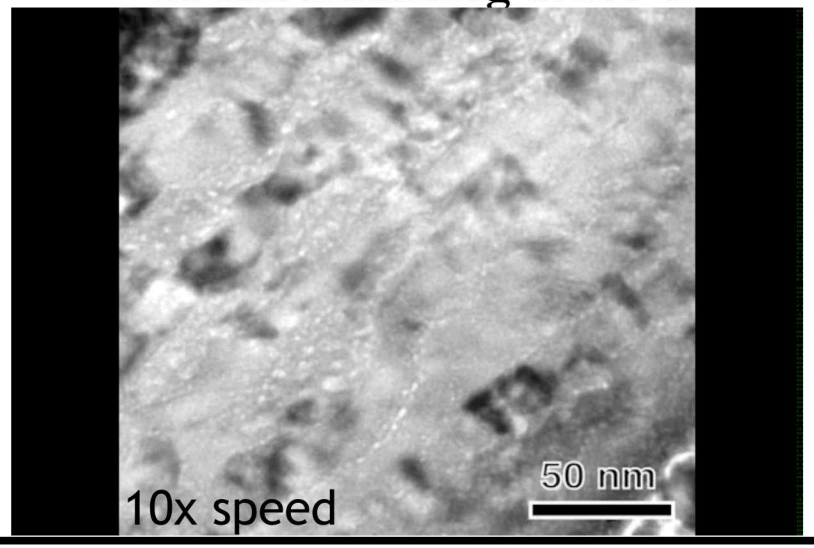


In-situ Helium Implantation into ErD_2/Mo Multilayers - Structure 2



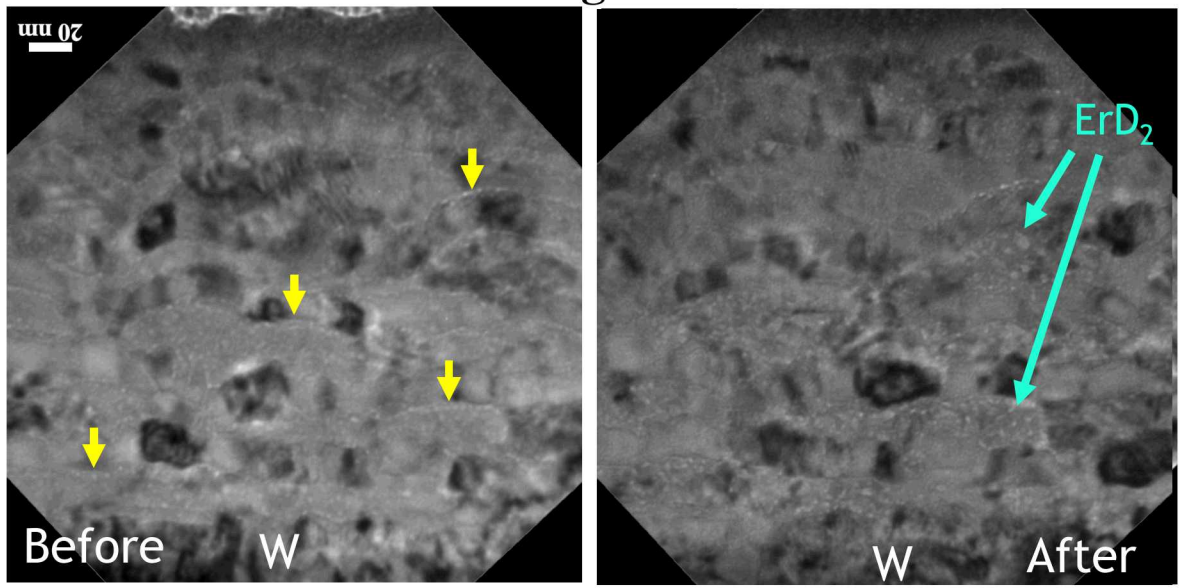
In-situ Annealing of Helium Implanted Multilayers - Structure 2

In-situ Annealing at 500°C



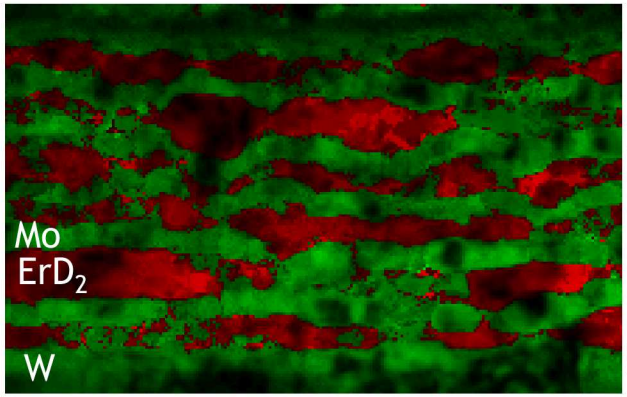
Mo grid

In-situ Annealing Before and After

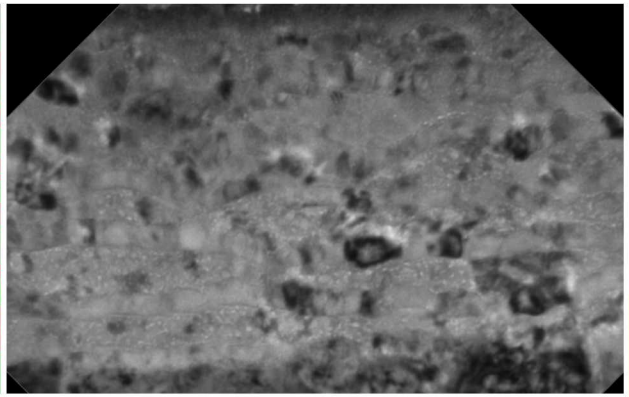


Post-Annealing PED to Verify Multilayer Locations

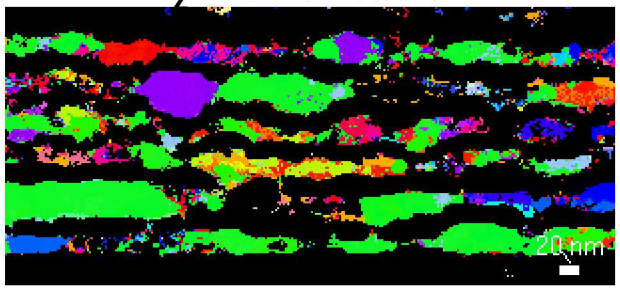
VBF+phase+phase reliability



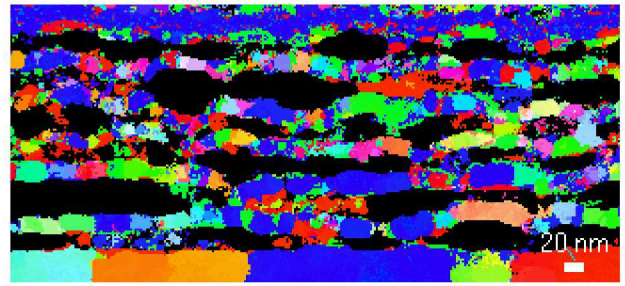
BF TEM Image



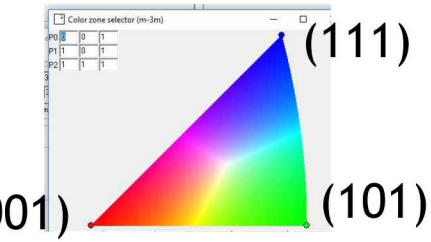
ErD_2 z orientation



Mo z-orientation



- Annealing caused bubbles to grow larger in ErD_2 than Mo
- EDS showed oxide in the Er layers, more after loading. May trap He.

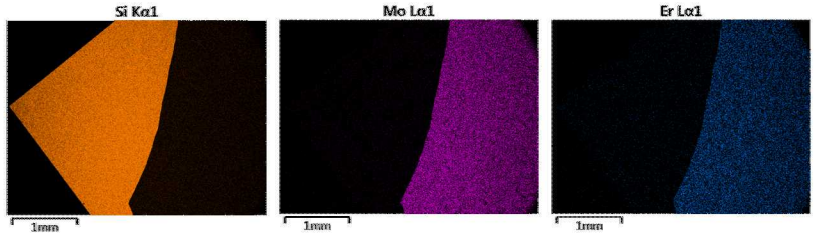


Conclusions

- In-situ He implantation provided a rapid, rough assessment of He behavior in multilayered structures.
- PED was effectively utilized to quickly differentiate oxide and metal grains in a large area, and quantify texture and grain size.
- Bubbles trapped at interfaces better with thinner layers
- Bubbles and multilayers were stable in both structures under in-situ annealing up to 500°C.
- Bubbles grew more in ErD_2 layers than Mo layers, presumably due oxide in the ErD_2 layers.

Future Work

- Perform bulk He implantations to study:
  1. He evolution in the absence of thin film effects
  2. Determine bubble size as a function of He concentration
  3. Quantify possible blistering and film spalling effects
- Fix spalling issues that would pose a tritium contamination hazard



- Prepare and age ErT_2/Mo multilayer films and repeat TEM analysis to see how microstructure would evolve in a real tritium storage material.
- Explore oxide interfaces

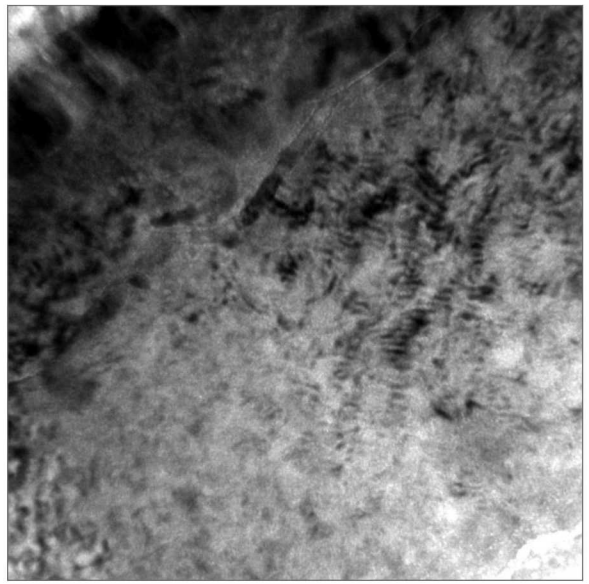
Pacific Northwest NATIONAL LABORATORY

Center for Integrated Nanotechnologies — DISCOVERY, PERFORMANCE, INTEGRATION, EDUCATION — CINT — Sandia, Los Alamos

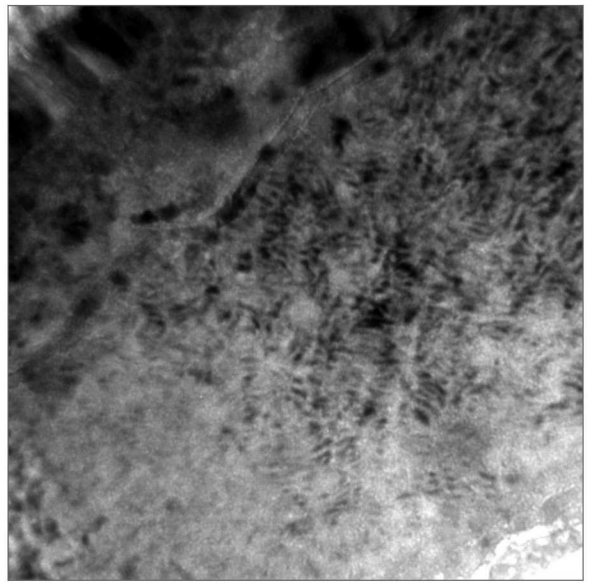
Backup Slides

In-situ Annealing of As-Loaded Multilayers - Structure 1

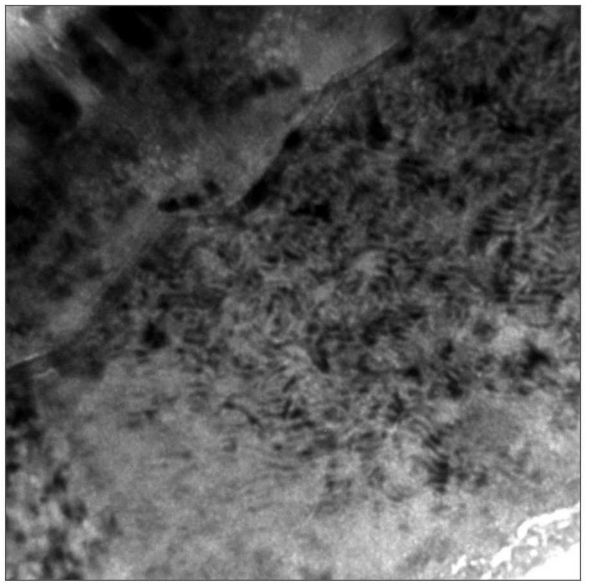
100°C



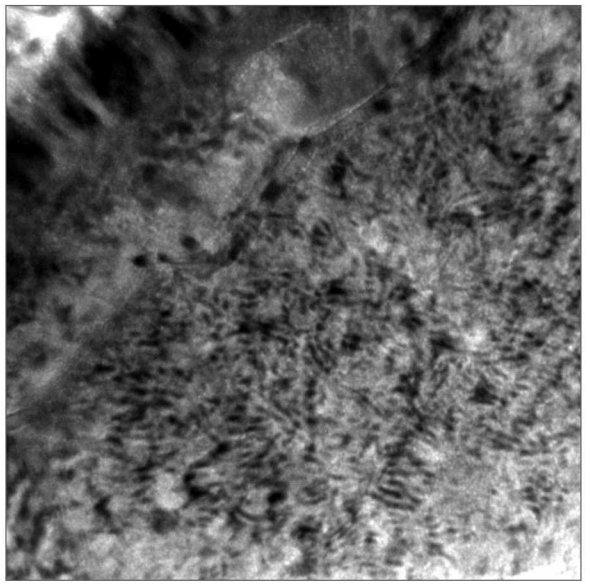
150°C



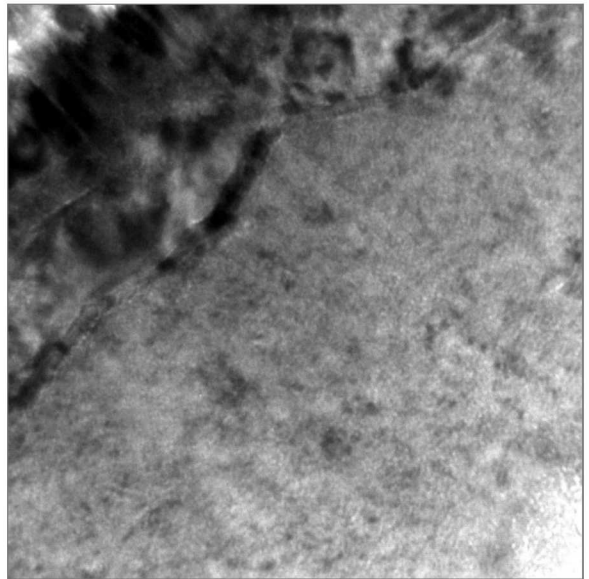
200°C



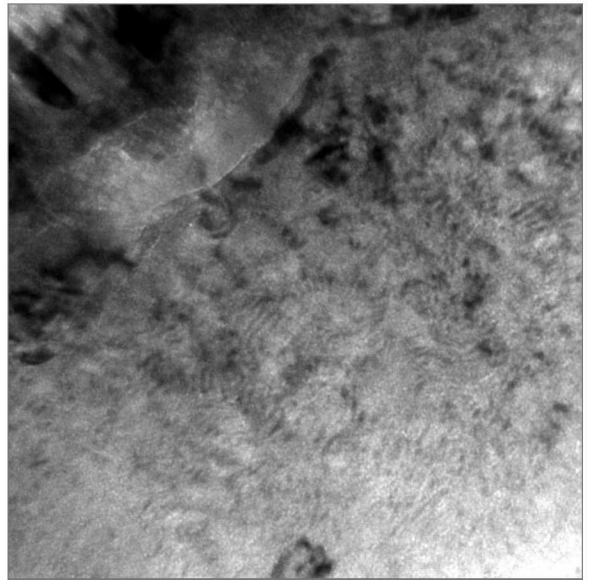
250°C



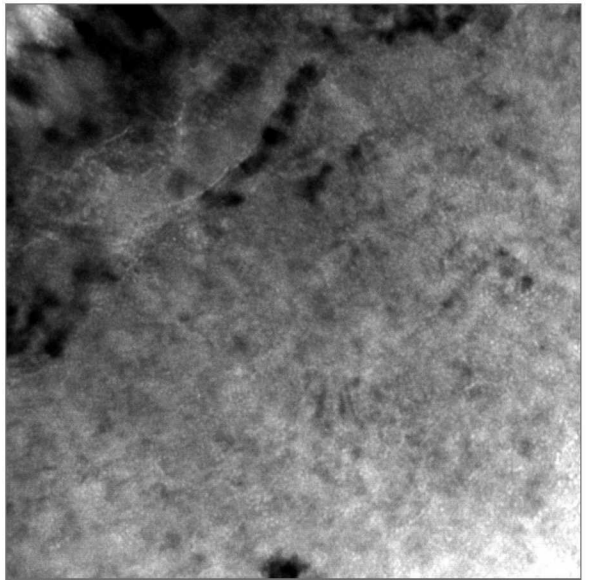
300°C



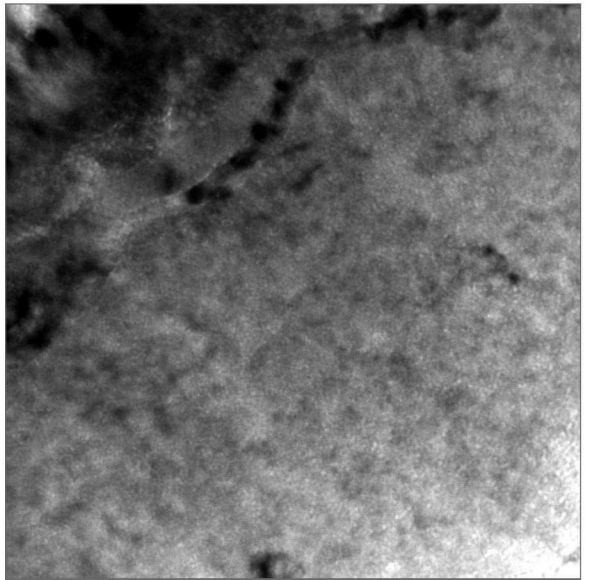
350°C



400°C



450°C



In-situ Annealing of Helium Implanted ErD_2/Mo Multilayers - Structure 2

Images after annealing at each temperature for 10 min.