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Helium Bubble Evolution in Implanted Erbium Deuteride Bulk and Multilayered Structures

PRESENTED BY

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co-authors are listed in the acknowledgements ☺

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Outline

Objectives: 1) to understand the fundamental mechanisms behind accelerated He release in tritium storage materials, 2) and to understand how He interacts with interfaces in multilayered structures

- **Background**
  - tritium storage and helium in metal tritides
- **Part I: Bulk ErD_2**
  - microstructural changes after He implantation into ErD_2
- **Part II: Multilayers**
  - development of an ErD_2/Mo multilayered hydride structure and initial He implantation results
- **Summary**

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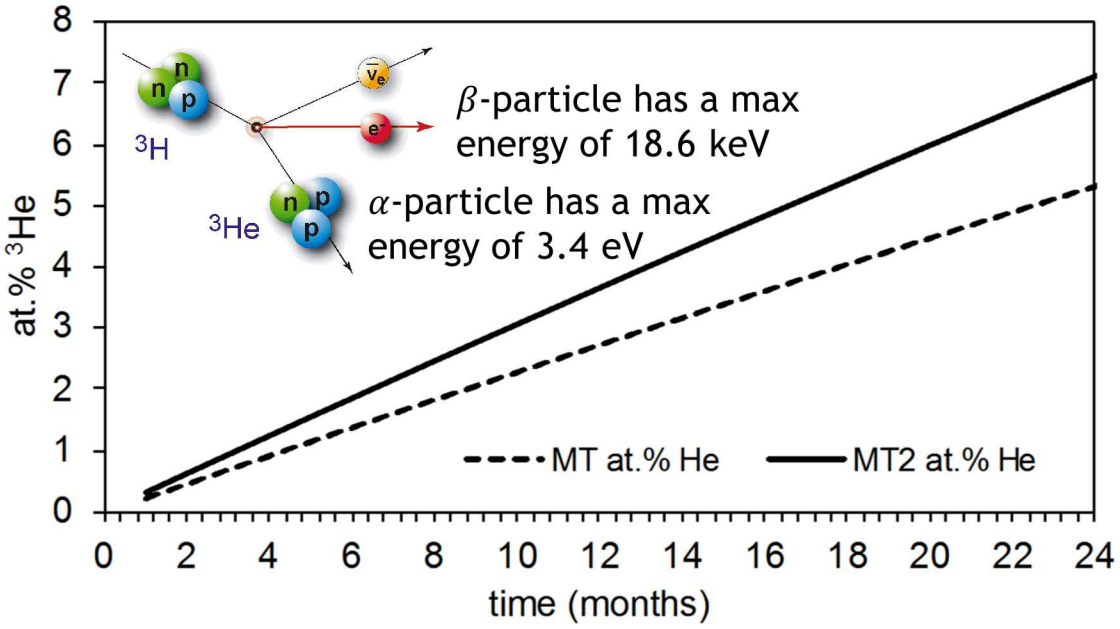
Metal Hydrides are Used for Tritium Storage

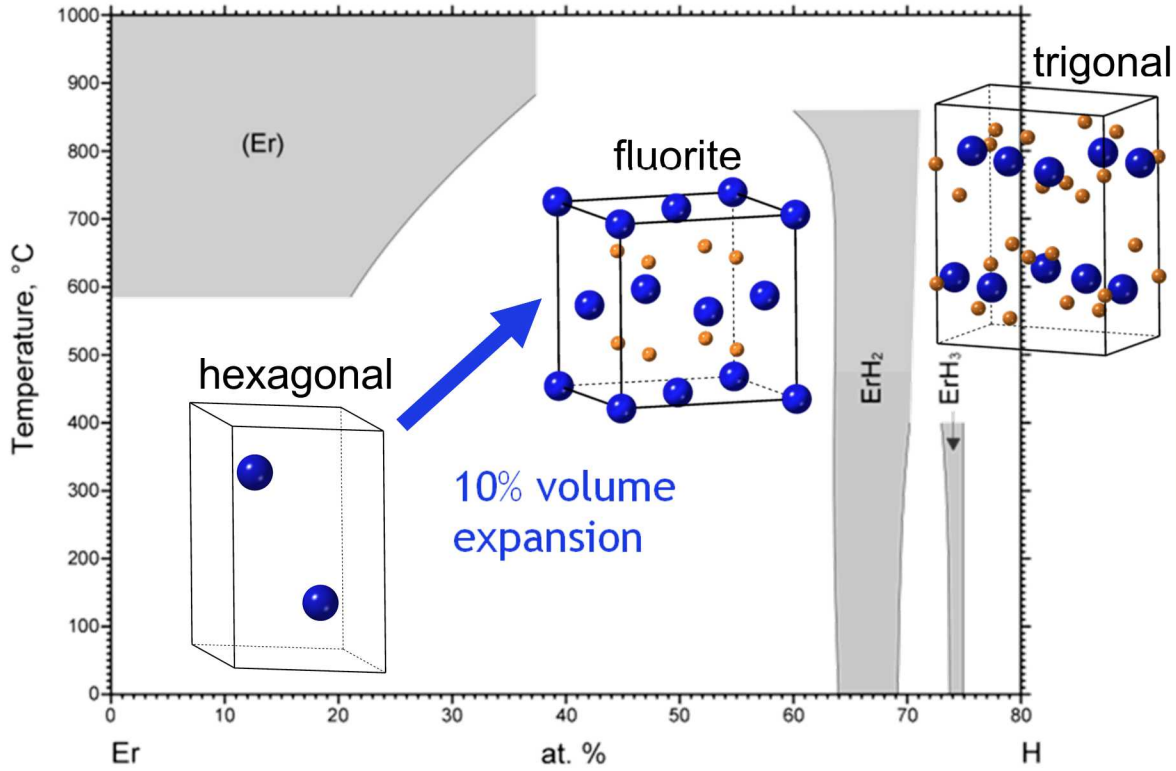
Tritium Storage

Thielmann

AG Materials

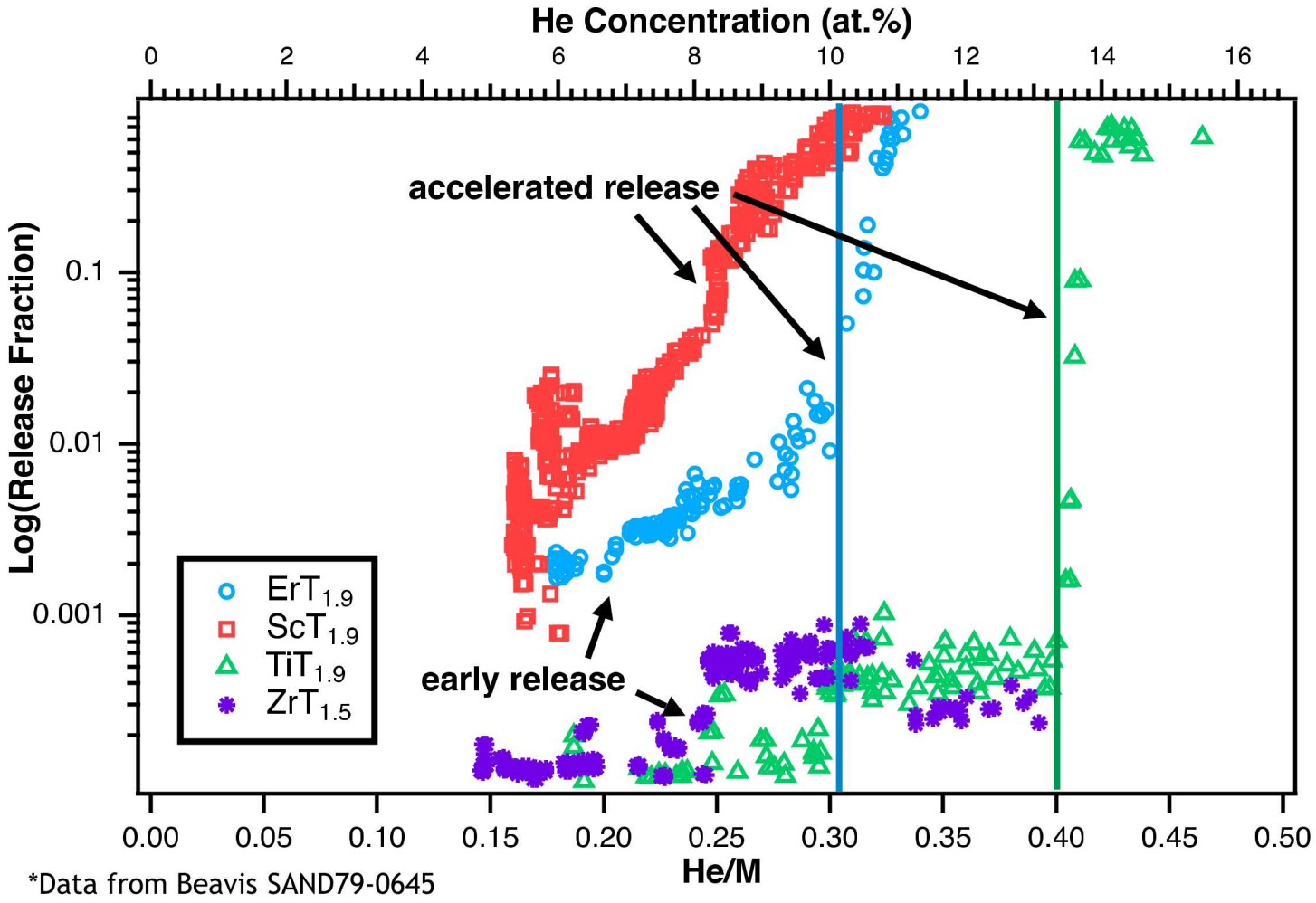


Metal to Hydride Phase Transformation



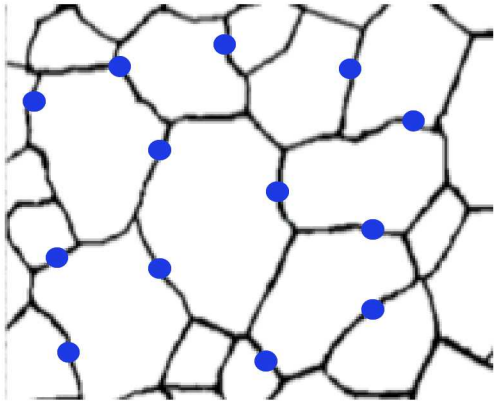
- Transition metals (groups III & IV), lanthanides, and actinides are used because they form stable hydrides with a density ≧ solid H_2.
- Phase diagrams can be quite complex. Most hydrides have several phases.

Tritides Exhibit Accelerated He Release when ^{3}He Capacity is Reached

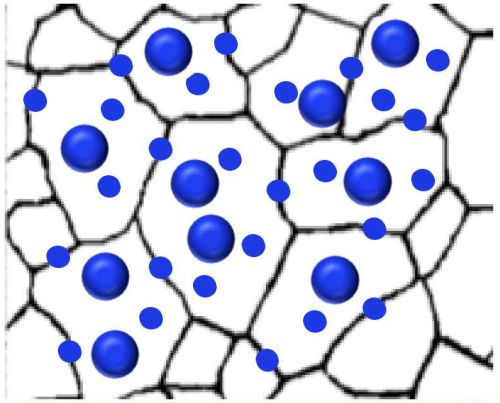


*Data from Beavis SAND79-0645

Early release occurs from ^{3}H decay in grain boundaries



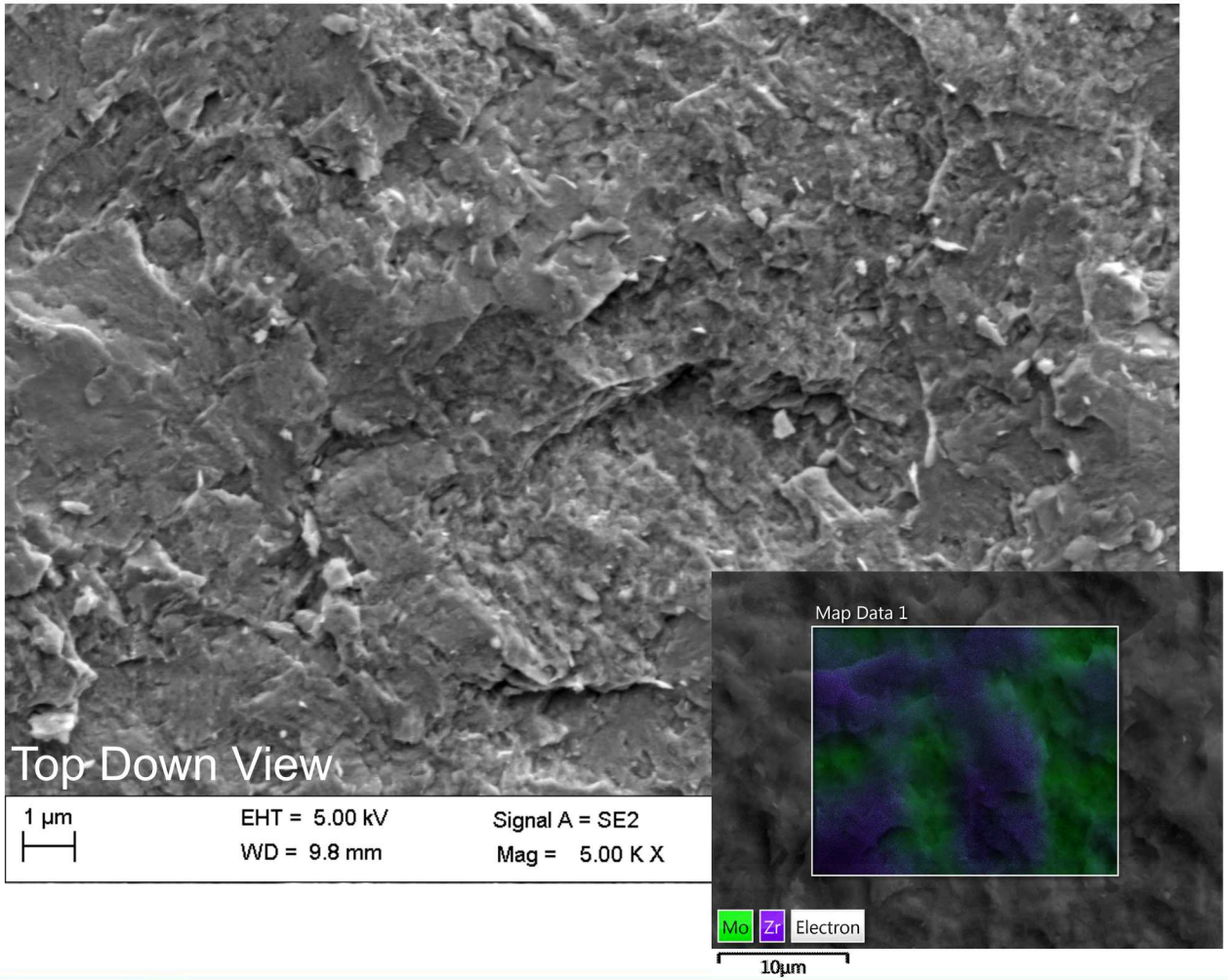
Based on Wolfer theory, **accelerated release** probably occurs when 1) lattice stresses are such that loop punching and therefore He bubble growth can no longer occur or 2) inter-bubble fracture causes cracking



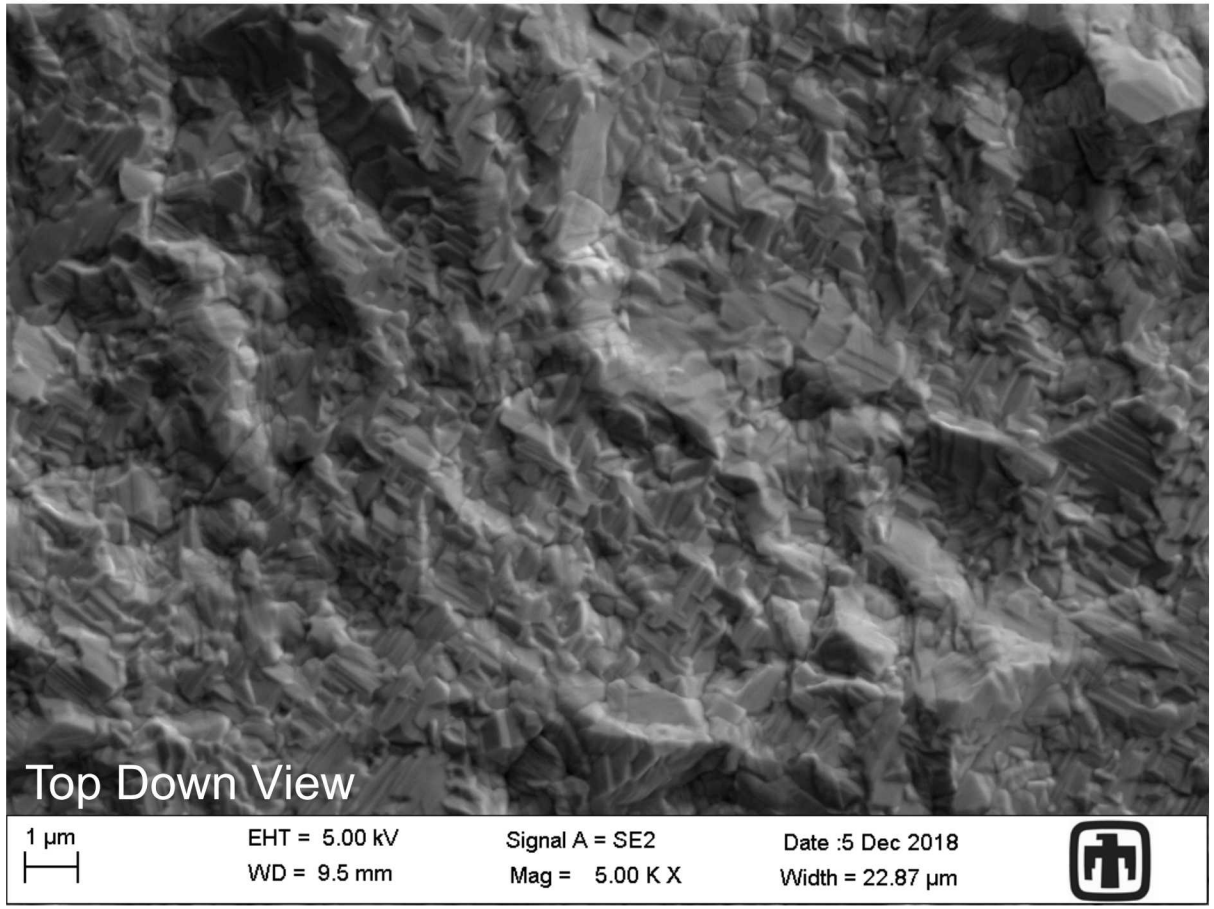
- Accelerated release occurs when {He release rate} = {He generation rate}
- Timescale is 0 months for ScT_2, ~35 months for ErT_2, ~48 months for TiT_2

Spalling can Occur with Age, Especially Near Accelerated Release

ZrT_2 Film in Accelerated Release (69 months)

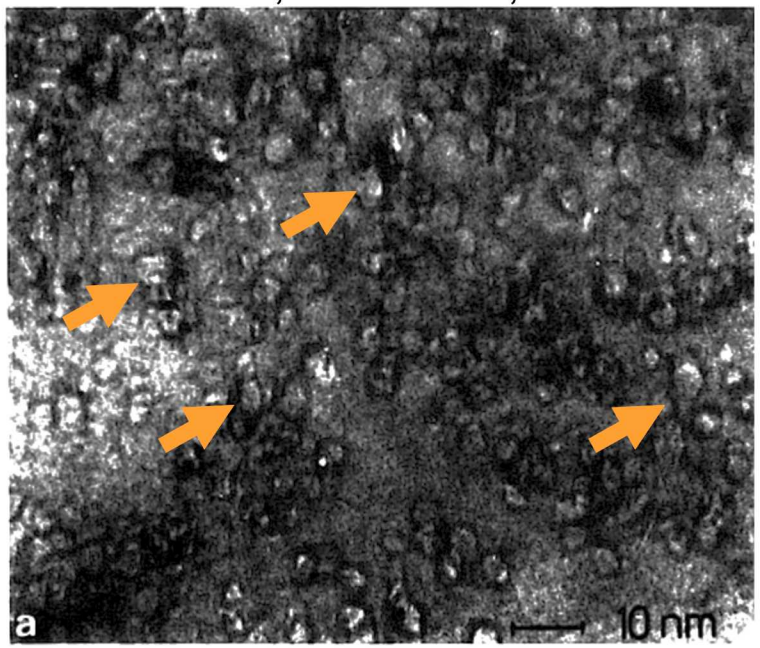


ZrT_2 Film in Early Release (22 months)

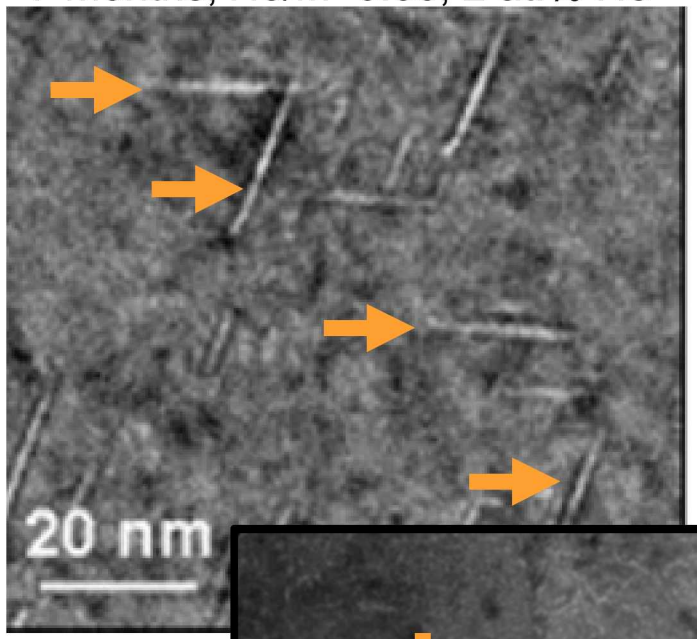


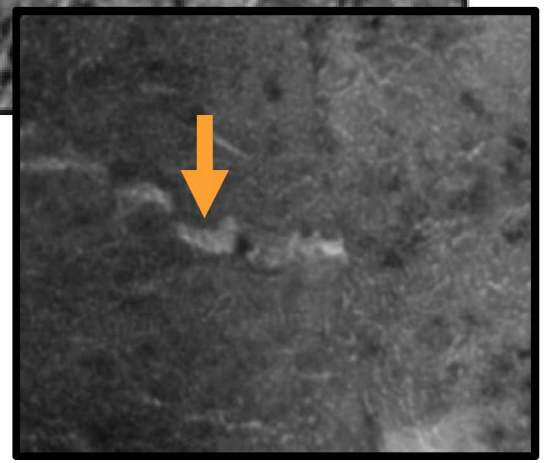
Nanometer Sized He Bubbles form During Early Release Stage

δ-$ZrT_{1.6}$ (fluorite)
27.5 months, He/M=0.24, 8 at.% He



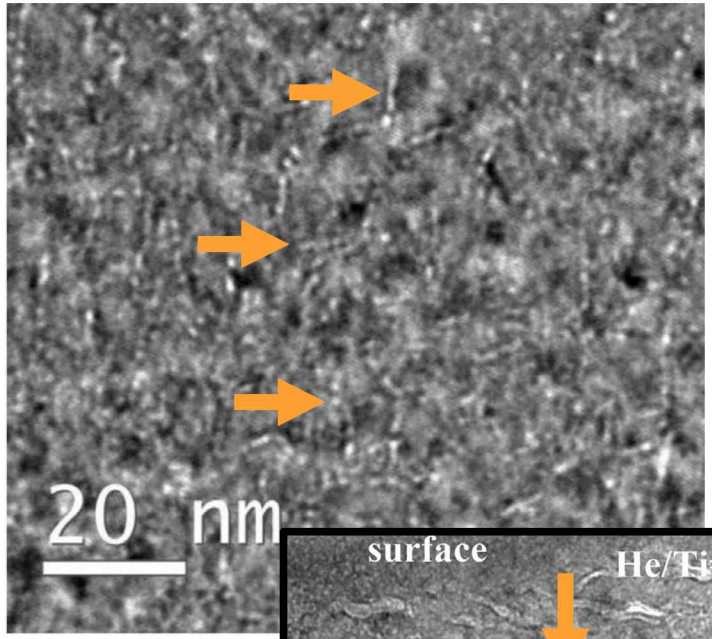
β-ErT_2 (fluorite)
7 months, He/M=0.06, 2 at.% He

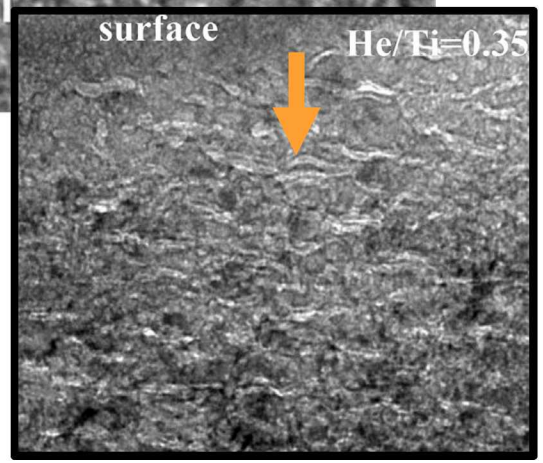




49 months, He/M=0.4,14 at.% He

β-TiT_2 (fluorite)
7 months, He/M=0.06, 2 at.% He





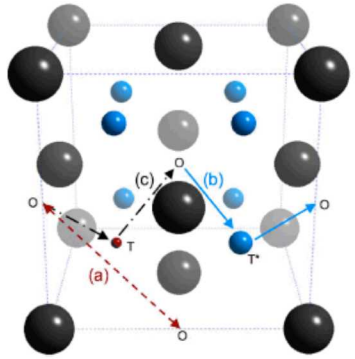
42 months, He/M=0.35,12 at.% He

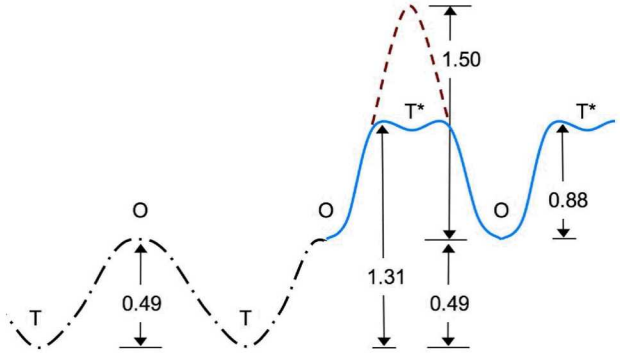
- Bubbles become faceted in $ZrT_{1.6}$, so far no evidence of platelet or crack formation.
- He platelets form in ErT_2 and TiT_2, eventually connecting to form large cracks that appear to reach the surface in some cases.
- No publications have connected surface microstructure with bubble microstructure (SEM to TEM).

Zr work: Schober et al JNM 141-143 (1986) 453-457.
Er work: Bond et al, J. Appl. Phys 107 (2010) 083514 & Snow et al JNM 453 (2014) 296-306.
Ti work: Wang et al, JNM 509 (2018) 700-706

He Bubble Nucleation, Diffusion and Growth in Metal Tritides

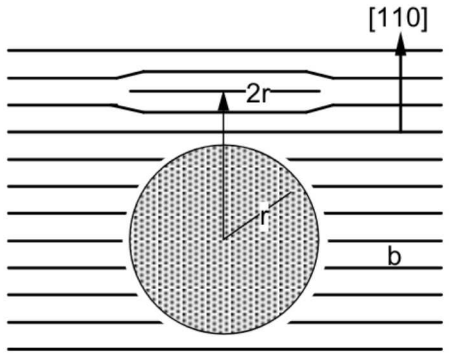
Helium Traps in T-site & Migrates through T-T diffusion in β-ErT_2

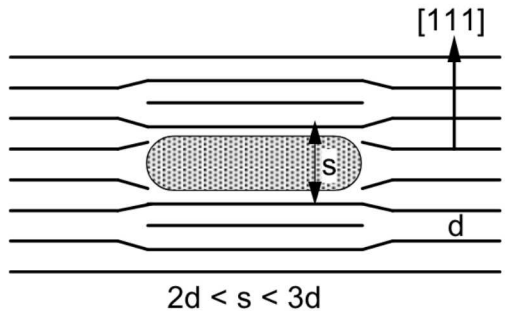




Wixom et al JAP 103 (2008) 123708

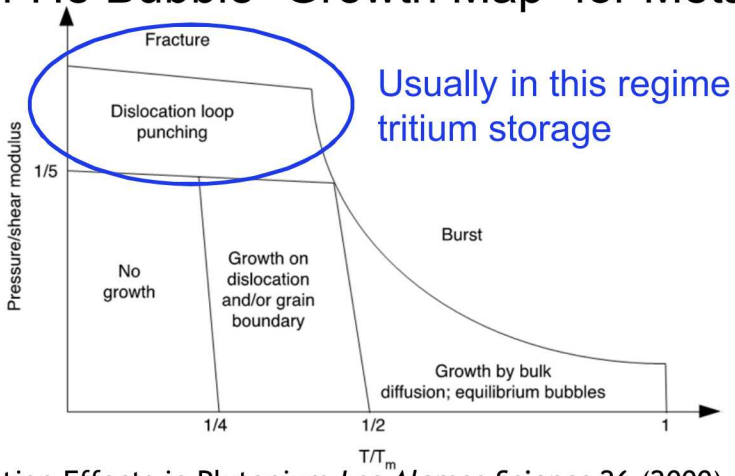
Spherical Bubbles Growth by "Dislocation Loop Punching" and Platelets can Grow by "Dislocation Dipole Expansion"





Cowgill, IHISM Workshop, St. Petersburg, Russia, 2-6 July 2007

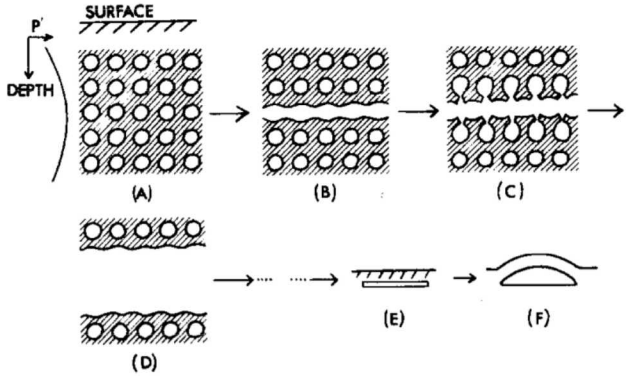
Wolfer He Bubble "Growth Map" for Metals



Usually in this regime for tritium storage

Wolfer Radiation Effects in Plutonium *Los Alamos Science* 26 (2000)

Inter-Bubble Fracture Accelerated Helium Release Mechanism

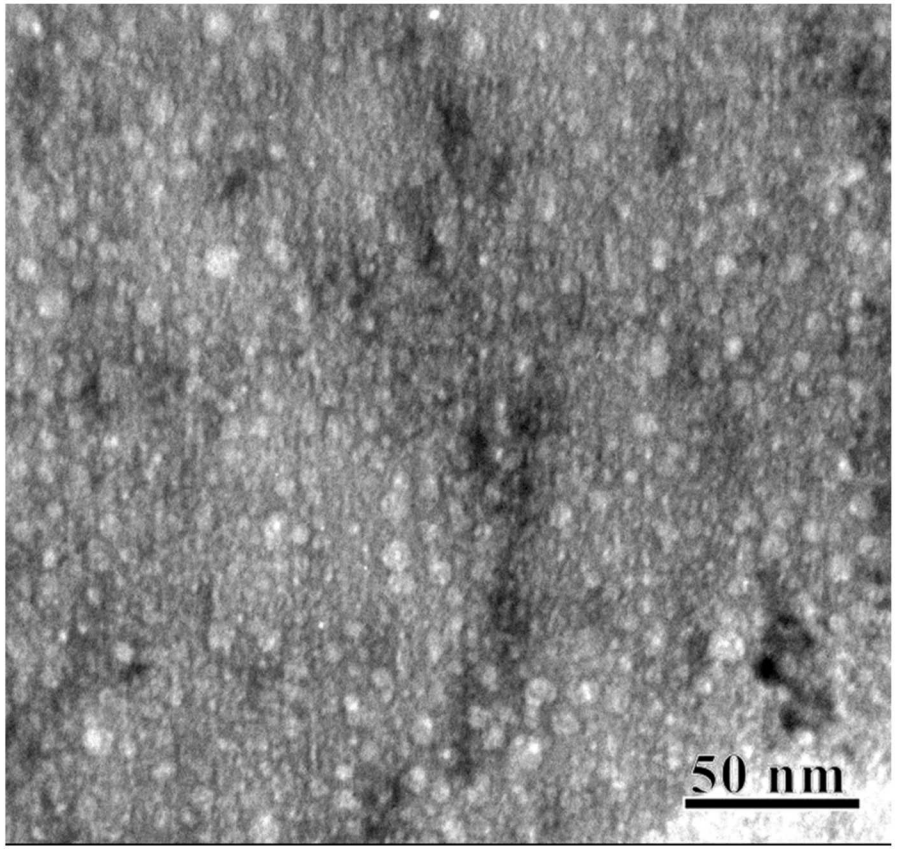


Evans JNM 68 (1977) 129-140 & Evans JNM 1978 (76 & 77) 228-234.

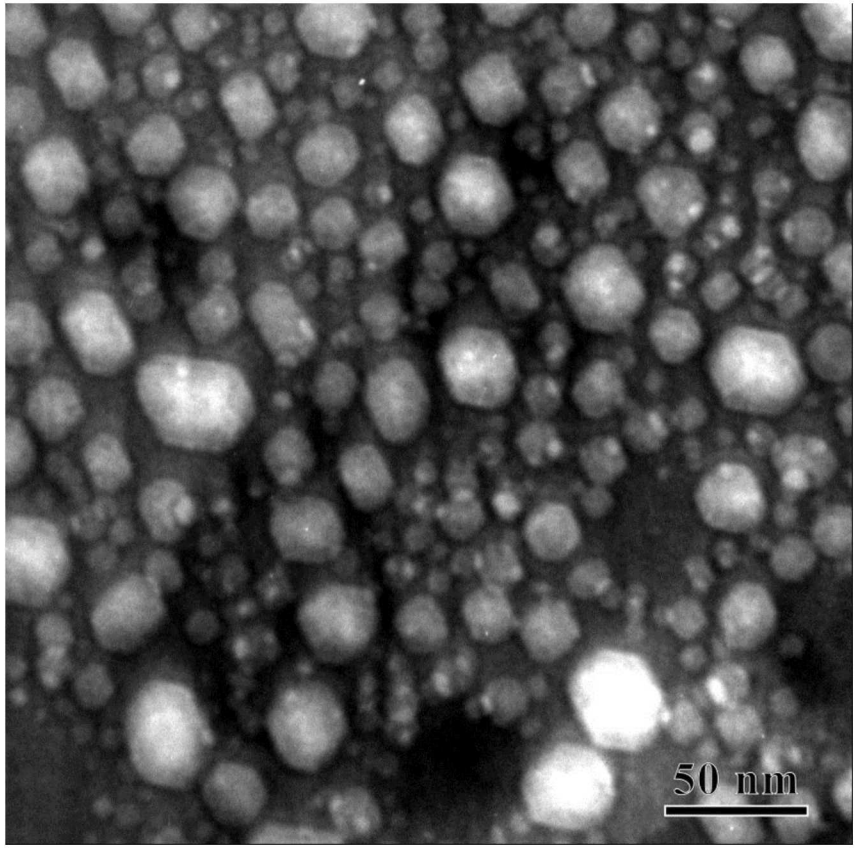
He Bubble Growth Increases with Storage Temperature

In-situ TEM anneal of **tritium aged Pd- 5% Ni** alloy containing ~12 at.% He

In-situ annealing at 400ºC , $T/T_M = 0.37$



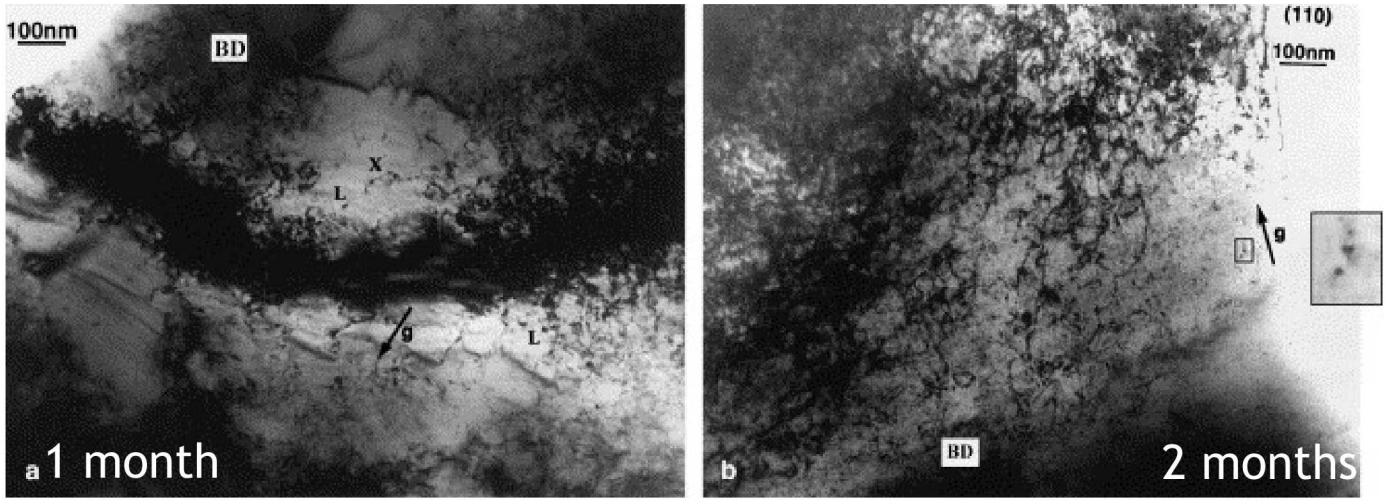
In-situ annealing at 900ºC , $T/T_M = 0.64$



- Since bubble density is extremely high in tritides, growth occurs by 1) He diffusion to bubble or 2) absorption of nearby cavities (potentially by nanoscale inter-bubble fracture between cavities?). No cavity migration.

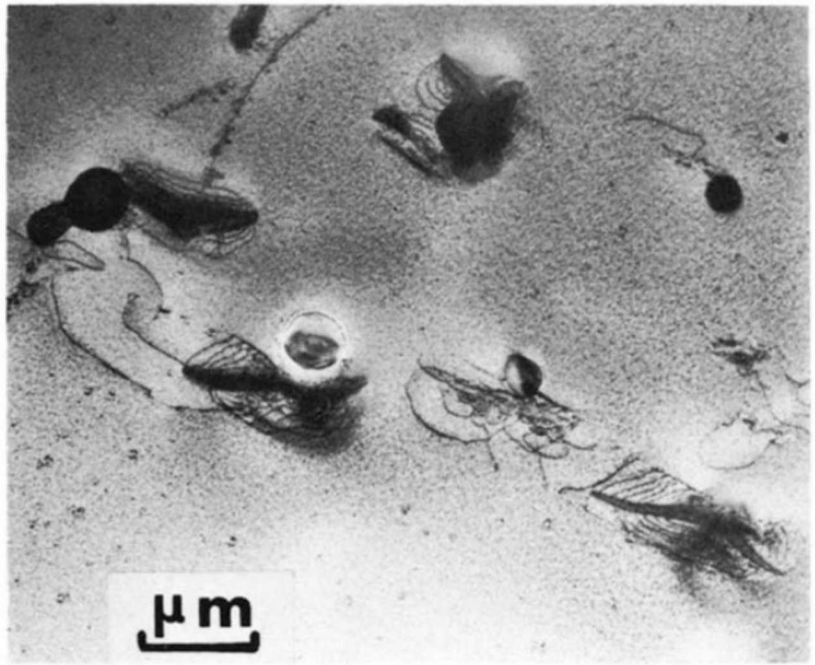
Intrinsic Defects are Produced During the Hydriding Process

Dense Dislocation Network has been Imaged in PdT



Thiébaut et al JNM 277 (2000) 217-225

Dislocations Induced by Zr Hydride Nucleation in Zr metal

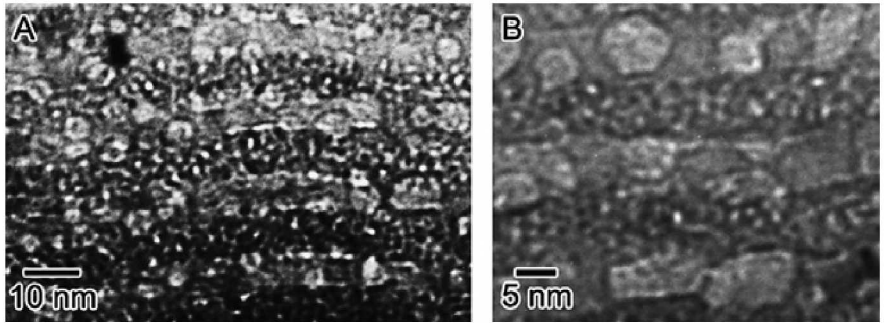


Carpenter JNM 48 (1973) 267-276

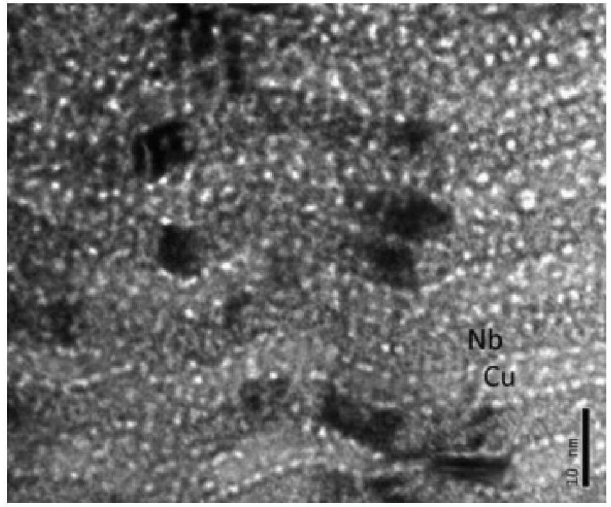
- Dislocations are created in the metal phase during hydride formation.
- Dislocation density continues to increase with hydriding/de-hydriding cycles.
- Hydriding-induced dislocations may act as trapping sites for He as metal tritides age.

Engineered Nanostructures Have Been Shown to Trap He at Interfaces

Multilayered Nanocomposites

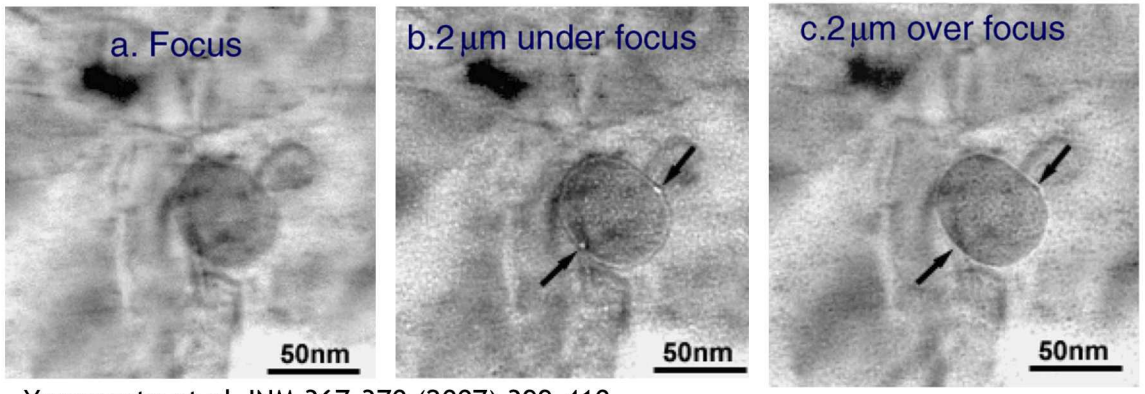


Hattar *et al*. Scripta Materialia 58 (2008) 541-544

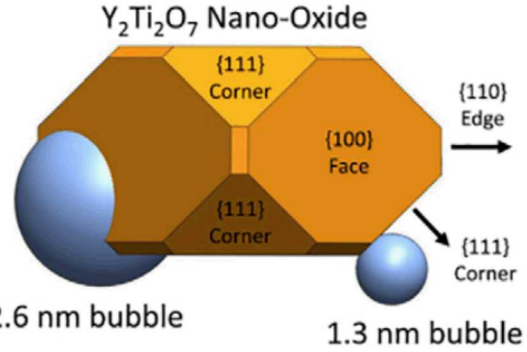


Demkowicz et al Curent Opinion in Solid State and Materials Science 16 (2012) 102-108

Nanostructured Ferritic Alloys (NFAs)



Yamamoto et al JNM 367-370 (2007) 399-410



Odette Scripta Materialia 143 (2018) 142-148

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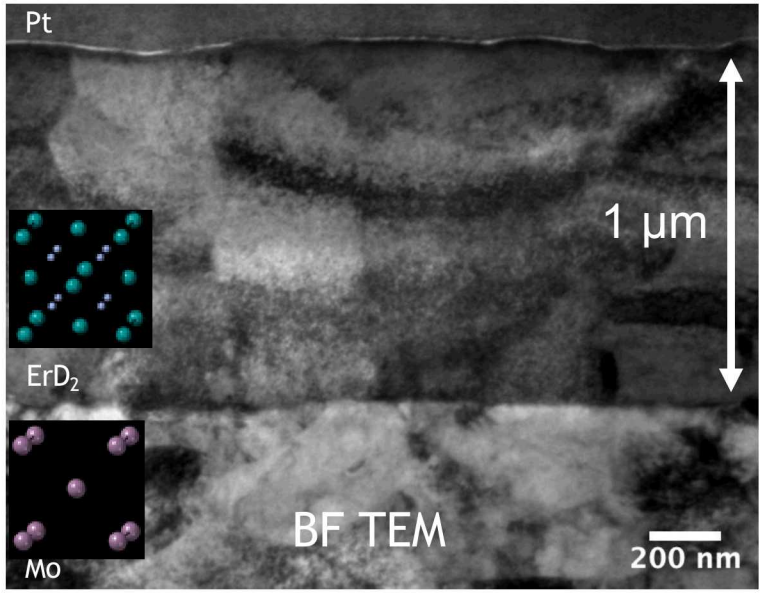
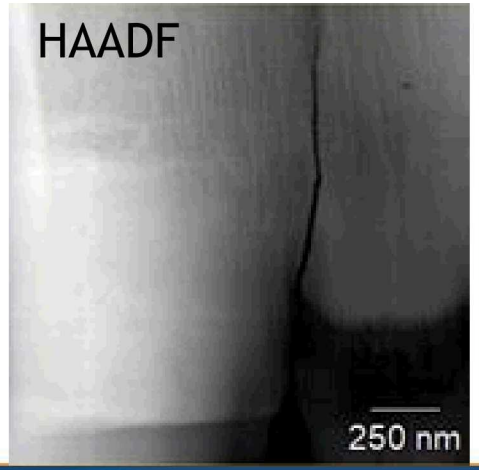
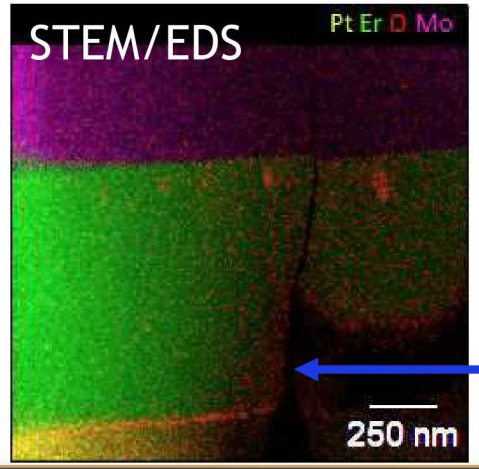
As-Deposited/Loaded ErD_2 Samples were Characterized with TEM & XRD

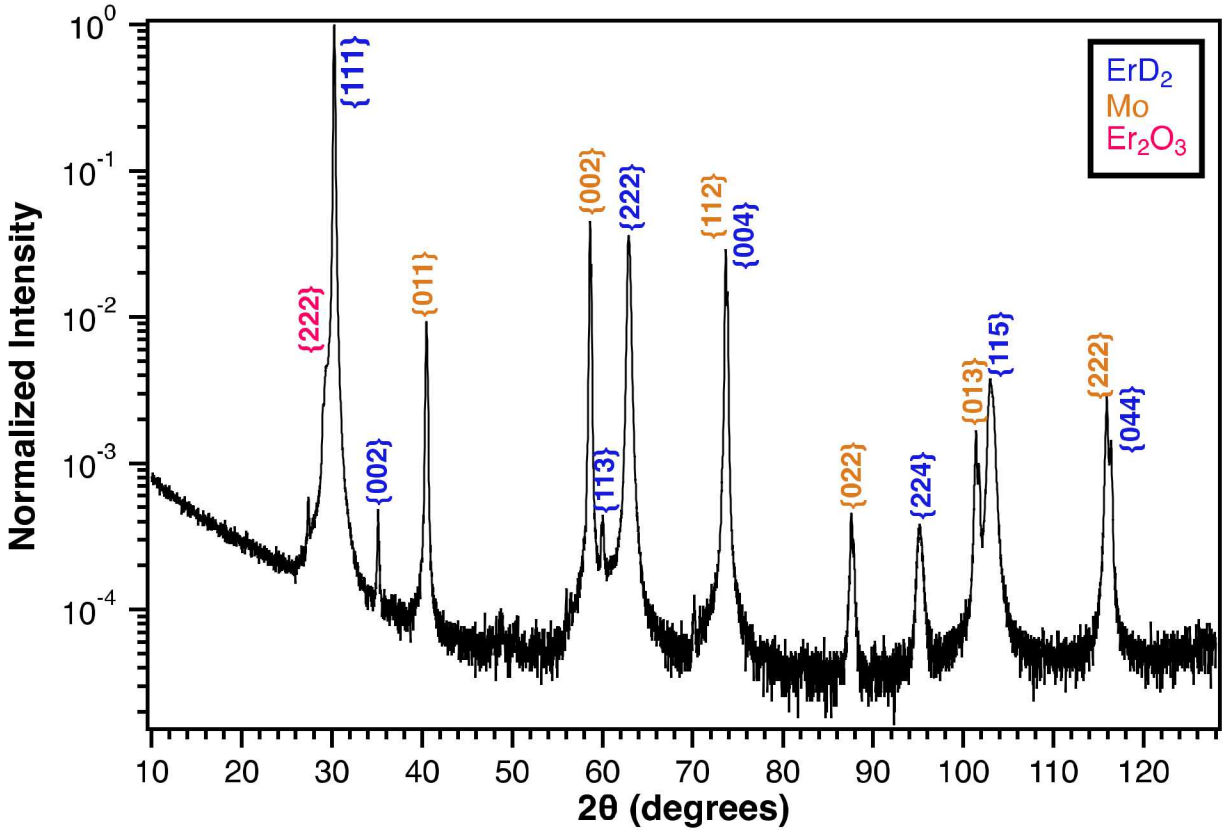
- 1 μm thick Er films were evaporated onto polished Mo substrates and loaded with ^2H, a surrogate for ^3H.







Oxide present at interfaces likely formed during FIB



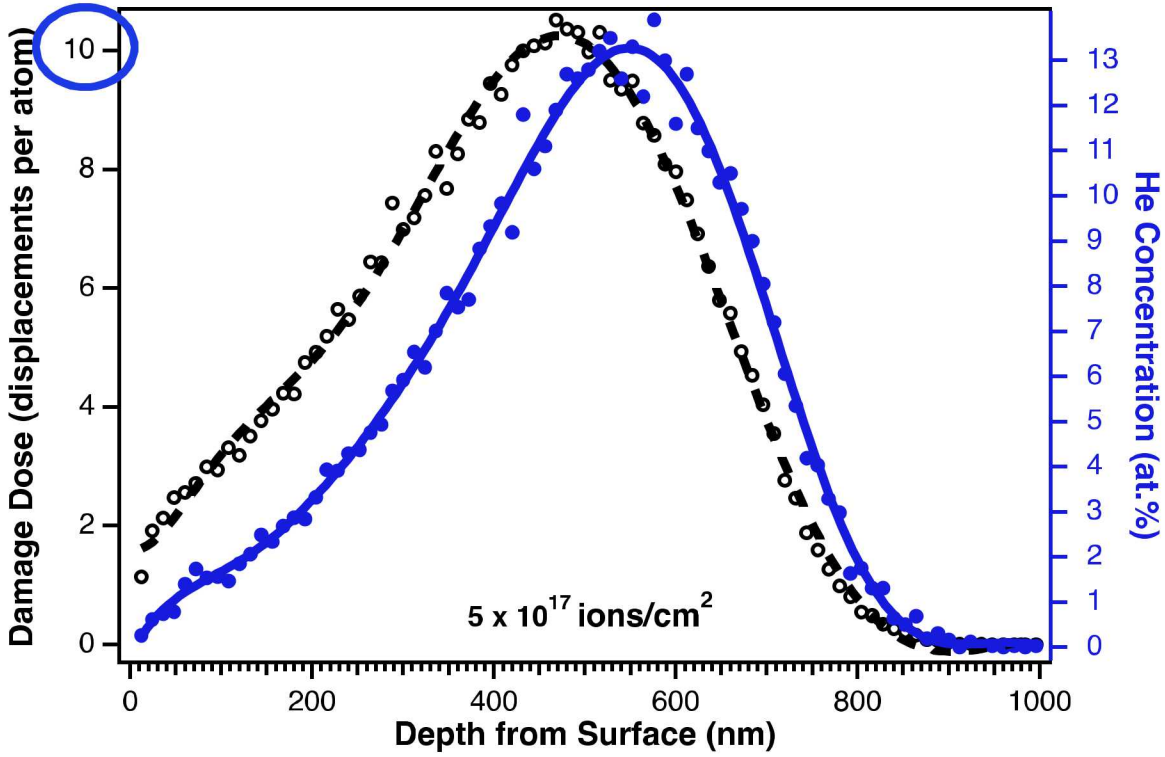
- Very little oxide in XRD pattern

Samples were He Implanted to Simulate Long-Term Tritium Decay

Danfysik Implanter @ LANL

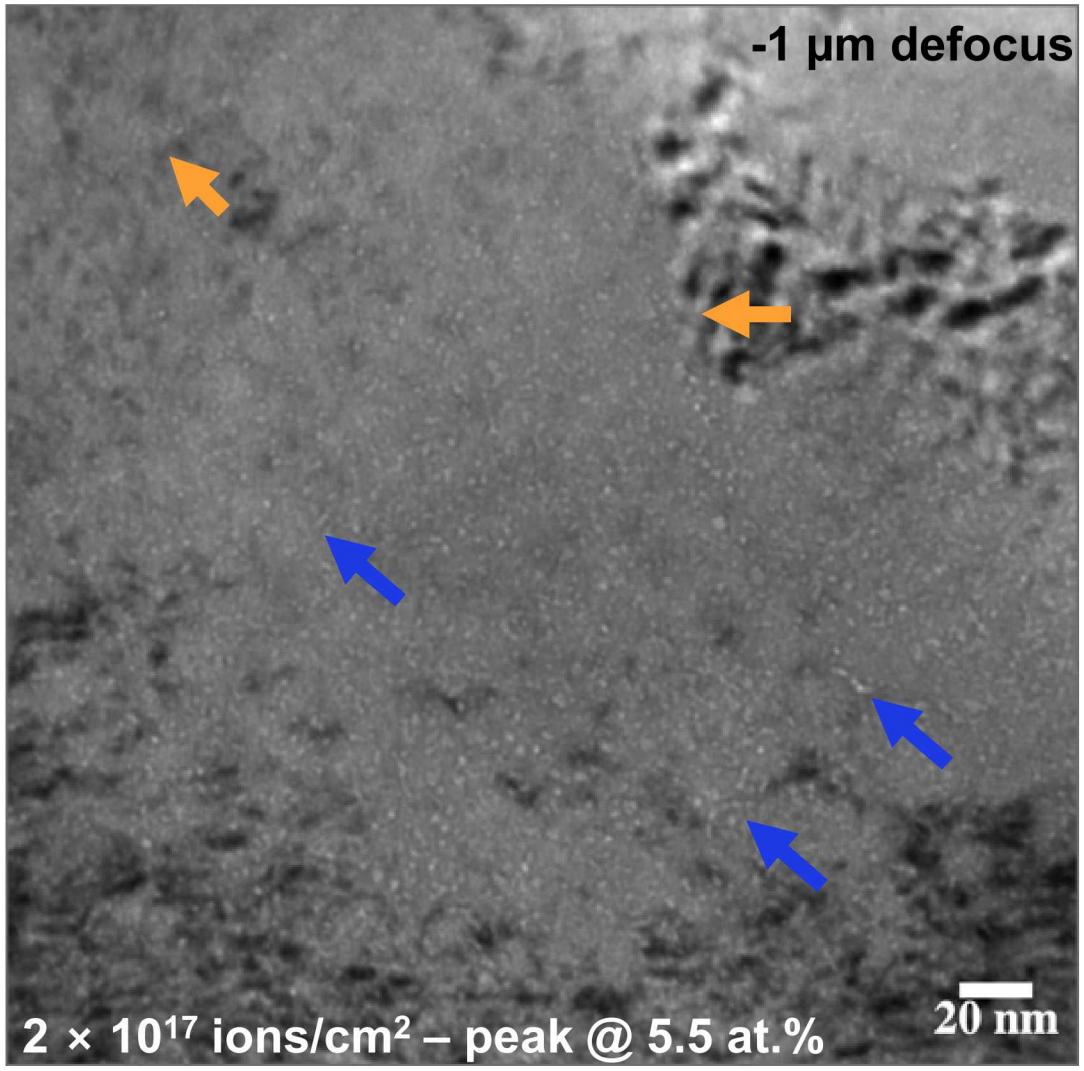
LANL IBML Website: https://www.lanl.gov/science-innovation/science-facilities/ion-beam-materials-lab/

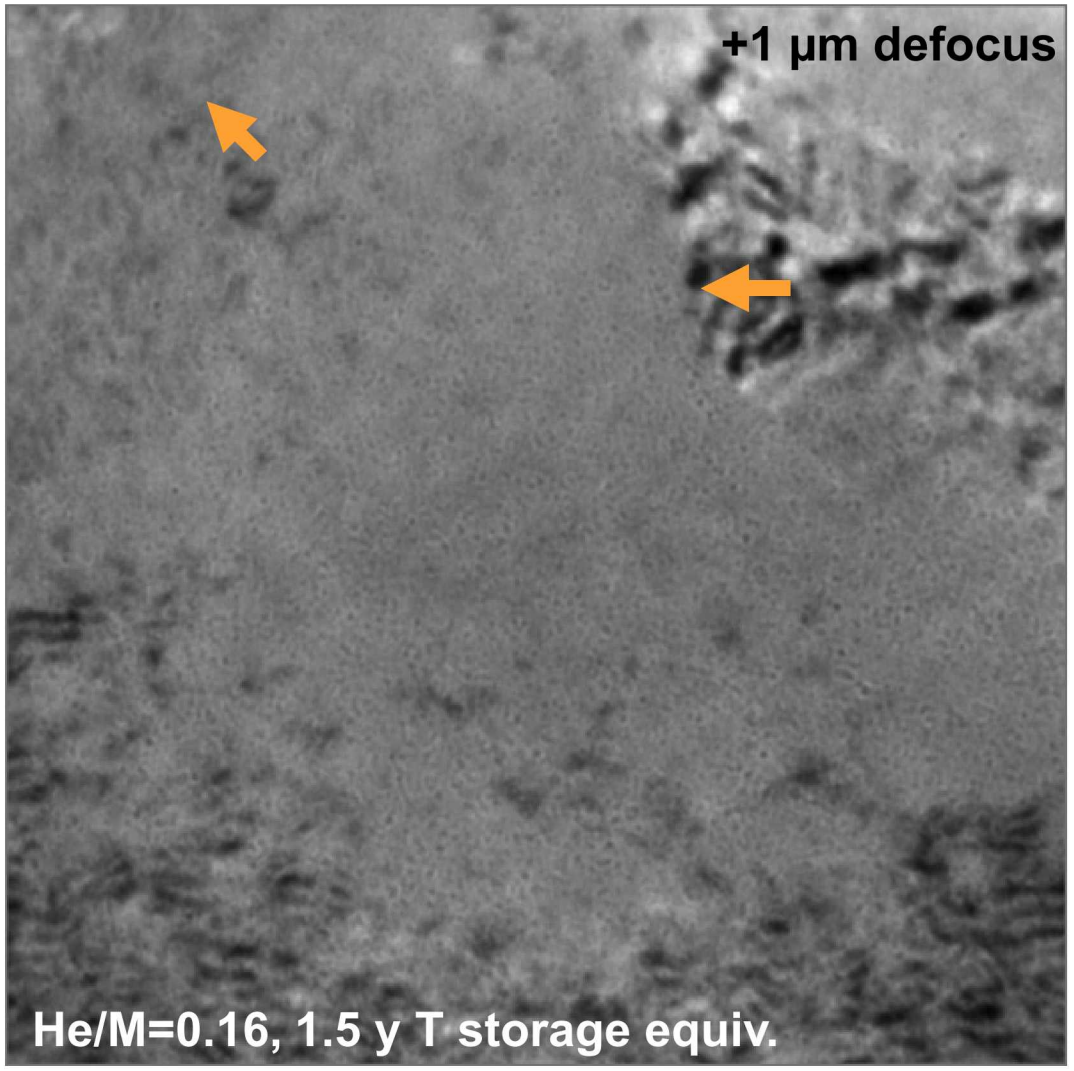
Bulk Implantations were done using 120 keV ^4He



- He implantation is used to reach "accelerated release" level He concentrations (>10 at.% He) in a day, rather than several years. Removes radioactive contamination hazards.
- Implantation is not an exact surrogate for ^3H β-decay, which causes zero atomic displacement damage and continuously removes H from the lattice.

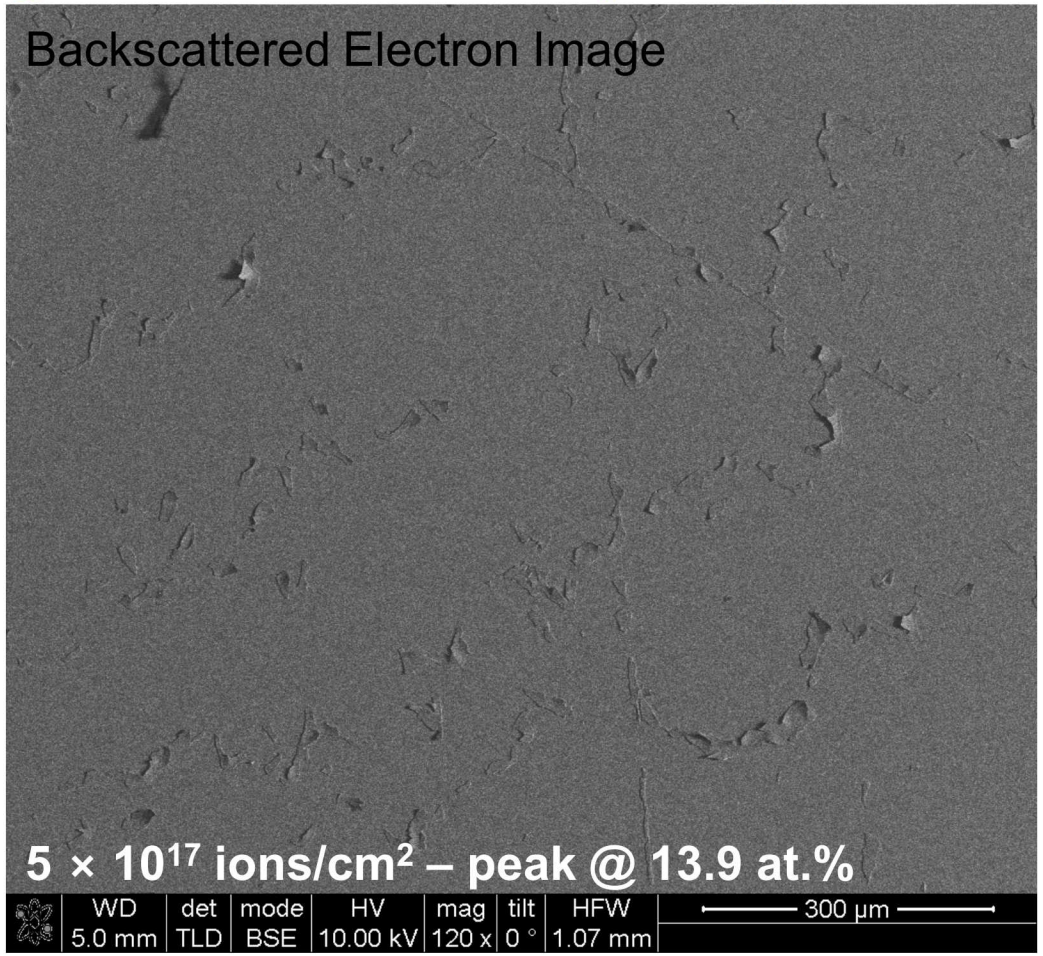
Nanometer Sized He Bubbles were Observed After 1-3 at.% He

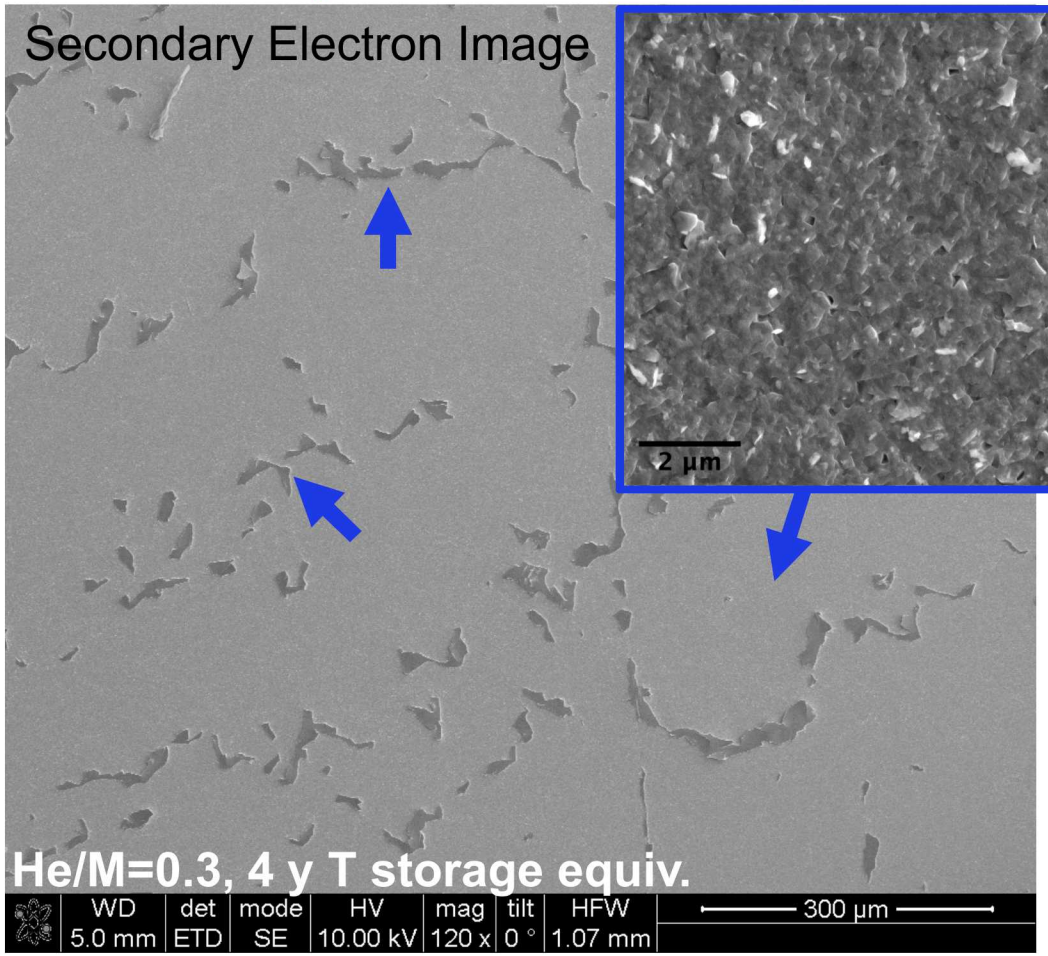




- He bubbles were found starting at 1.7 at.% (low density). Grain boundary nucleation & some evidence of linkage.

Significant Surface Spalling Occurred after Implantation to High Dose

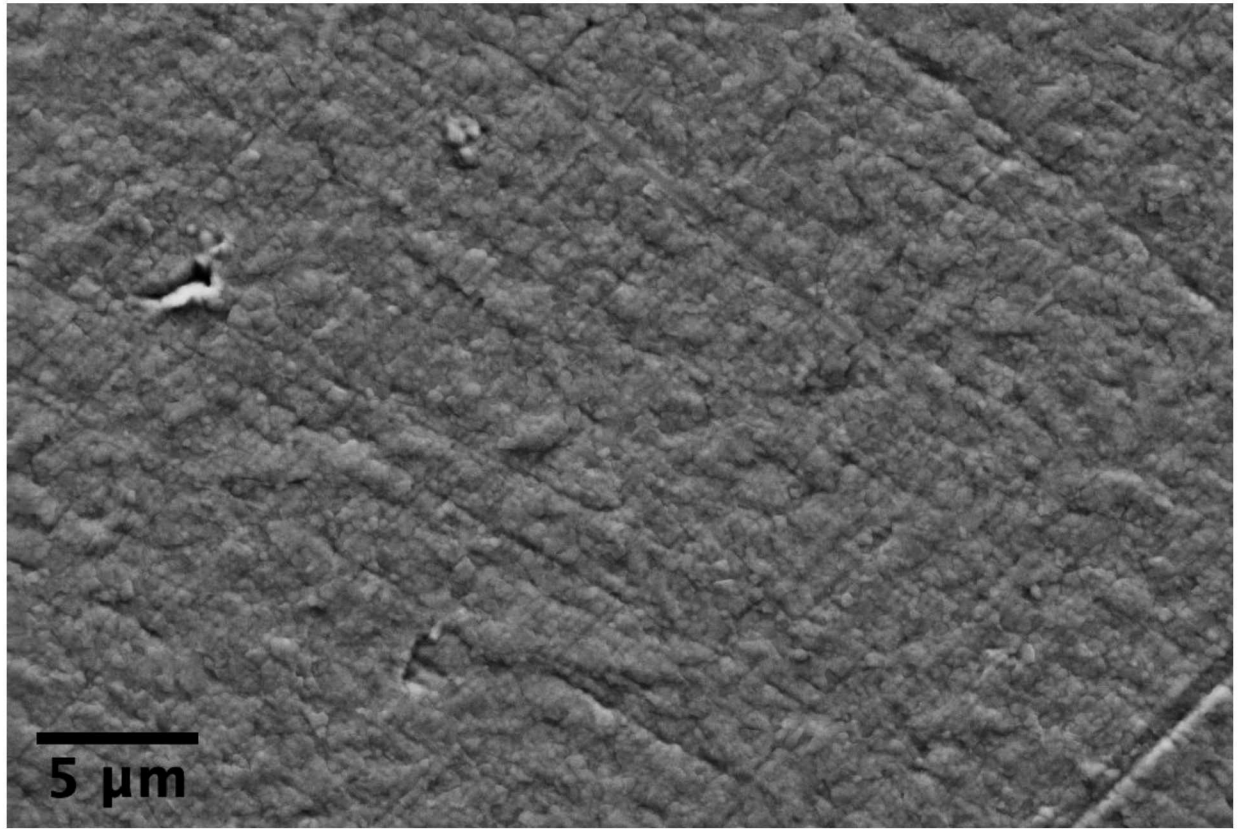




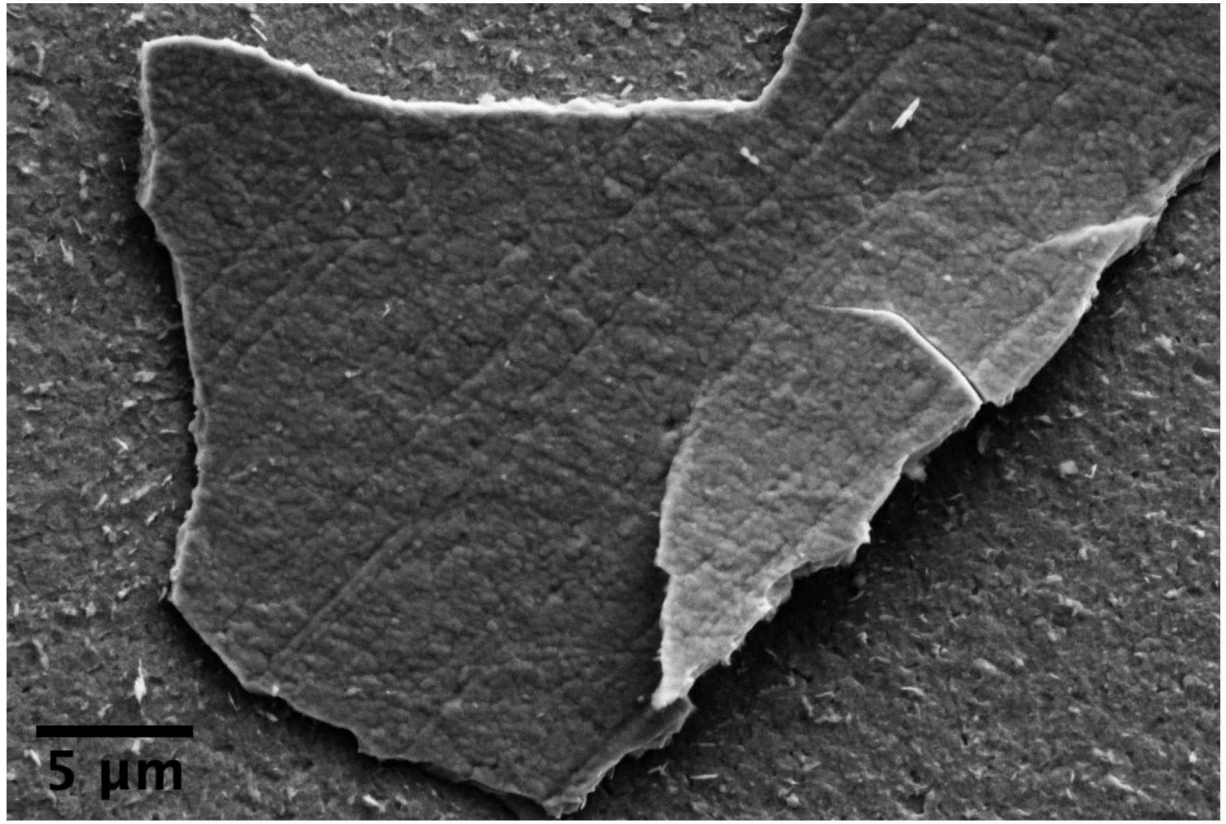
- SE image shows that most of the surface spalled off, leaving a few un-spalled areas. Lack of contrast in BSE image shows that spalling occurred within the 1 µm film thickness, not at the substrate.
- Fracture surface does not appear to show intergranular fracture, no obvious failure mechanism.

No Evidence of Blister Formation in Un-Spalled Regions

Unirradiated Surface

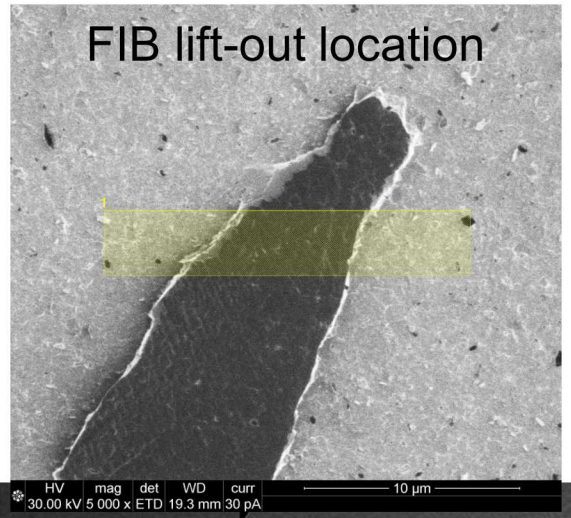


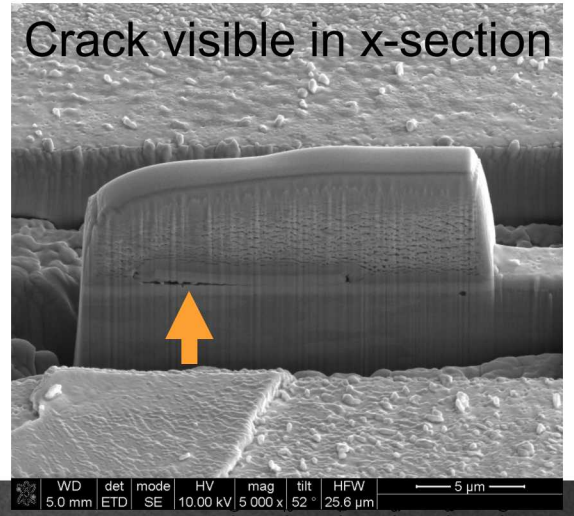
Spalled Surface (5×10^{17} ions/cm^2)

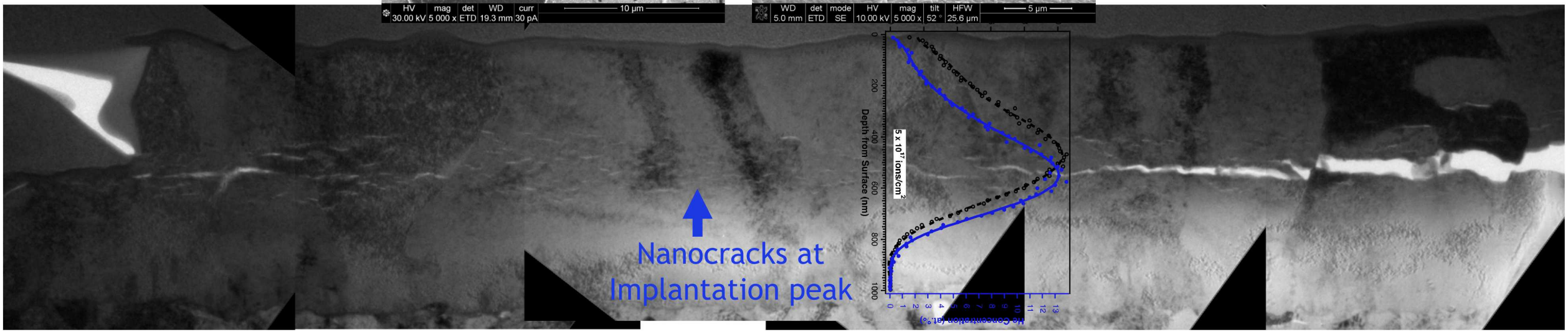


- Un-spalled surfaces appear nearly identical to the unirradiated sample surface, with the exception of cracks and flaked regions.
- Edges of un-spalled areas appear very jagged, not round as one would expect if blisters had burst to form them.

Nanosized Cracks were Observed in the Un-Spalled Areas

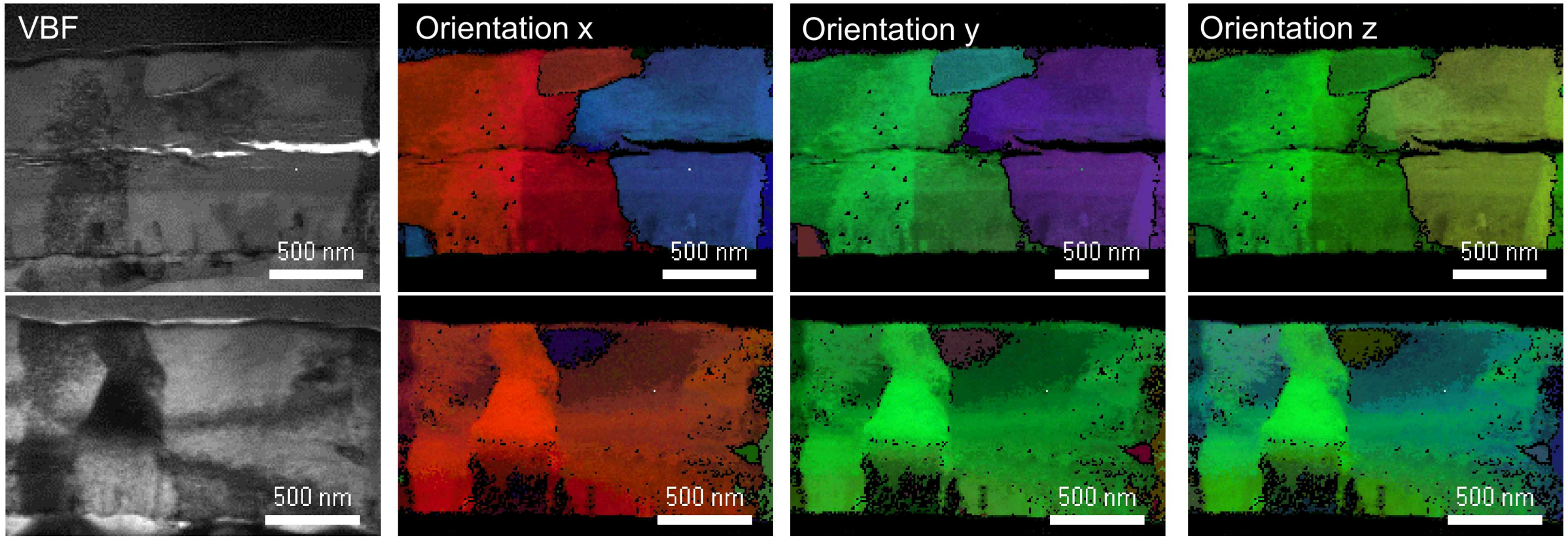




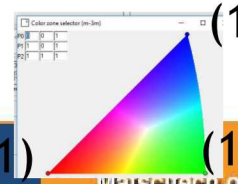


- Nanocracks appear after ~7.5 at.% He. Stress between cracks causes linkage at the implantation peak, forming larger cracks that cause spalling.

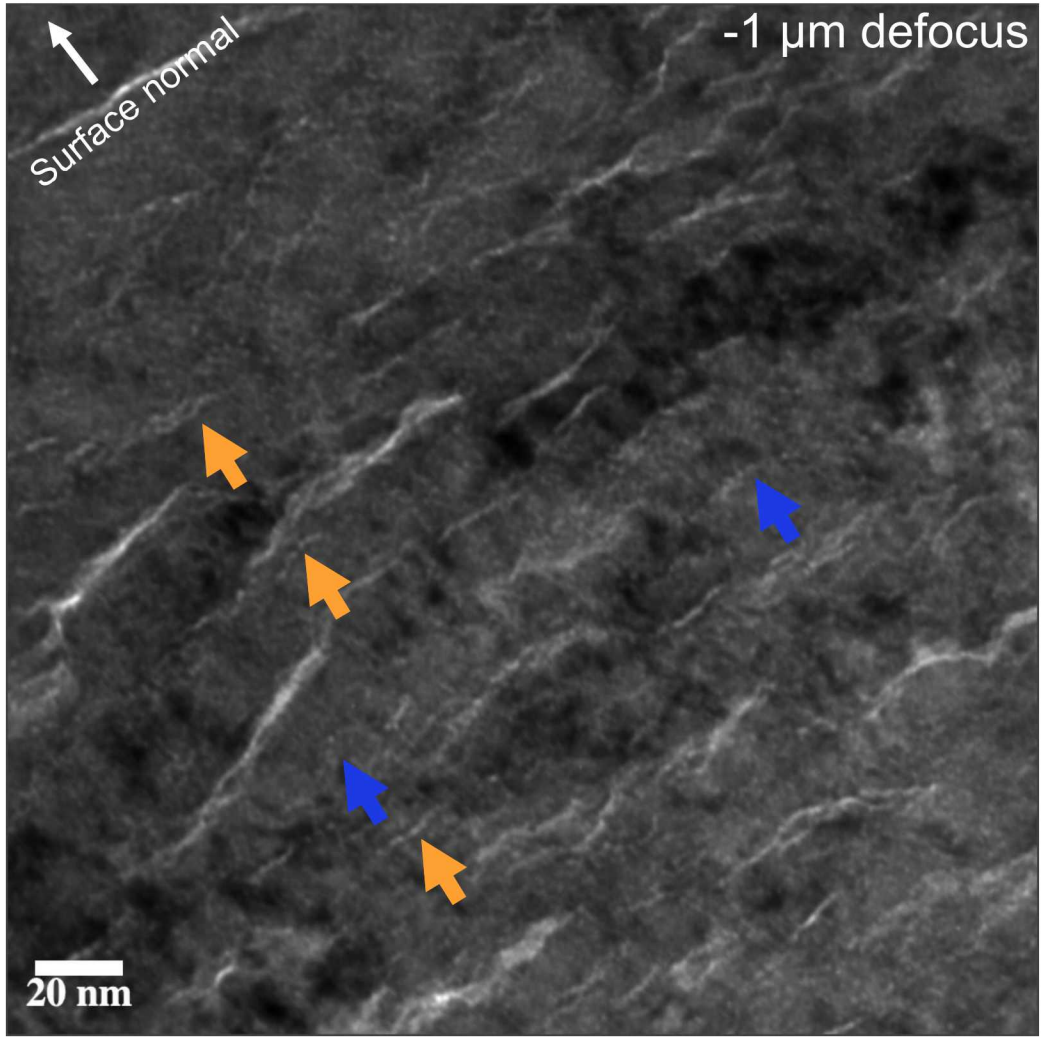
Precession Electron Diffraction Confirmed Intragranular Cracking

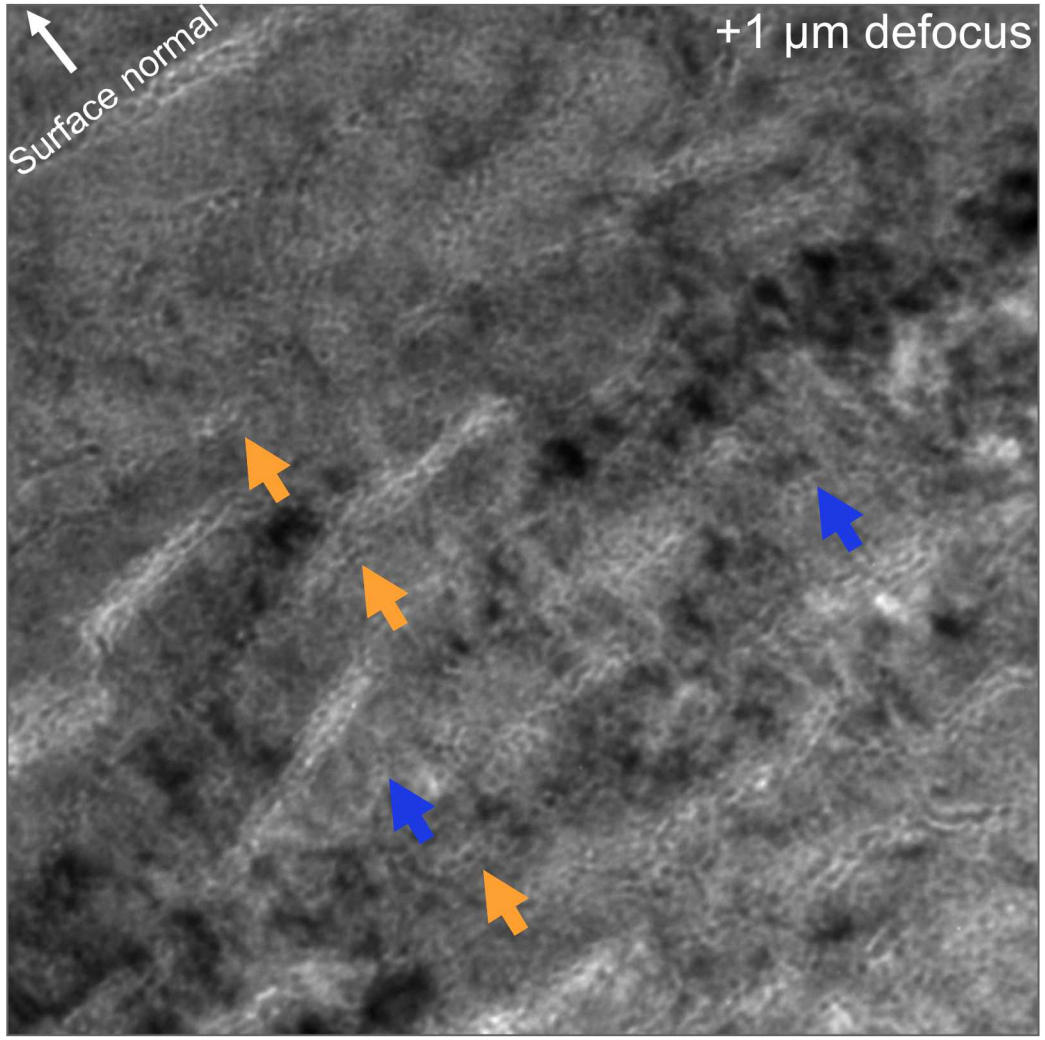


- Crack clearly initiates inside the grain and propagates intragranularly.
- Small misorientations (<15°) were measured near the near the crack region in some samples but were believed to be due to bending in the FIB lift-out, as they are also present in the pristine (unirradiated) sample.



Bubbles Appear to Form Chains that Lead to Nano-crack Formation





- Nano-cracks are spaced 4-15 nm apart and not always exactly parallel with the surface. In some cases, the bubble chains appear to be forming along interfaces or defects.

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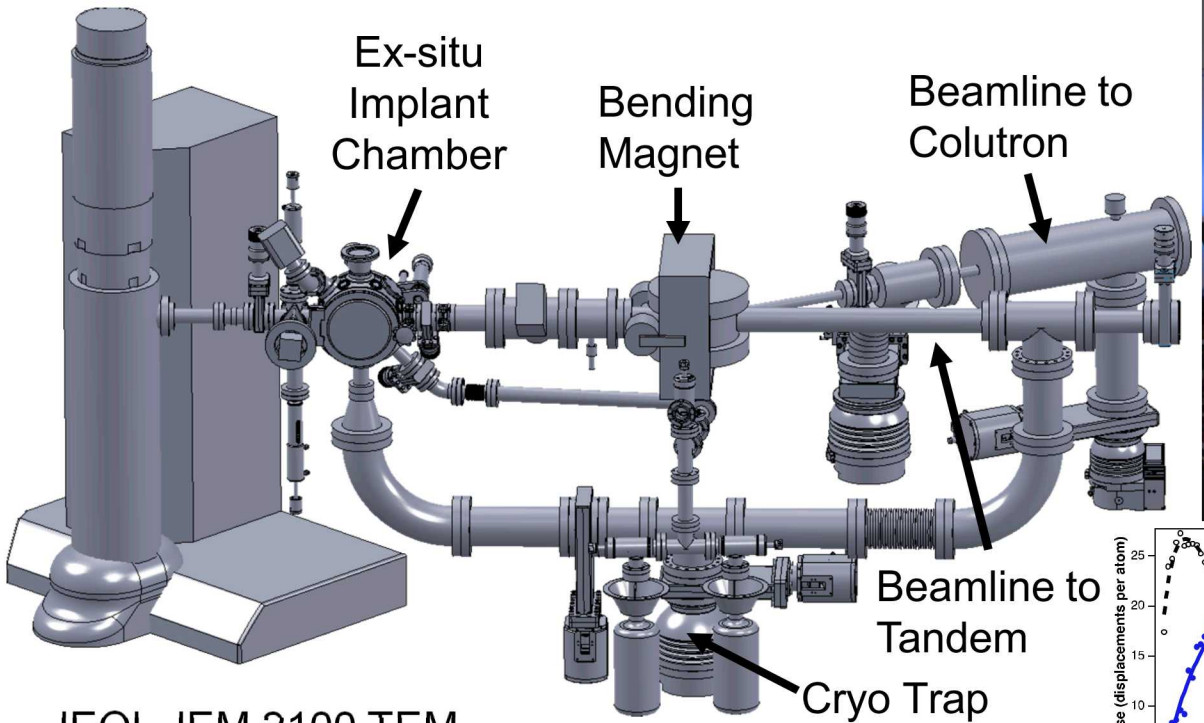
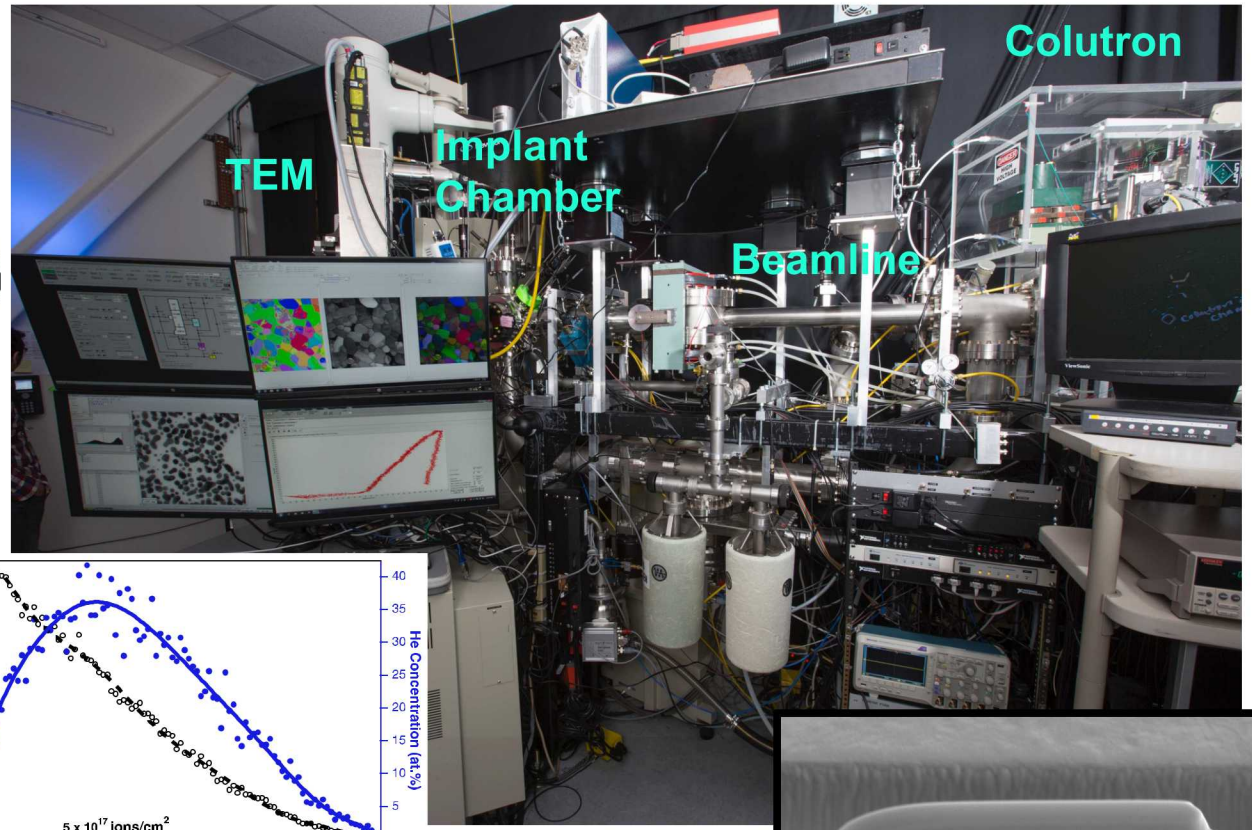
- **Summary**

In-situ He Implantation Using Sandia's In-situ Ion Irradiation TEM (I^{3}TEM)

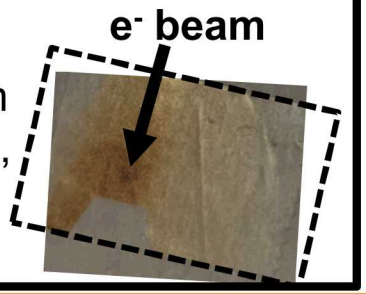


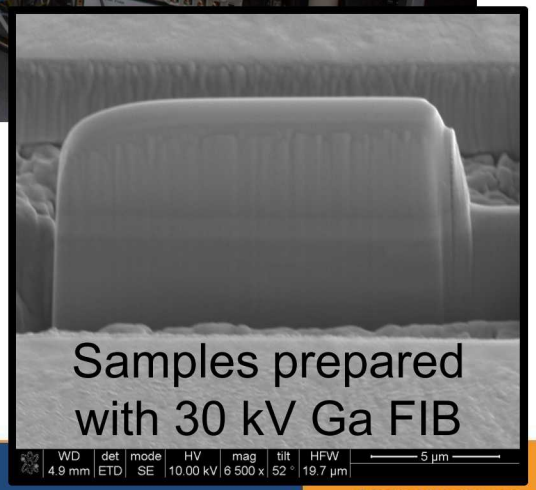
JEOL JEM 2100 TEM



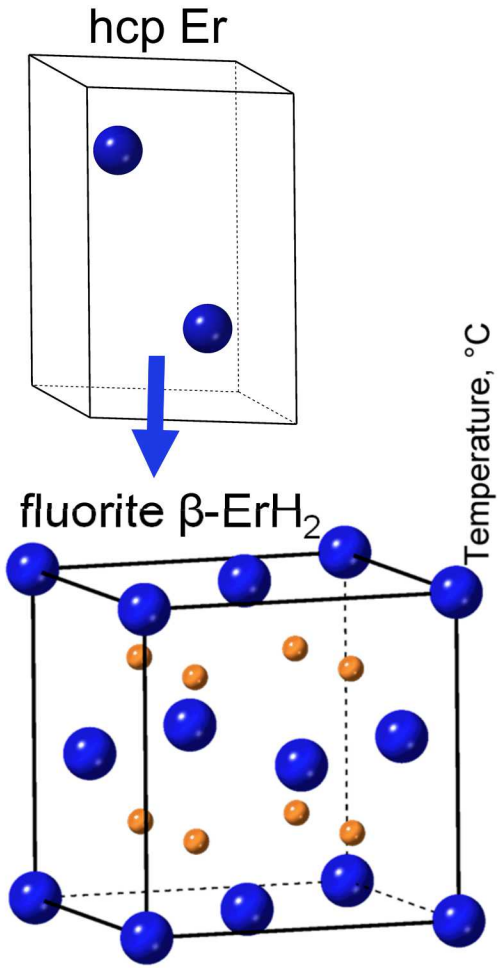
- Bubble evolution can be quantified in the same location as a function of He concentration
- System is equipped with heating stages and Nanomegas Precession Electron Diffraction (PED)

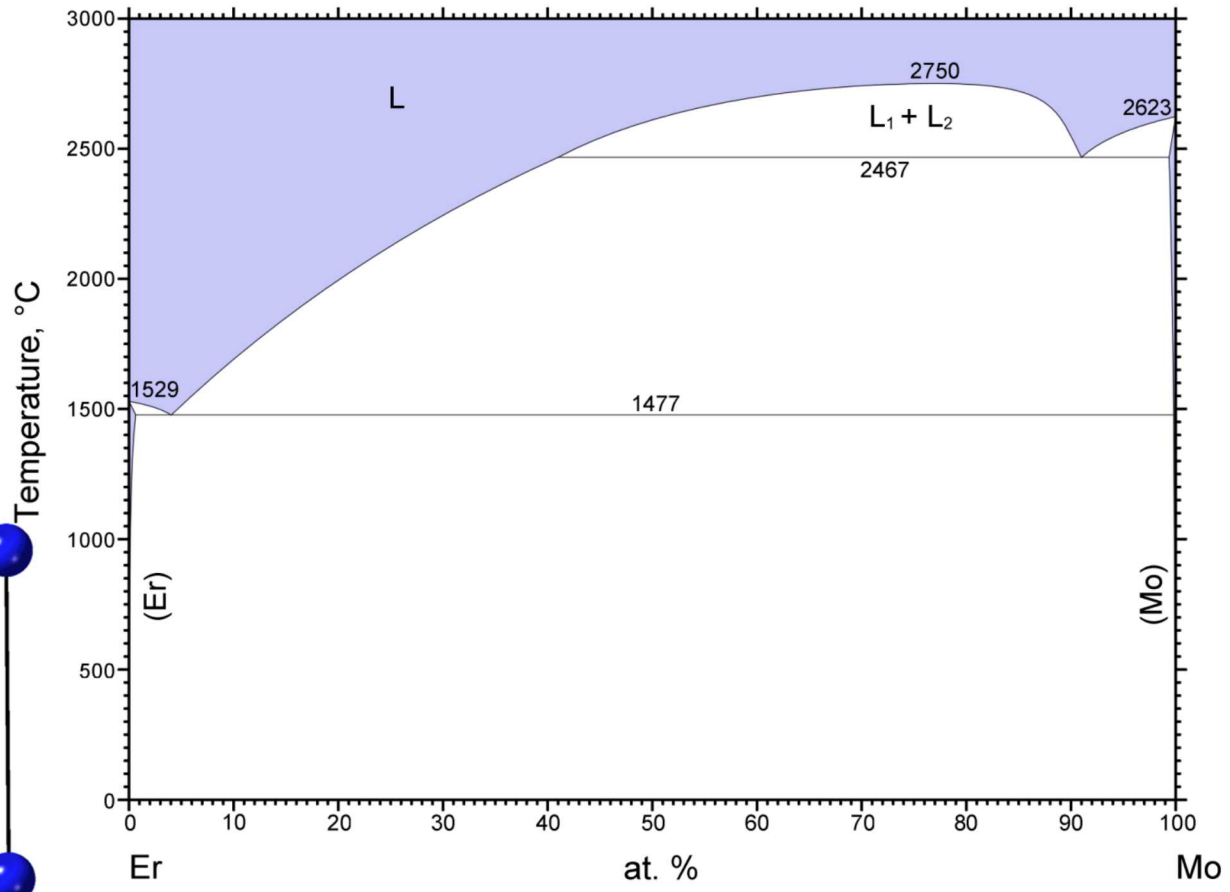
10 keV He Beam
Spot in Low Mag,
+30° tilt in x

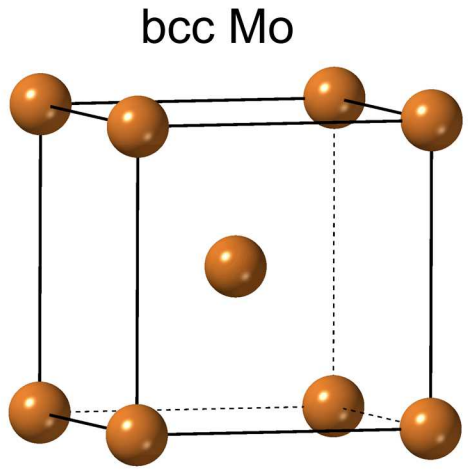




All Multilayered Structures were Prepared with Er and Mo

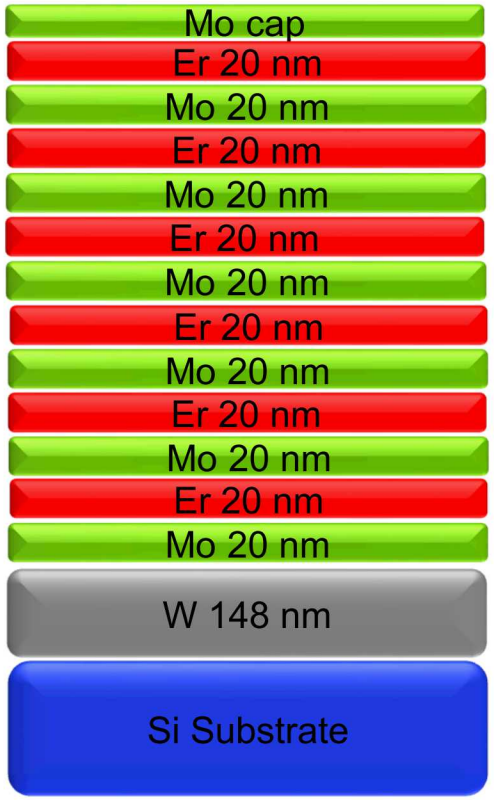




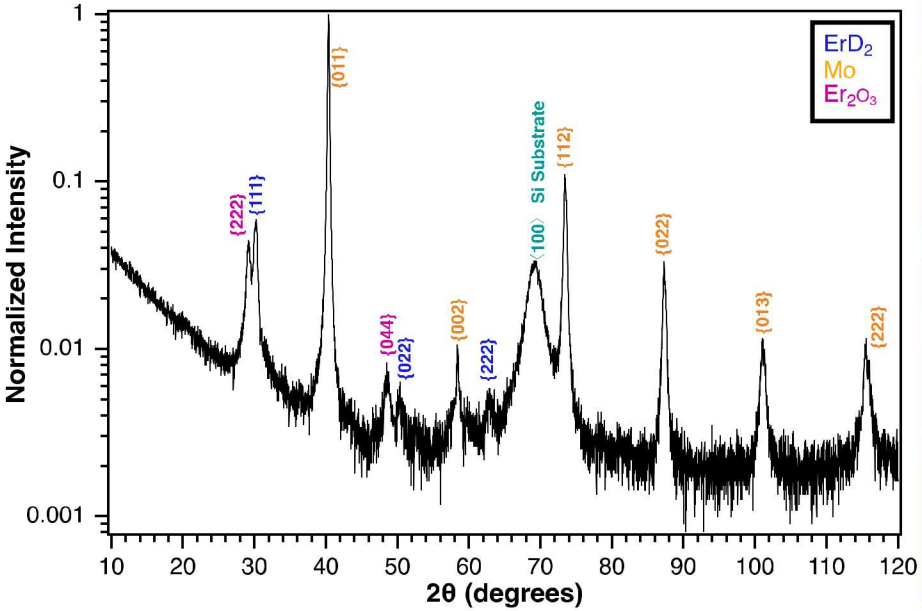


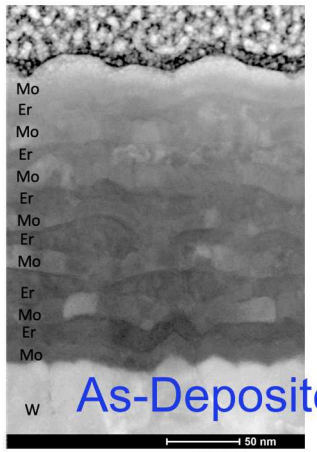
- Er and Mo are fully immiscible up to 1477ºC and remain immiscible after hydriding.
- Hydriding induces a 10% volume expansion, so significant residual stress is expected in the multilayered structure.
- Big Question: Can we initiate the hydride reaction in a multilayered structure?

Multilayer ErD_2/Mo Films were Deposited and Successfully Hydrided

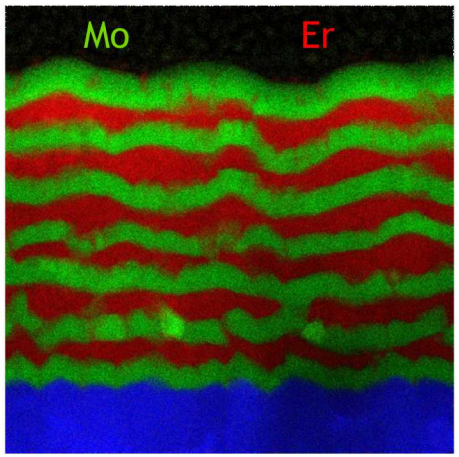


- W adhesion layer was sputter deposited at room temperature onto a Si substrate. 13 Er/Mo layers were electron beam evaporated.
- Samples were diced into 1 x 1 cm squares & successfully loaded with deuterium, as evidenced by the absence of hcp-Er & presence of fcc-ErD_2 in the XRD pattern.
- STEM/EDS maps of as-deposited/loaded structures showed no diffusion of adhesion layer, less oxide than previous films.

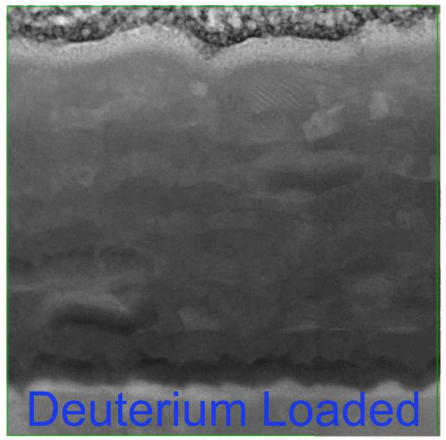




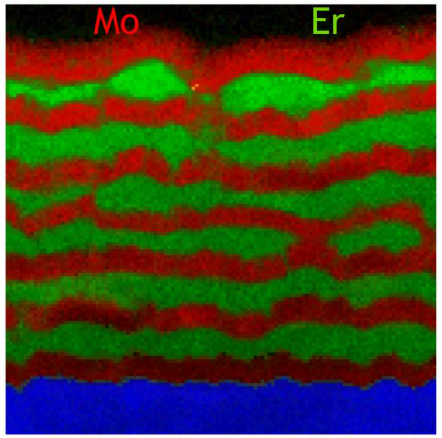
As-Deposited



250 nm field of view



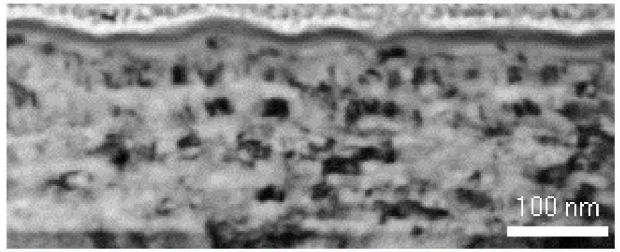
Deuterium Loaded



250 nm field of view

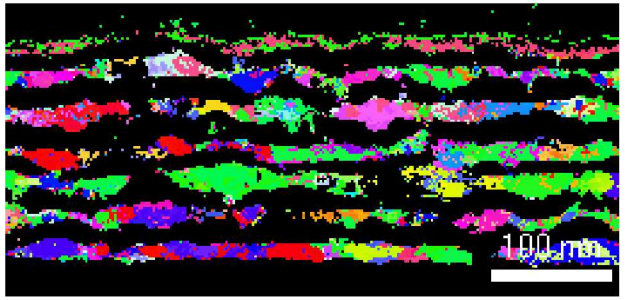
Grain Structure Changes were Characterized After Hydriding

Er/Mo (as-deposited) Multilayers

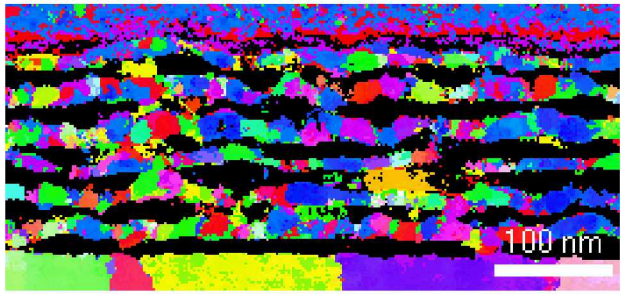


Max Er grain size: **31 nm**
Max Mo grain size: **33 nm**

Er z orientation



Mo z-orientation

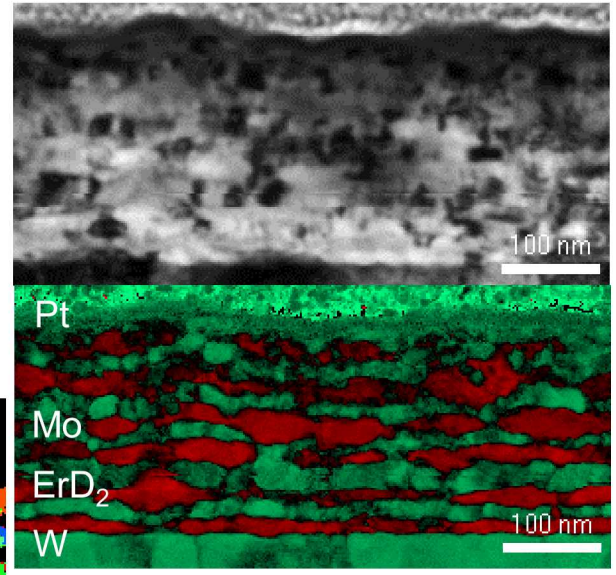


PED parameters
2 nm step size
Smallest condenser
Spot 5, α = 3
0.1° precession angle

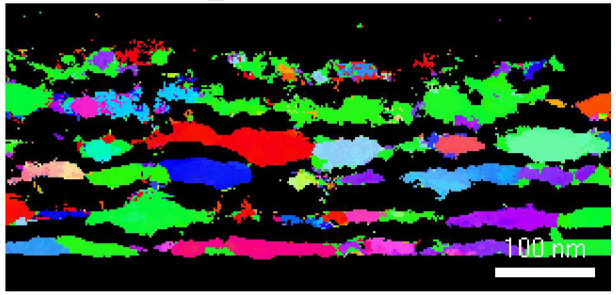
*images were cropped for grain size analysis

ErD_2/Mo (as-loaded) Multilayers

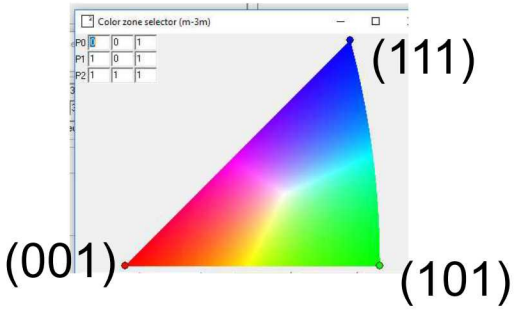
Max ErD_2 grain size: **62 nm**
Max Mo grain size: **37 nm**



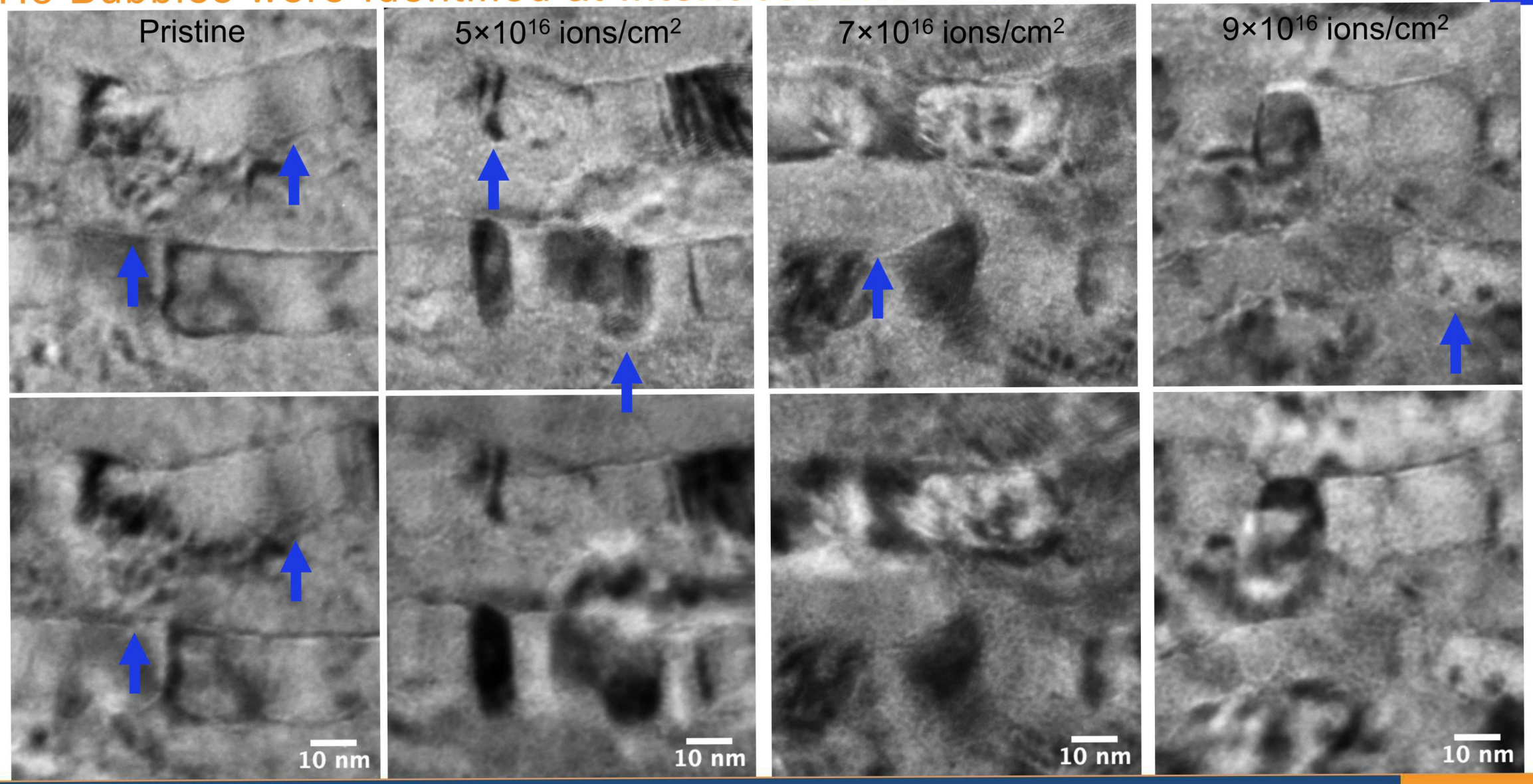
ErD_2 z orientation



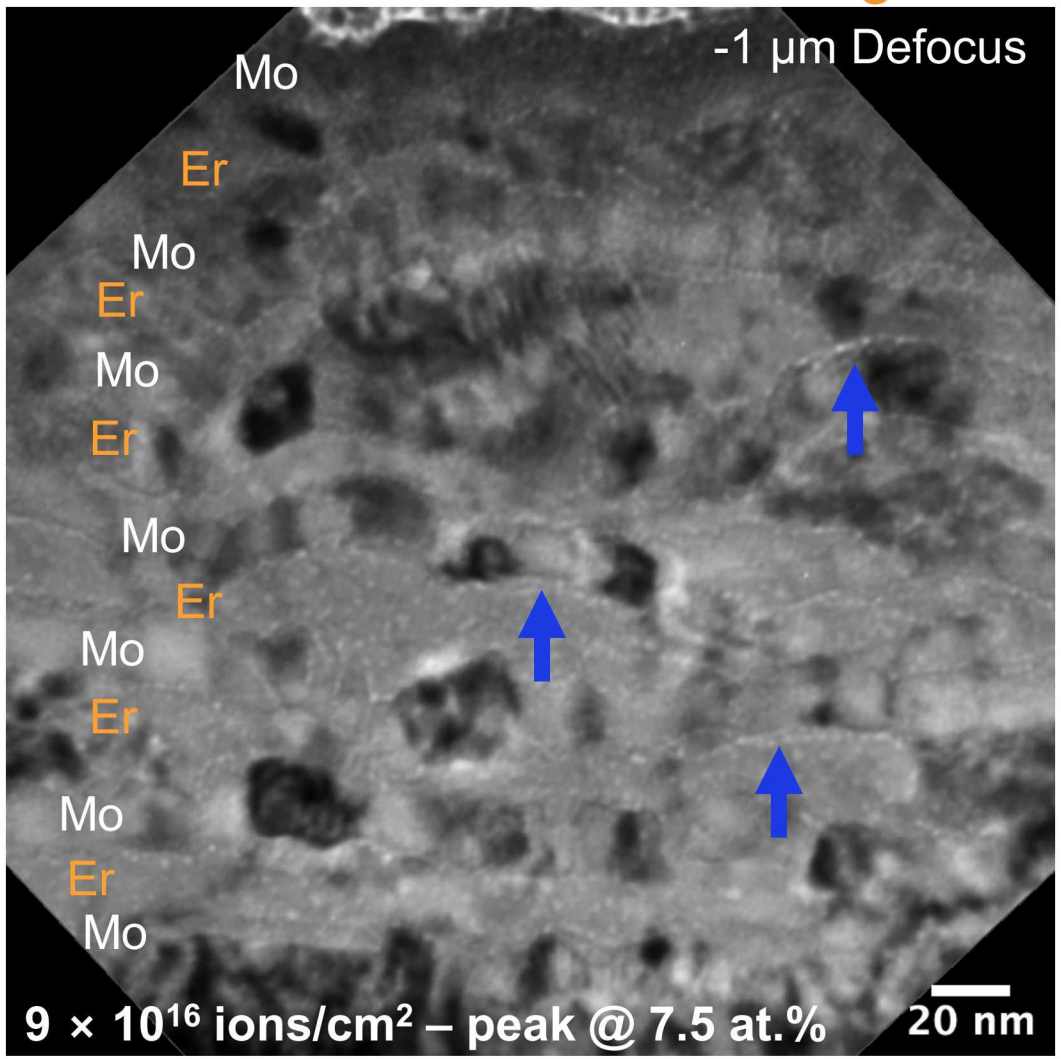
Mo z-orientation

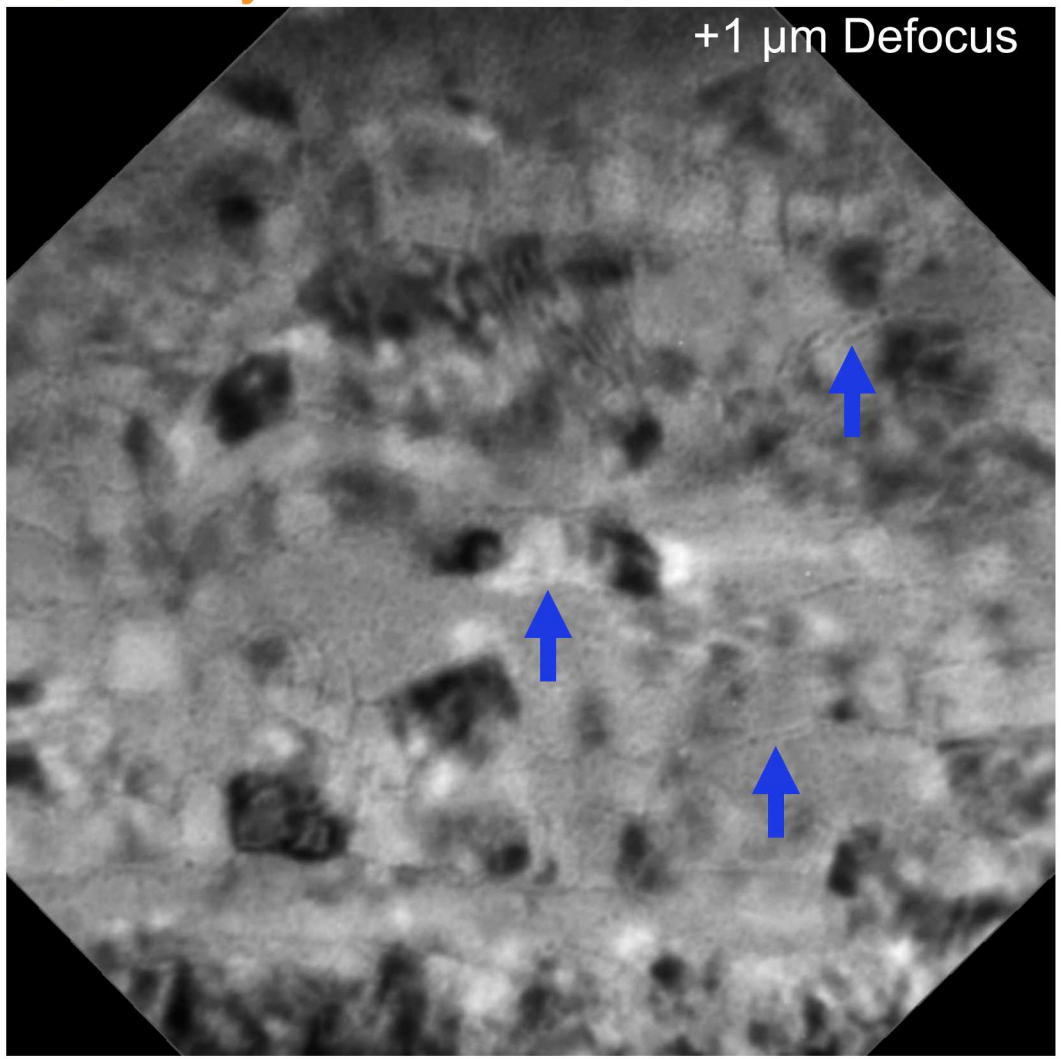


He Bubbles were Identified at Interfaces and in Matrix



Bubble Distribution is Inhomogeneous, Likely due to Oxide





- Layers are not uniform due to hydriding induced swelling, so PED was used to identify them.
- Helium bubbles likely inside the ErD_2 layers because of interstitial oxygen or Er_2O_3 precipitates

Outline

- **Background**
  - tritium storage and helium in metal tritides
- **Part I: Bulk ErD_2**
  - microstructural changes after He implantation into ErD_2
- **Part II: Multilayers**
  - development of an ErD_2/Mo multilayered hydride structure and initial He implantation results
- **Summary**

Summary

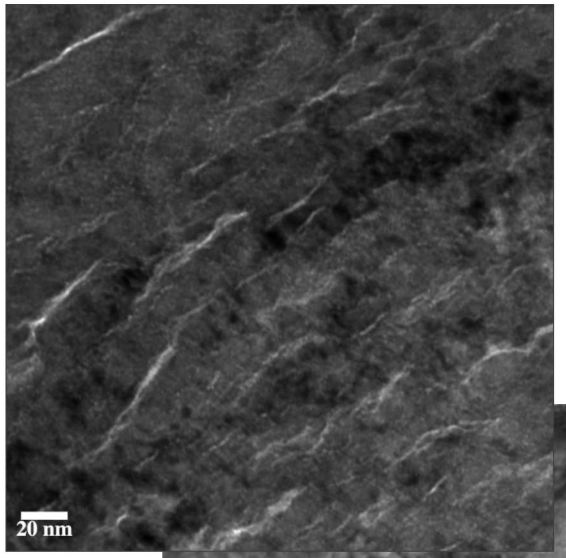
Objectives: 1) to understand the fundamental mechanisms behind accelerated He release in tritium storage materials, 2) and to understand how He interacts with interfaces in multilayered structures

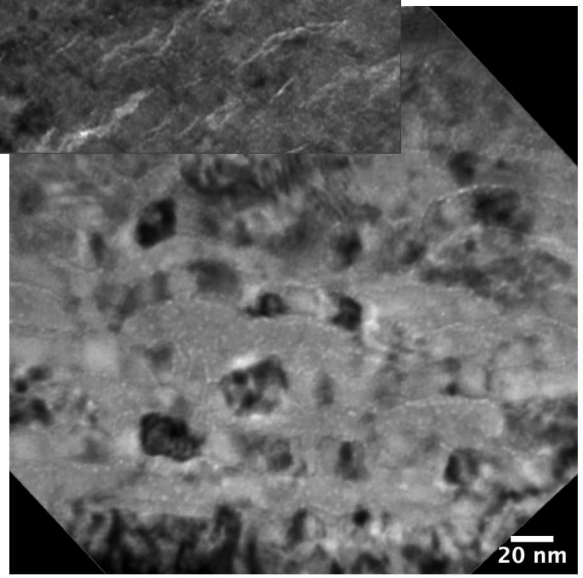
Helium implantation into ErD_2

- Intragranular nano-cracks were identified parallel to the surface in un-spalled areas of the implanted film.
- As stresses between the cracks increase, the cracks eventually link, forming larger cracks that cause spallation.
- A similar release mechanism may be occurring in ErT_2, where stresses between He platelets may cause linkage.

Multilayered ErD_2/Mo nanocomposites

- Helium was found to trap at multilayered interfaces.
- Helium is being trapped inside the ErD_2 layers, likely at oxide interfaces.





Acknowledgements

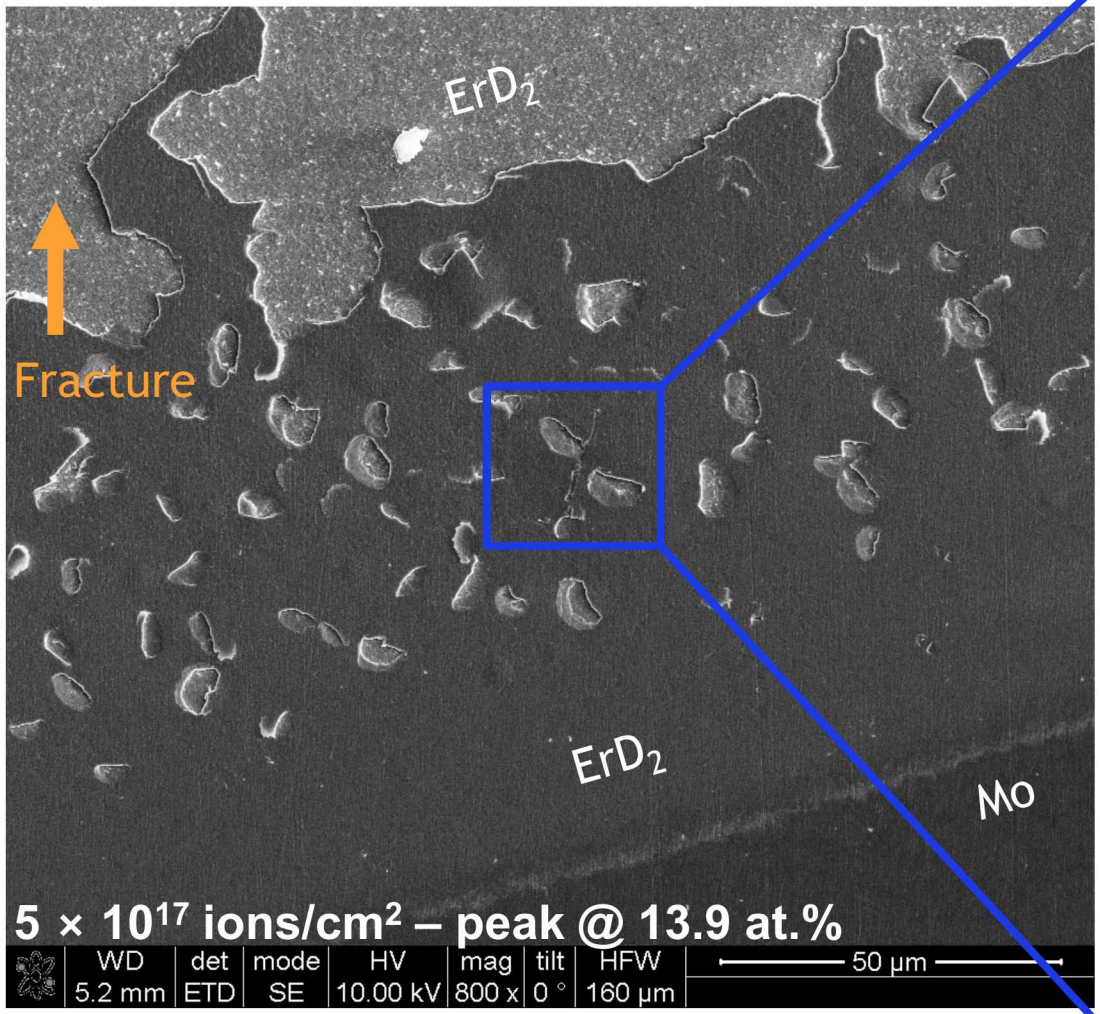
- STEM/EDS: Paul Kotula (SNL), Bethany Matthews (PNNL), Bruce Arey (PNNL)
- Film Deposition: Ron Goeke (SNL), Clark Snow (SNL)
- I^3TEM Facility: Khalid Hattar (SNL)
- XRD: Dale Zschiesche (SNL)
- Bulk He Implantation: Yong Wang (LANL)
- EELS (in progress): Joshua Sugar (SNL-CA)

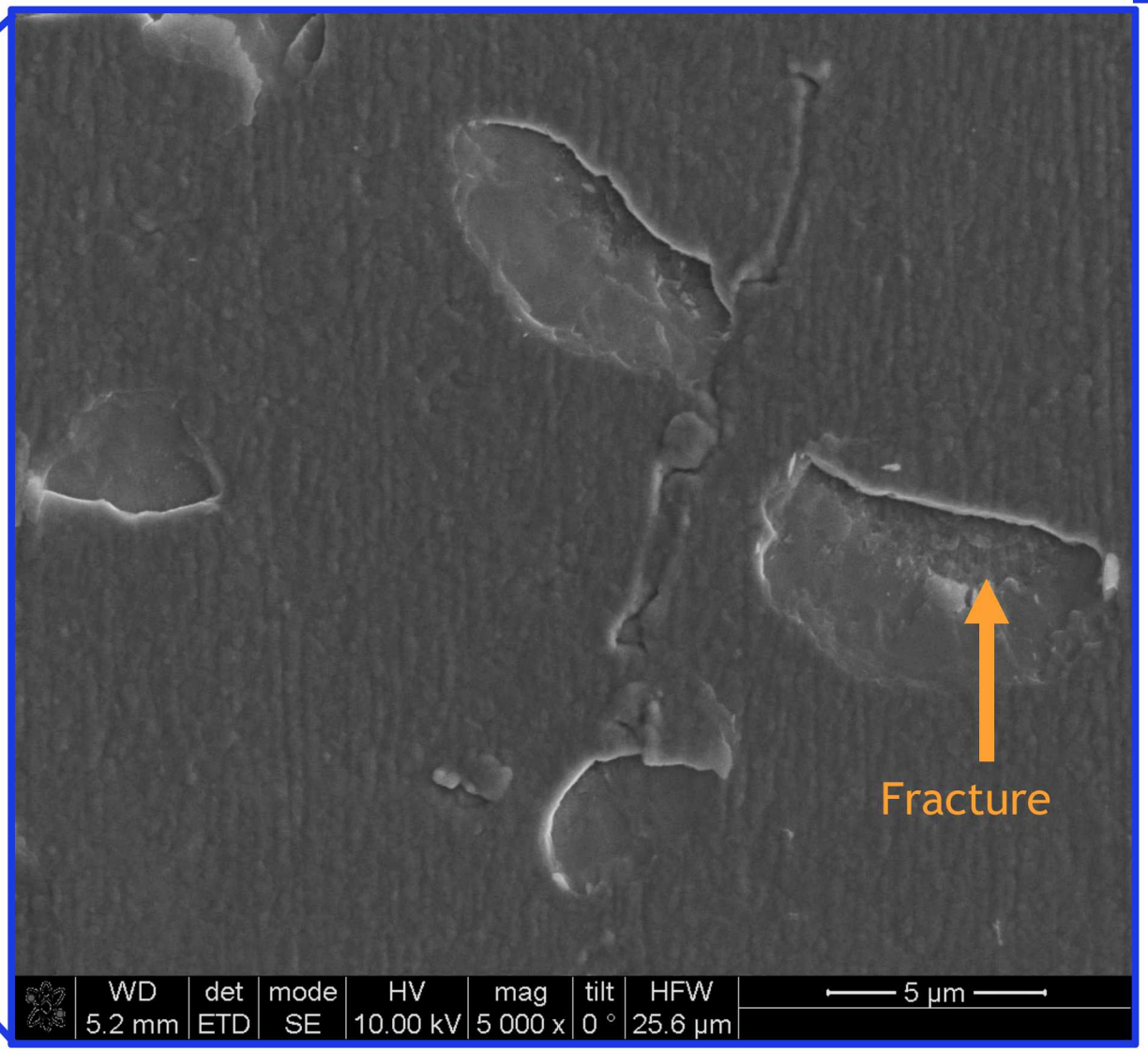
The Following CINT Facilities were Utilized for this Work:

- In Situ Ion Irradiation TEM (SNL-NM)
- FEI Nova Focused Ion Beam (SNL-NM)
- LANL Ion Beam Laboratory (LANL)

Extra Slides

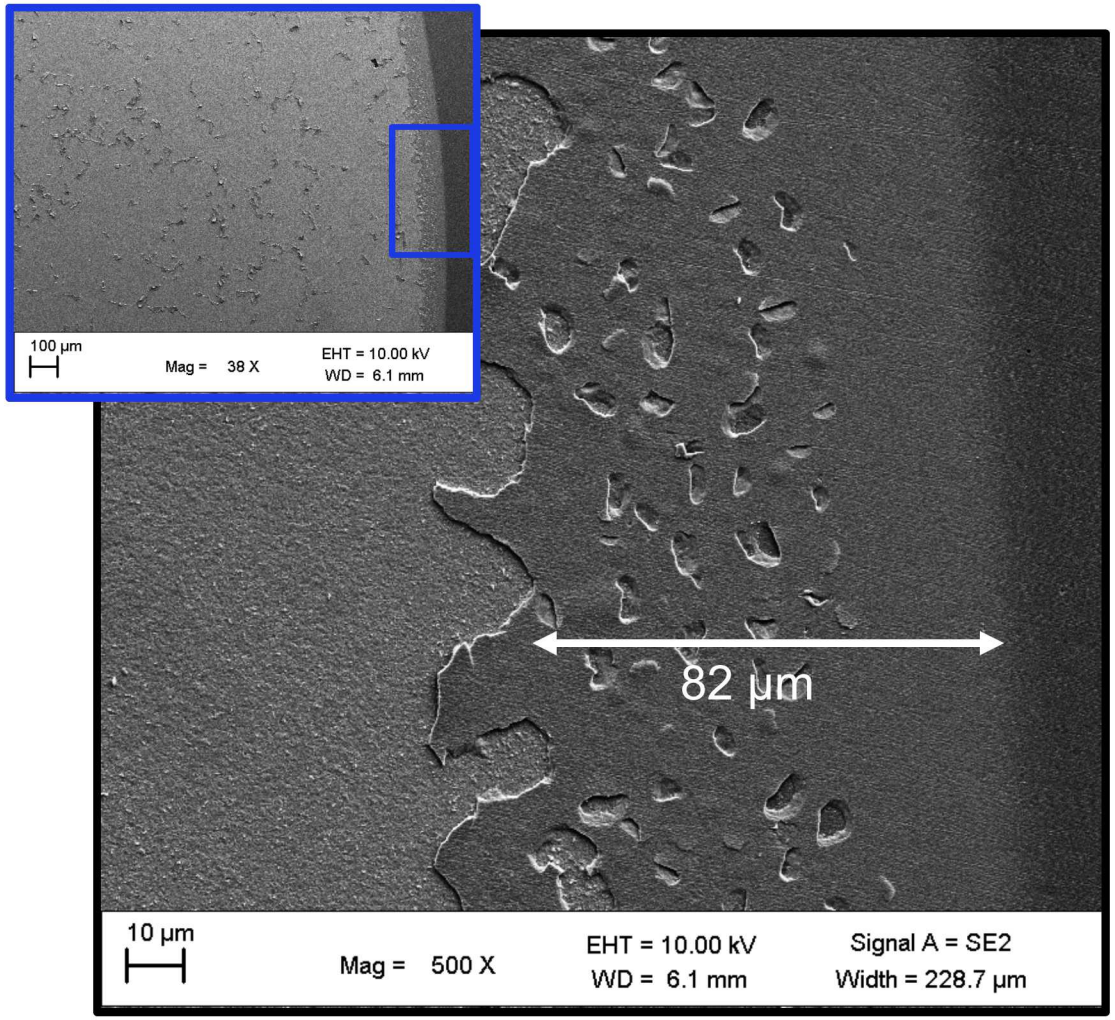
Blister Microstructure Present at Film Perimeter



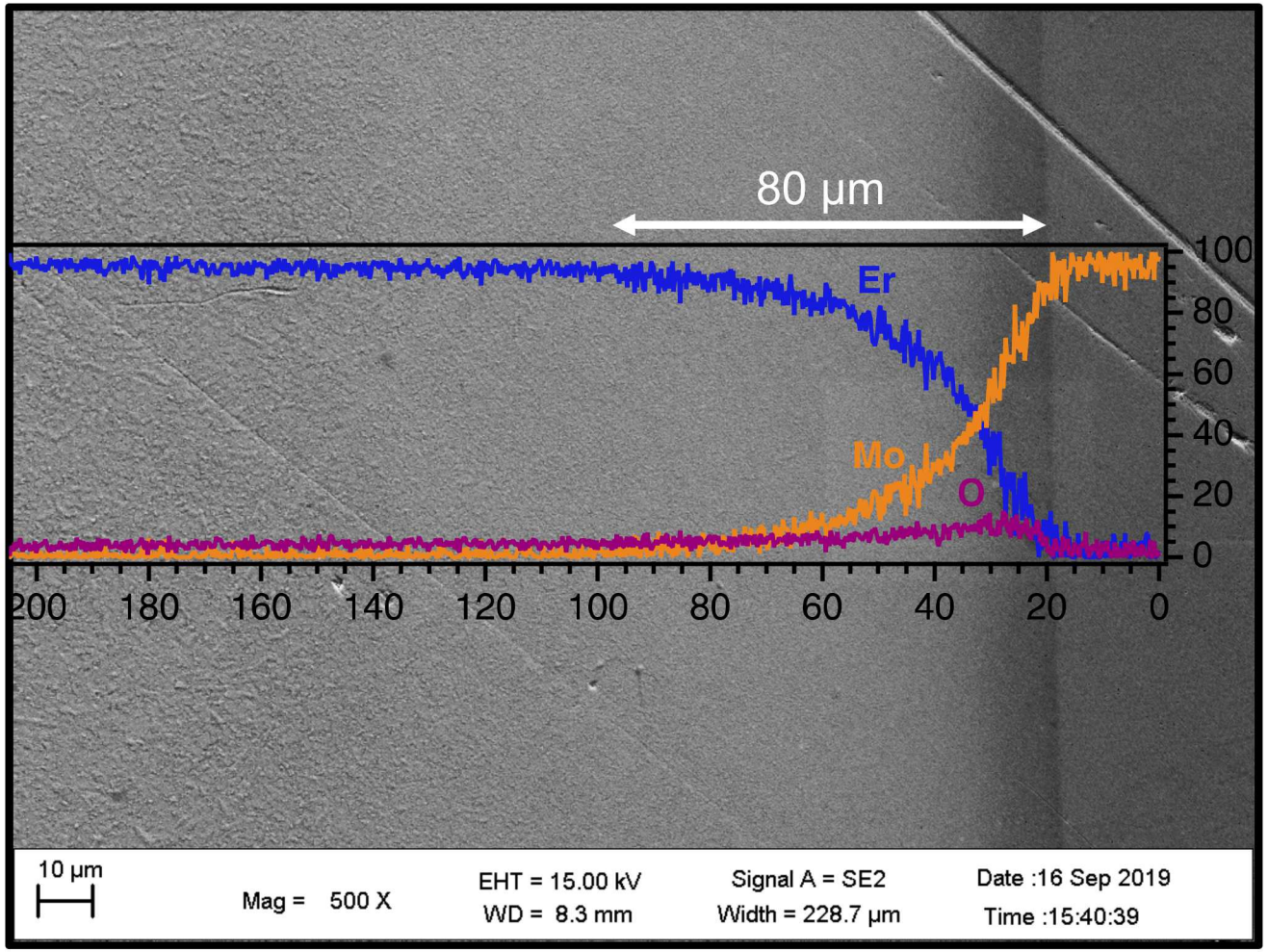


Minor Chemistry Changes Result in Different He Effects

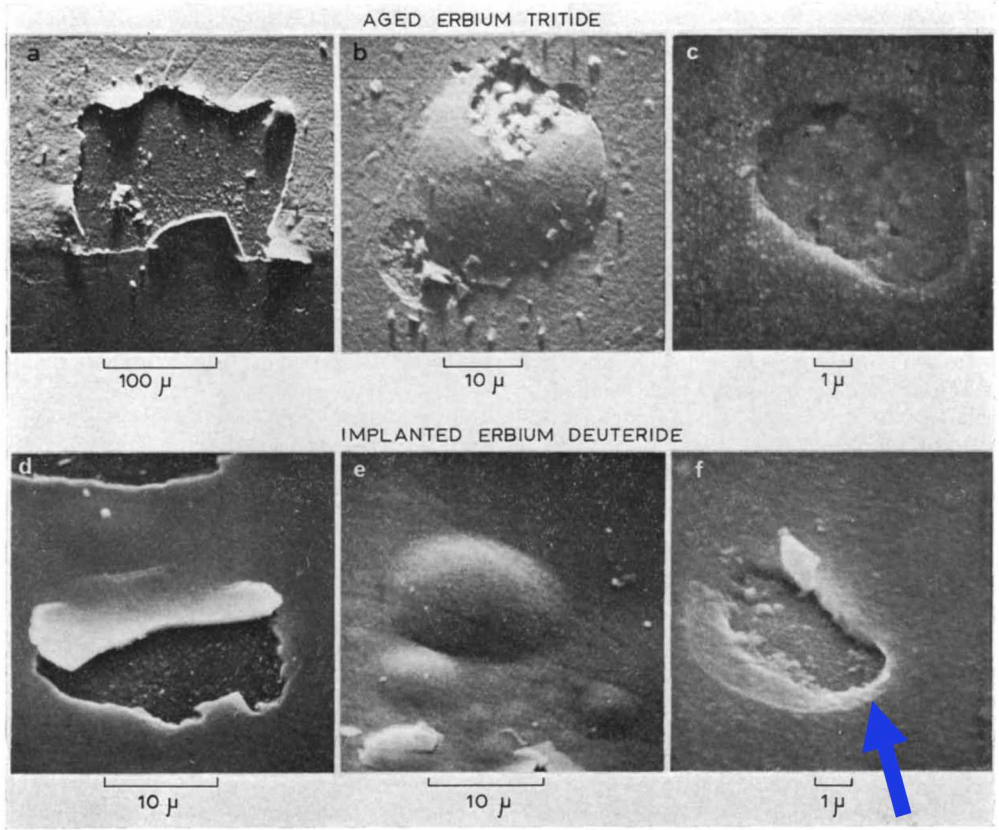
Edge of Sample Implanted with 5 × 10^{17} ions/cm^2



Edge of Pristine Sample has Thinner Er Layer and More Oxide



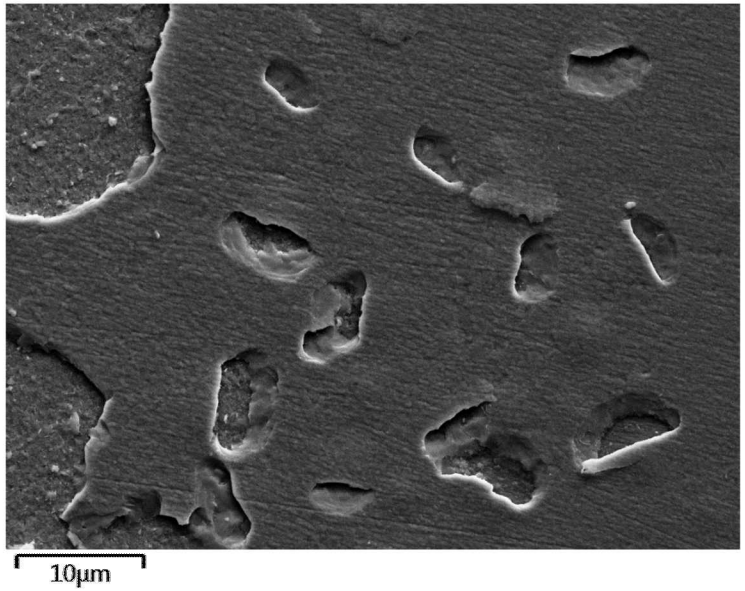
Literature Reports Blistered Microstructure after He Implantation

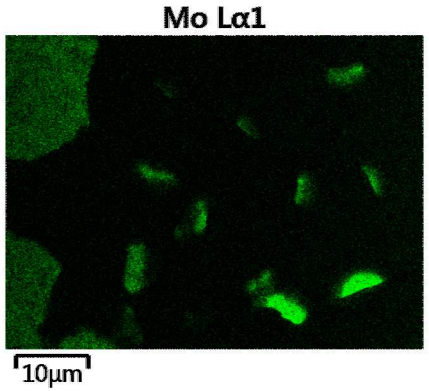


Blewer and Maurin JNM 44 (1972) 260-278

Extends to substrate

Similar Features in this Work

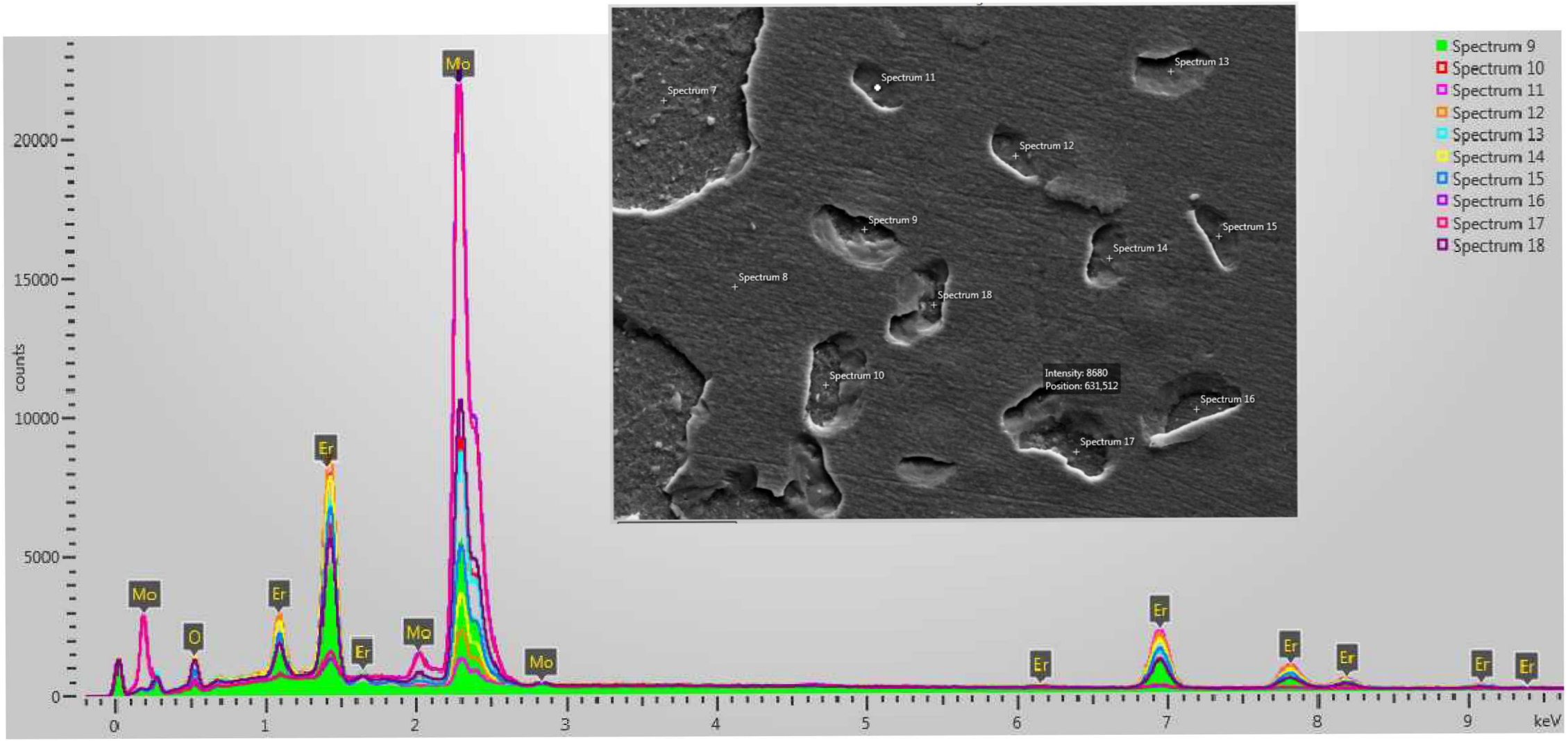




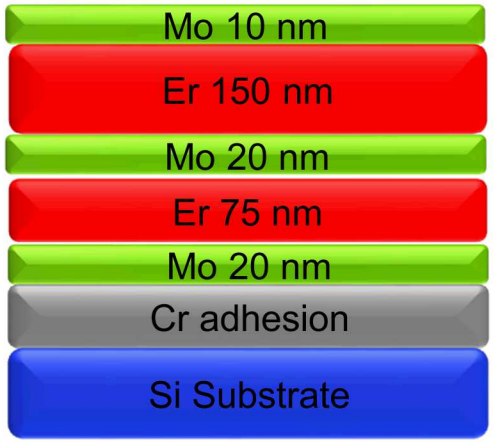
Some Extend to Substrate

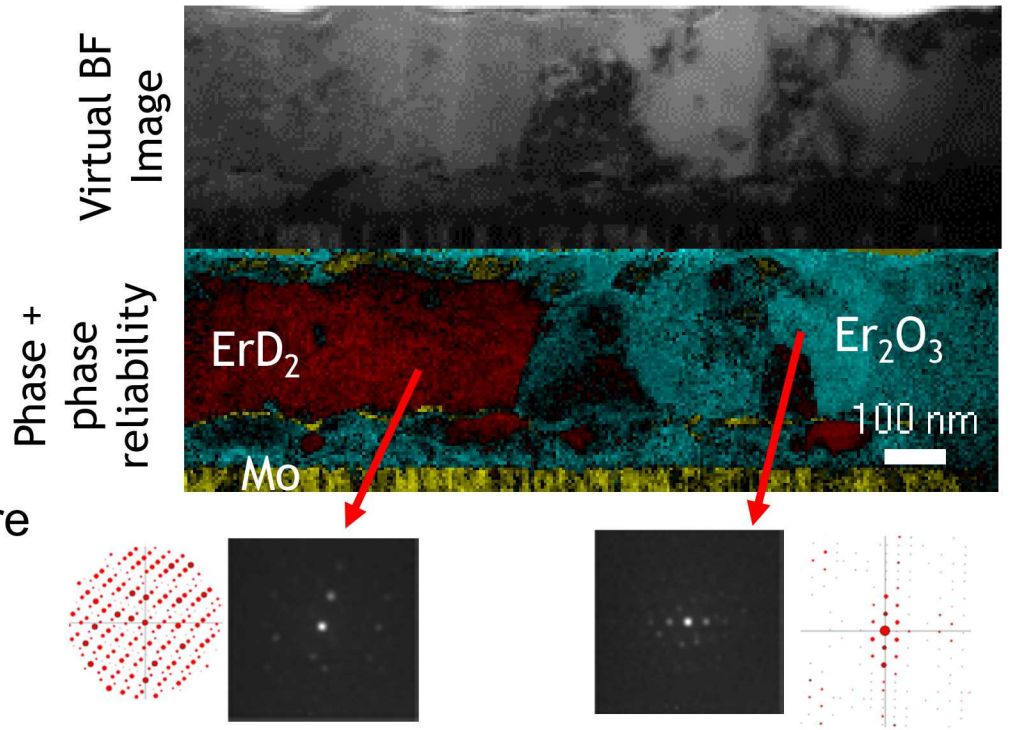
- Previous results using 120 keV ^4He produced blisters and craters in the material, similar to the microstructures present on the perimeter of the samples implanted in this work.
- This microstructure was similar to the aged ErT_2 images available in literature.

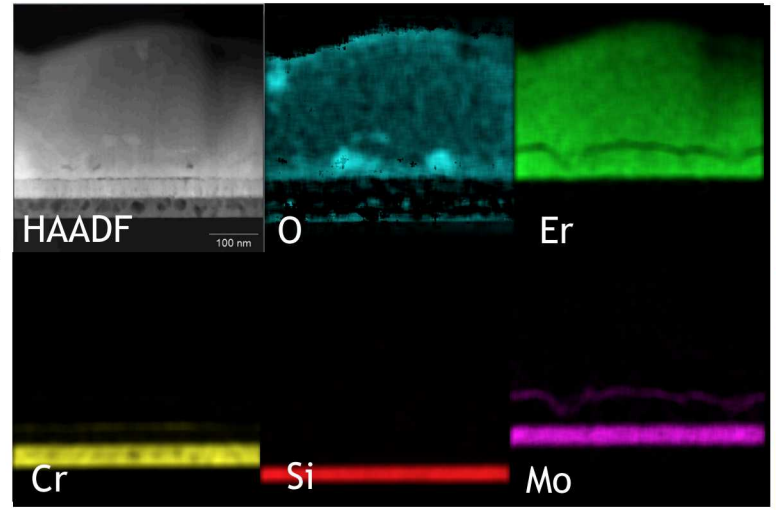
EDS Spectra from All Holes in ErD_2 Implanted with 5×10^{17} He/cm^2

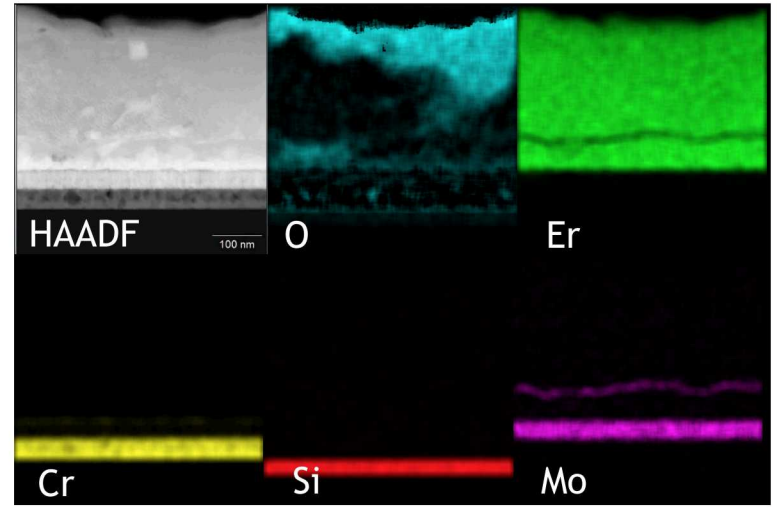


As a First Attempt, Samples were Prepared with a Single Mo Layer



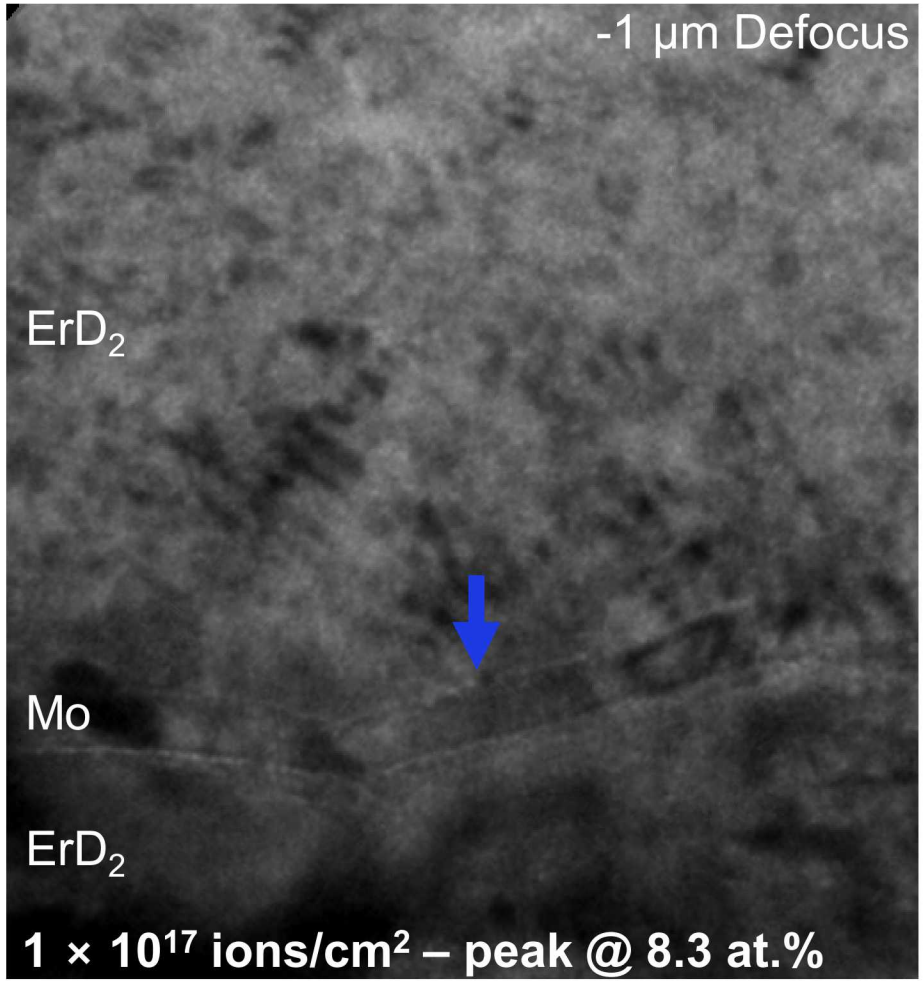


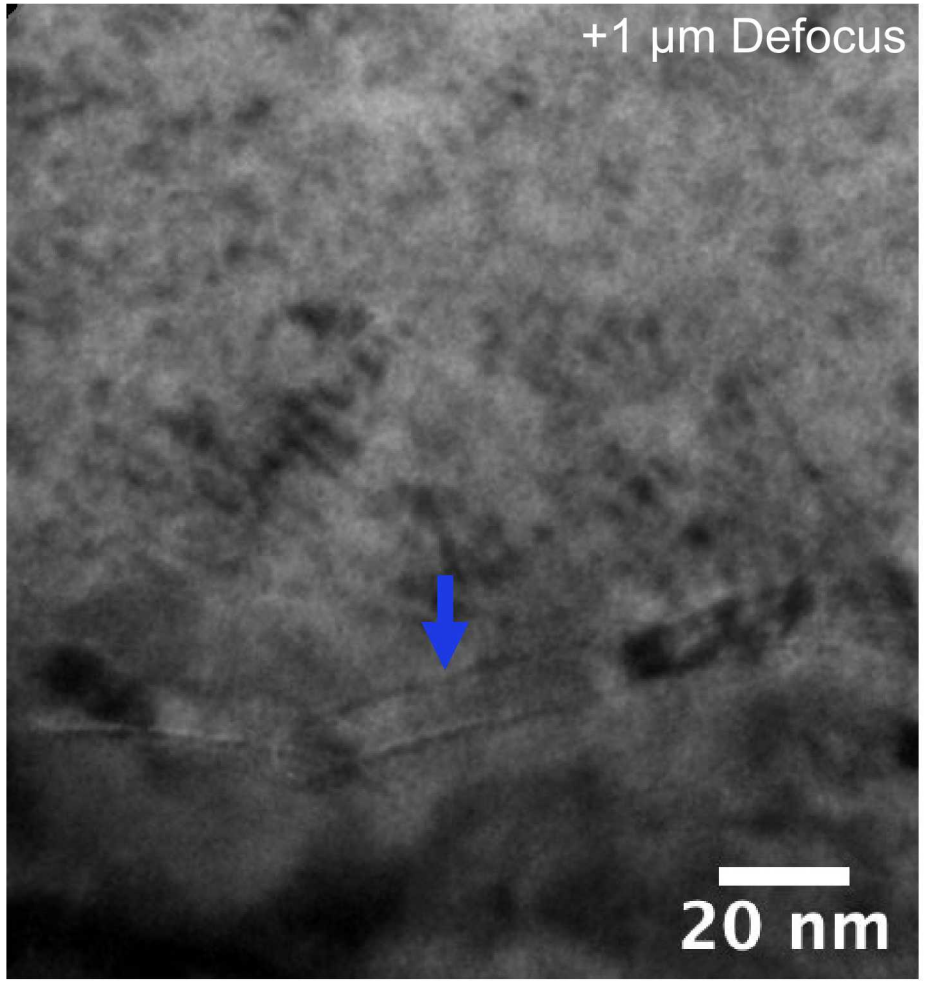




- Cr/Mo layers were sputter deposited at room temperature onto a Si substrate. 4 Er/Mo layers were electron beam evaporated.
- Samples were diced into 1 x 1 cm squares & loaded with deuterium.
- EDS maps of as-deposited structure showed Cr diffusion through the sputtered Mo layer and some Er_2O_3 grains.

He Clearly Traps at Mo Interfaces in ErD_2/Mo Structure





- Bubbles formed along the Mo interface after "in-situ" implantation to 8×10^{16} ions/cm^2 (6.7 at.%)
- After implantation to 1×10^{17} ions/cm^2 (8.3 at.%) bubbles were clearly visible inside grains and along boundaries.

Oxide Interfaces also Effectively Trapped He