Exploring the Thermal and Mechanical Stability of Amorphous and Nanocrystalline Tantalum Films

SAND2018-2604C

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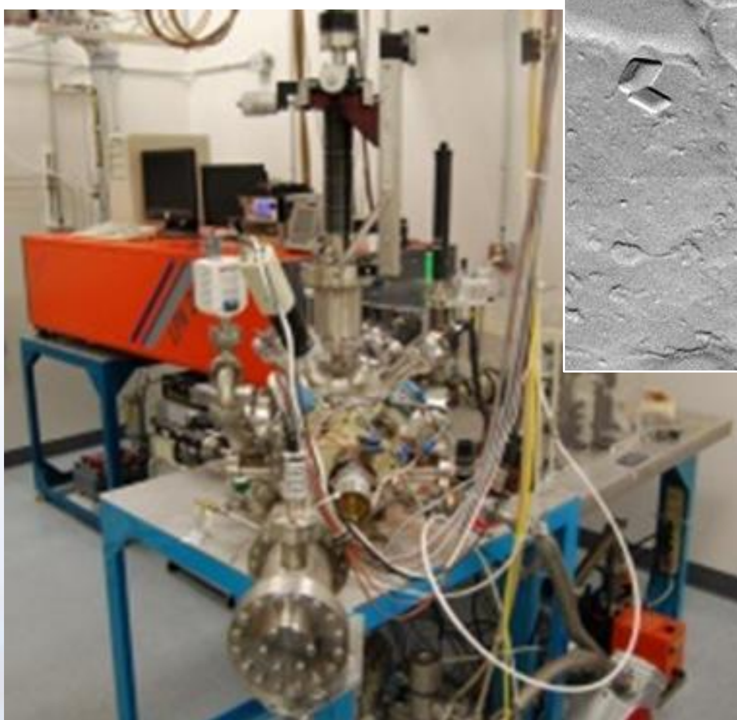
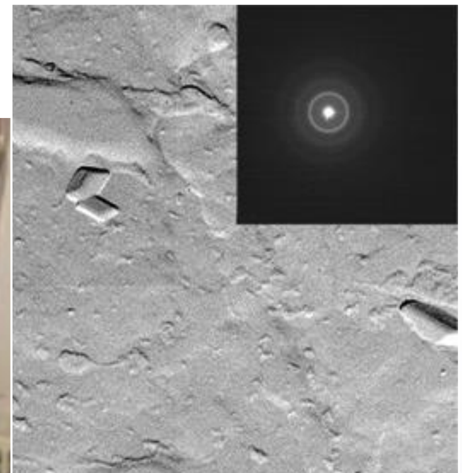
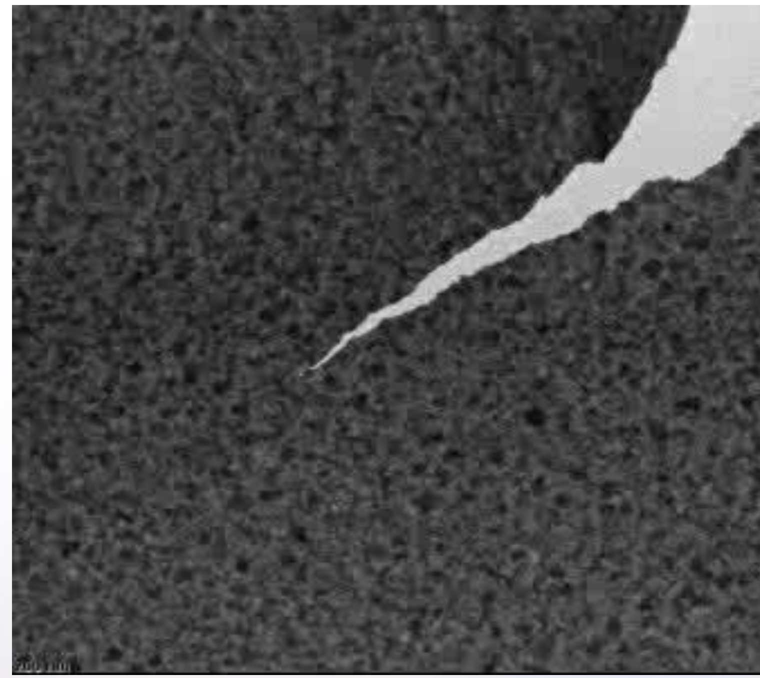
March 12, 2018







Thermal and Mechanical Stability of Amorphous and Nanocrystalline Ta are Explored

This work was supported by the US Department of Energy, Office of Basic Energy Sciences. Or other funding source.

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Materials in Extreme Environments

Collaborator: for work on this slide

Refractory metals classified by high melting point

- BCC crystal structure
- Corrosion resistant
- Useful in defense, nuclear, and energy applications

Nanocrystalline metals

- Maintain high strength and radiation tolerance at high temperature
- Thermally unstable

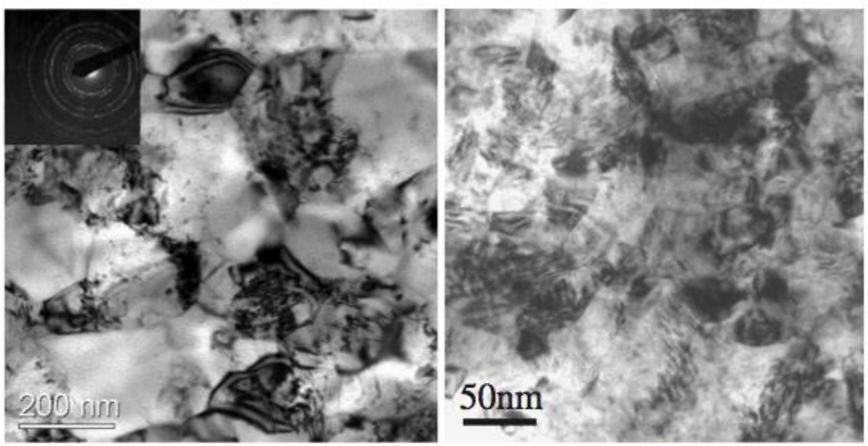
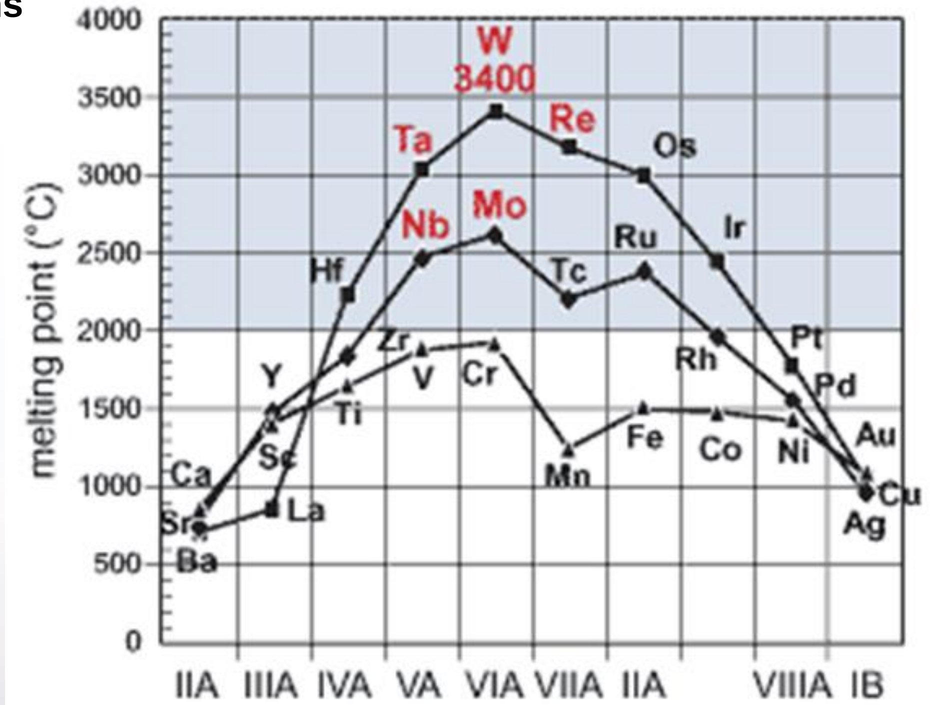


Figure 2. The microstructure of SPD Ni in both unirradiated (left) and irradiated (right) sample.

Nia, et al., Philosophical Magazine (2005)



http://www.personal.psu.edu/ius1/refract_metals.html

Stability must be predicted

Materials in Extreme Environments

Collaborator: for work on this slide

Motivation:

- Understand effect of high temperatures on metal thin films fabricated by pulse laser deposition (PLD)
- Characterize mechanical behavior of PLD amorphous and nanocrystalline thin films

In-situ microscopy techniques:

- Visualization of stability in amorphous and nanocrystalline structure at elevated temperature
- Observation of mechanical failure in Ta thin films
- Real time analysis of material behavior in extreme environments

Research questions:

1. Microstructural stability during annealing
2. Comparison of mechanical failure in amorphous and nanocrystalline thin films

73
Ta
tantalum
Melting pt: 3014°K
body centered cubic (α-Ta)
Tetragonal (β-Ta)

Based on values in the Handbook of Binary Phase Diagrams Volume 3 by Dr. William G. Moffatt

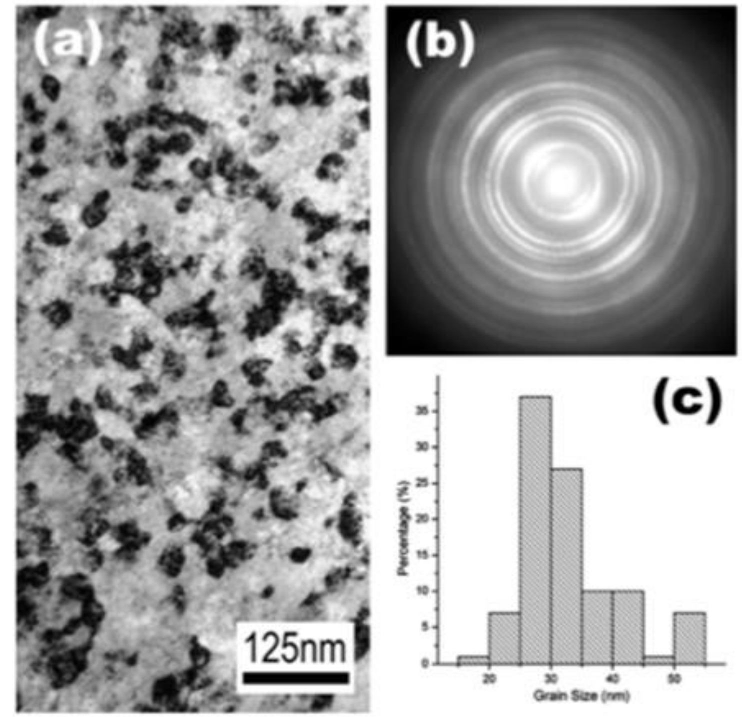


Figure 4. (a) TEM image of the planar view of a β-Ta thin film. (b) The corresponding electron diffraction pattern. (c) A histogram showing a statistical diameter distribution of the nanocrystalline Ta grains.

Zhang, et al., Scripta Materialia (2007)

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Pulsed Laser Deposition of Ta Films

Collaborator: for work on this slide

PLD used to synthesize nanocrystalline and amorphous Ta films

- **Krypton-Fluoride laser: λ = 248 nm**
- **Substrate: polished NaCl**
- **Pulse Rate: 35 Hz**

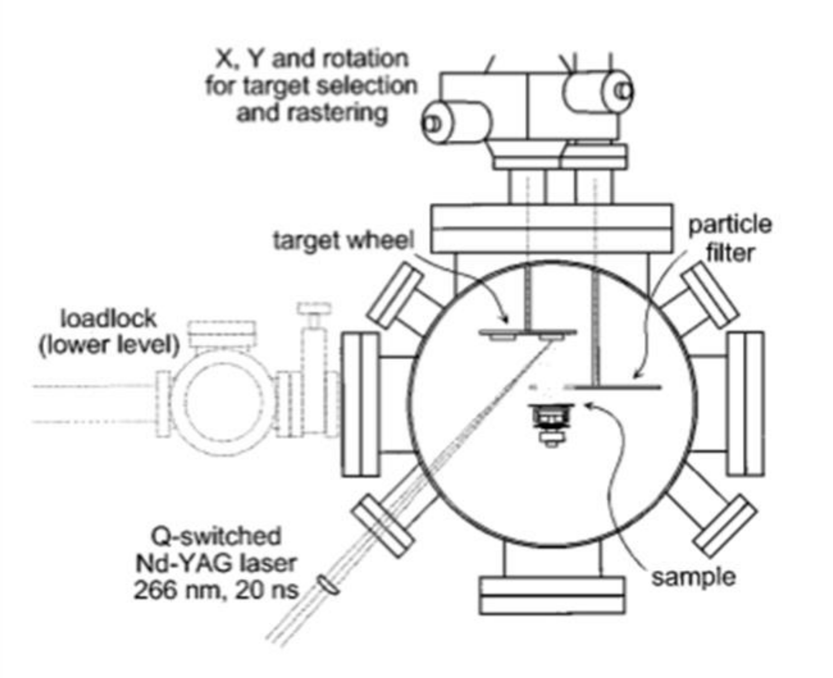
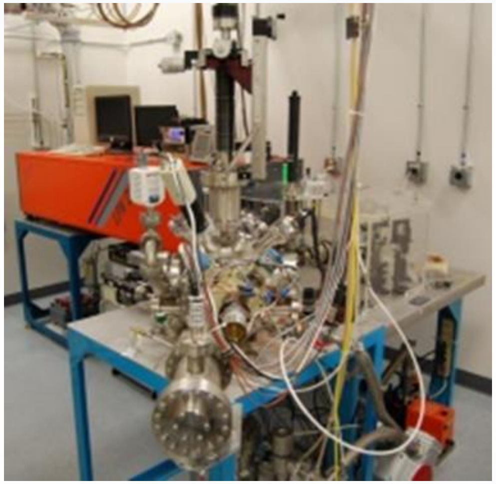


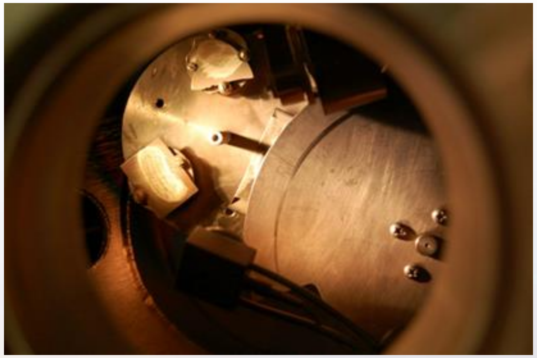
FIG. 1. Schematic of the pulsed laser deposition system.

Knapp, et al., Journal of Applied Physics (1996)



Pulsed laser Deposition system located in the Ion Beam Laboratory at Sandia National Laboratories, NM

PLD target disc at Sandia National Laboratories



Nominal thickness: 20-150 nm
Results in amorphous Ta films

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TEM Characterization

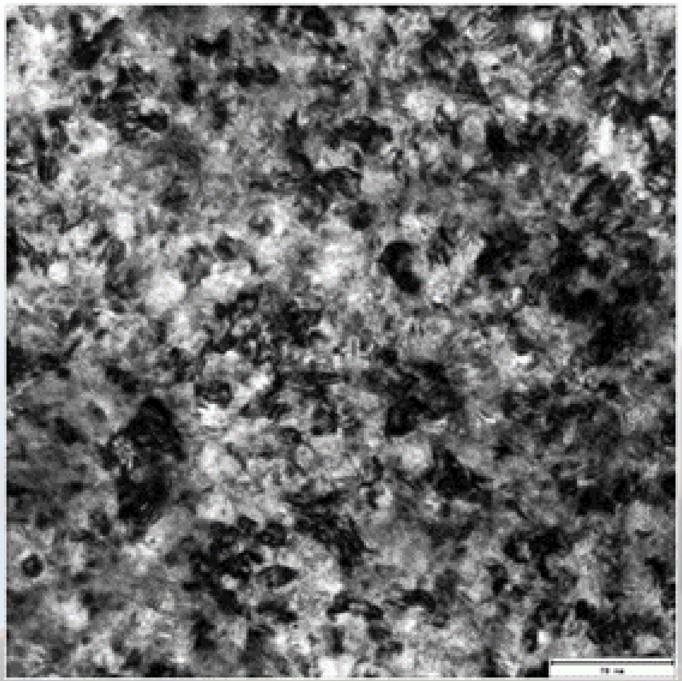
Collaborator: for work on this slide

Studies performed using TEMs at Sandia National Labs

- **Phillips CM-30**
- **JEOL JEM 2100**

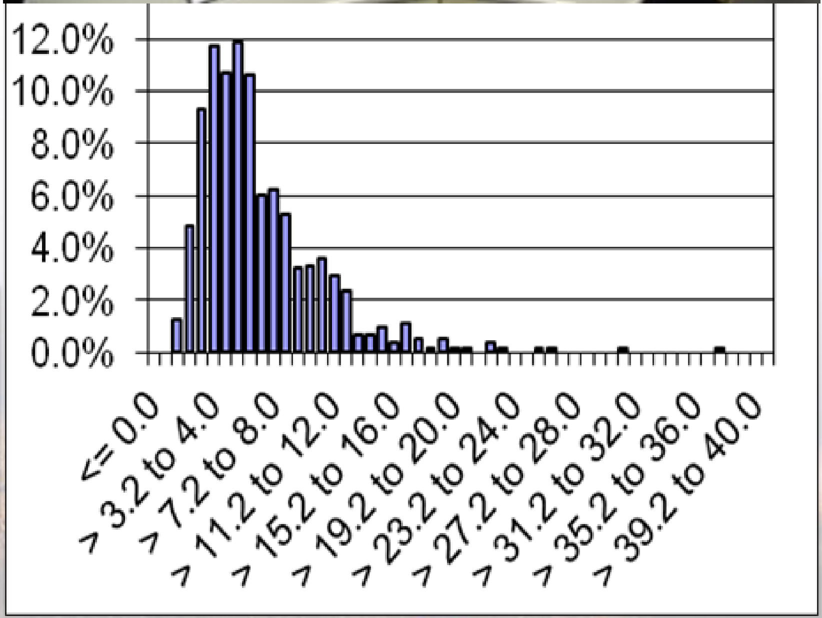
TEM studies:

- **In-situ annealing and bright field imaging**
- **Selected area diffraction analysis**
- **In-situ straining**



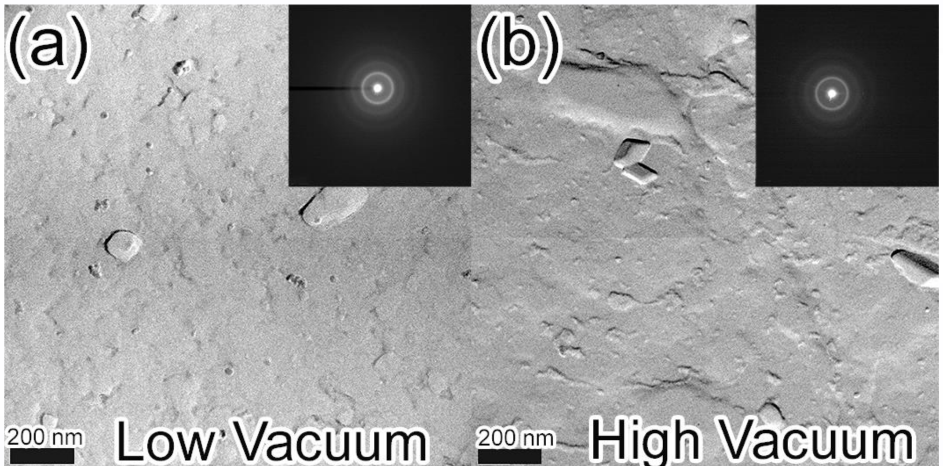
Grain Size Deposition Distribution

Mean grain size = 7nm

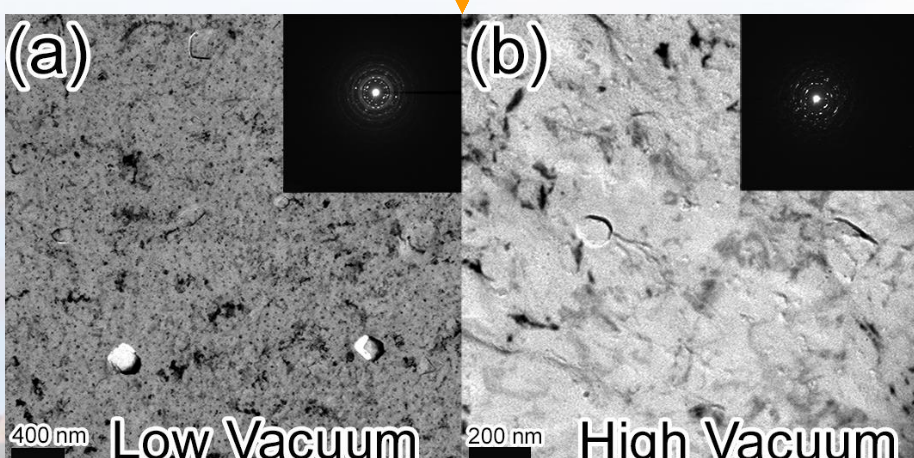


Initial imaging confirmed nanocrystalline tantalum films with grain size 3-12nm

As-deposited Tantalum Films



In Situ Anneal

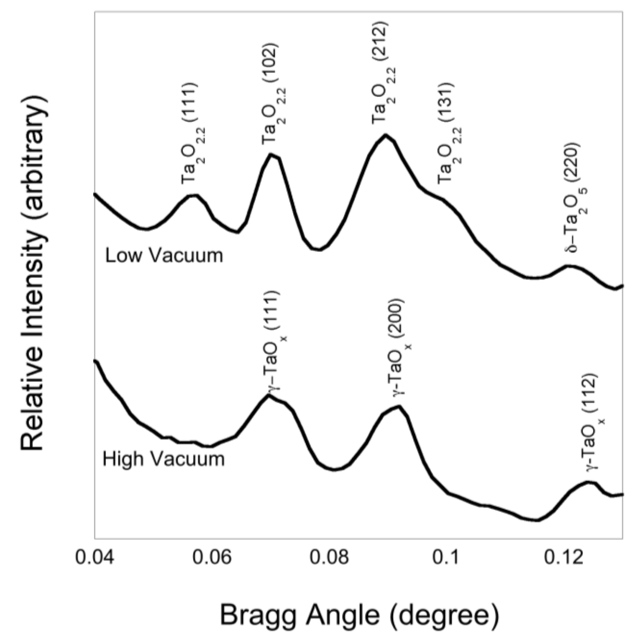


As deposited Ta films exhibited…

- **Bright field images and diffraction patterns characteristic of the amorphous state**

***In situ* detection of crystallization**

- **Moiré fringes and other contrast in BF and distinct reflections in the SAD patterns**
- **Low vacuum film crystallized at 1200°C while the high vacuum film at 1000°C**
- ***Different orthorhombic Ta oxide phases***



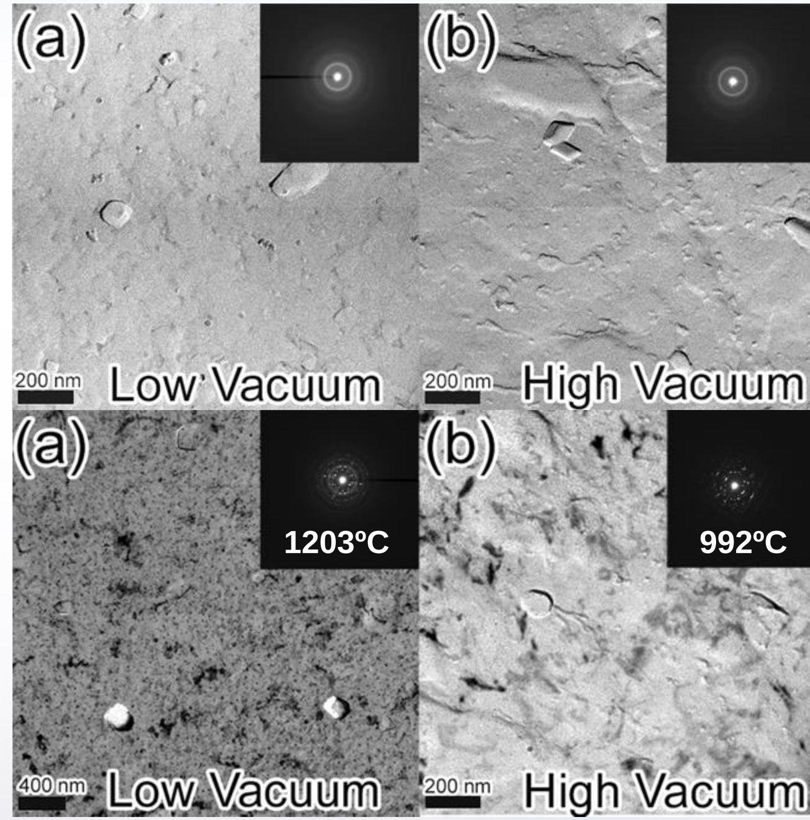
In-situ Anneal of Amorphous Films

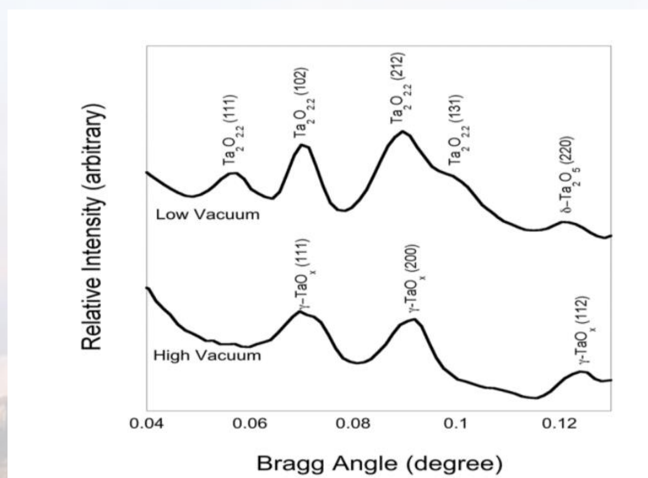
As-deposited amorphous Ta PLD films:

- Two vacuum conditions chosen to compare high and low pressure conditions during PLD
- Lack of grain contrast and diffuse rings substantiate amorphous structure

Annealed Ta films:

- Appearance of Moiré fringes; no distinguishable grain structure
- Diffuse rings present in low vacuum annealed sample; some fraction of amorphous phase remains
- Formation of different metastable tantalum oxides





Crystallization of low and high vacuum amorphous films results in formation of tantalum oxides

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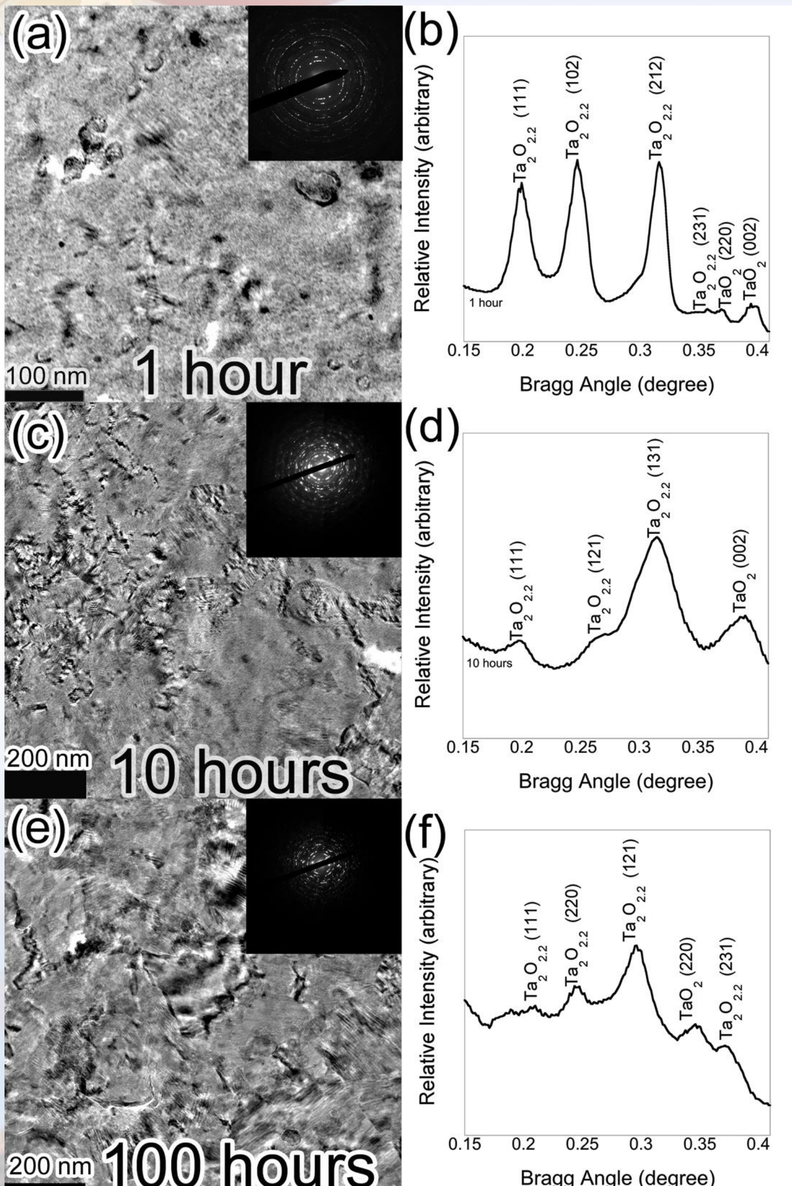
Devitrification and Annealing at 700ºC



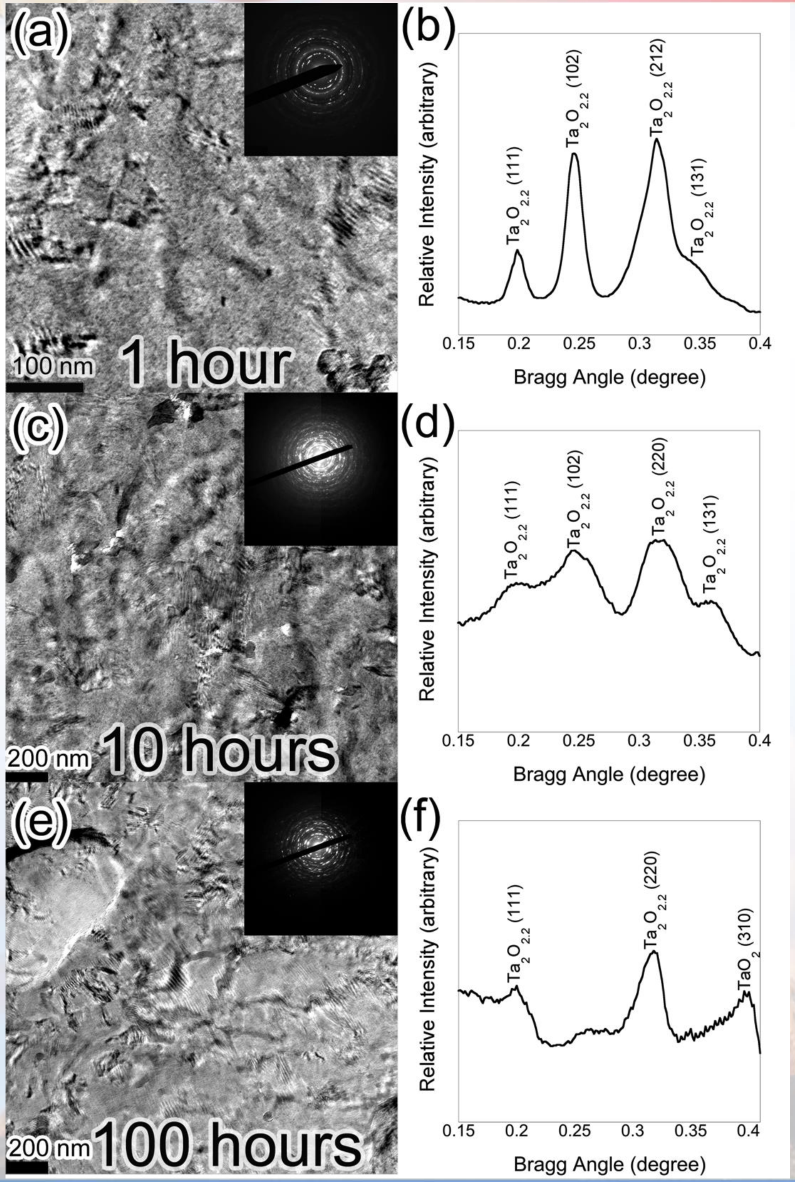
<u>Low vacuum</u> condition film exhibited…

- **Grain contrast after heating for 1 hour with nanocrystalline grains in the BF image**
- **Diffraction patterns confirmed the nanocrystalline state of the films**
- **Films remained nanocrystalline even after 100 hours at 700ºC**

Phase analysis revealed…

- **$Ta_2O_{2.2}$ and TaO_2 after heating for 1 hour**
  - ***$Ta_2O_{2.2}$: Orthorhombic crystal structure***
  - ***TaO_2: Tetragonal crystal structure***
- **Identical <u>metastable phases</u> remained following annealing for up to 100 hours**
- **Texture differences not necessarily related to structural evolution; likely just sampling variations depending on analysis location**

Devitrification and Annealing at 700ºC



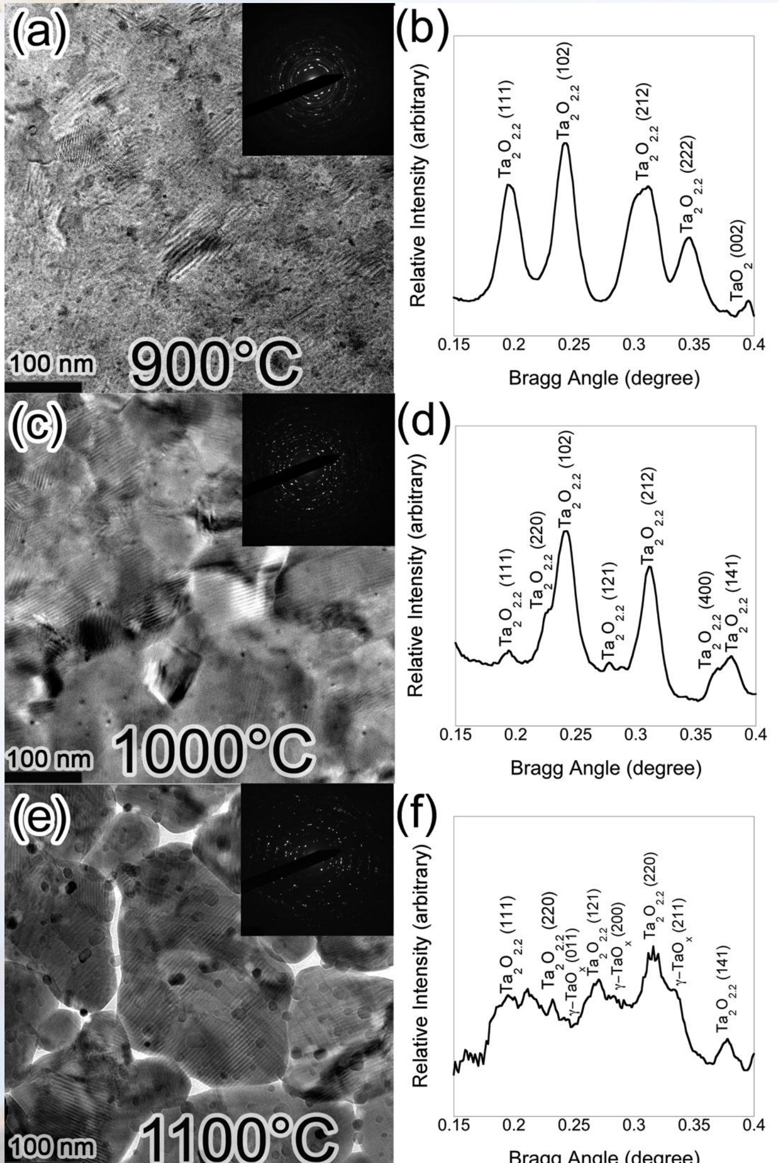
<u>High vacuum</u> condition film exhibited…

- **Nanoscale grain contrast and Moiré fringes in the BF image after heating for 1 hour**
- **Diffraction patterns confirmed the nanocrystalline state of the films**
- **Films remained nanocrystalline even after 100 hours at 700ºC**

Phase analysis revealed…

- **Only the orthorhombic $Ta_2O_{2.2}$ phase detected after the 1 hour anneal**
- **The tetragonal TaO_2 phase didn't appear until 100 hours at 700ºC**
- **The γ -Tao_x phase found during *in situ* imaging was absent at this temperature**
  - ***Suggests γ -TaO_x could be an intermediate phase that crystallizes in tantalum oxide***

The influence of temperature on phase evolution



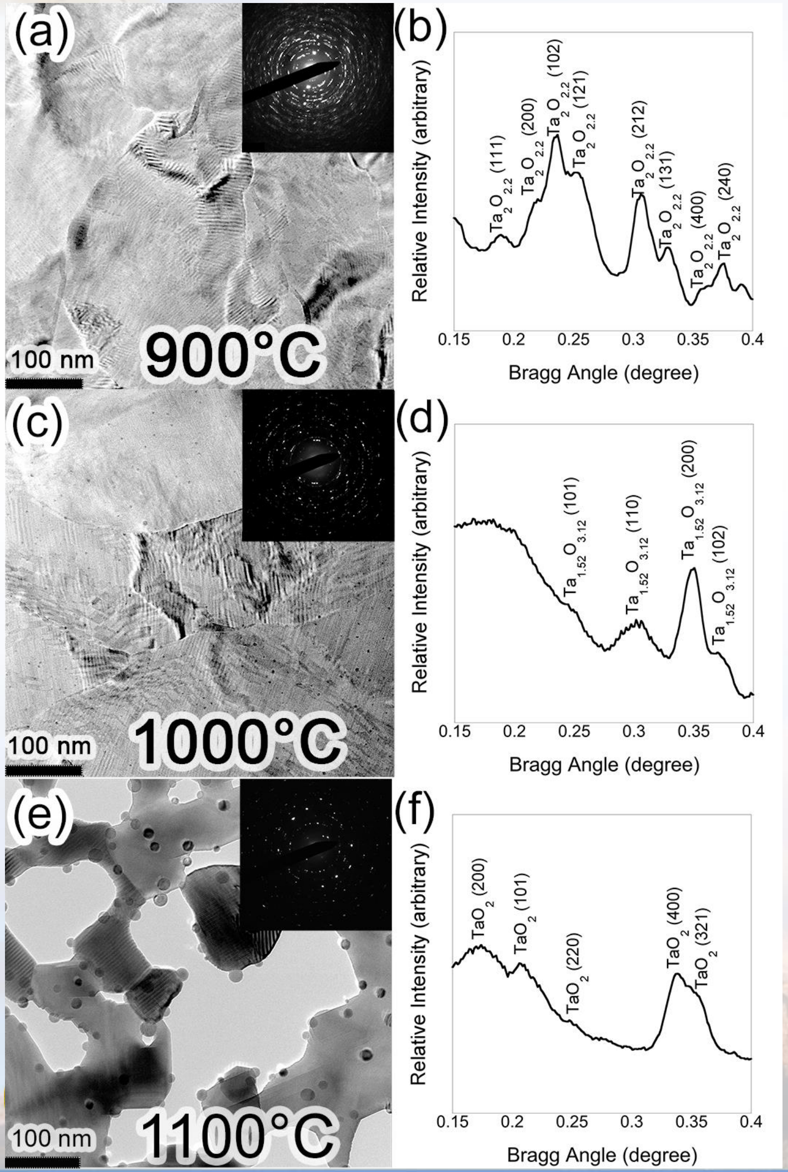
<u>Low vacuum</u> condition film exhibited…

- **At 900ºC, nanoscale grain contrast, Moiré fringes, and "dark spots" in the BF image**
- **Increasing the temperature to 1000ºC produced conspicuous grain contrast**
- **Film dissociation occurred at 1100ºC**

Phase analysis revealed…

- **Orthorhombic $Ta_2O_{2.2}$ and tetragonal TaO_2 in the films devitrified at 900 and 1000ºC**
  - ***Identical to the phases observed at 700ºC***
- **Film instabilities at 1100ºC accompanied by the appearance of the γ-TaO_x phase**
- **Dark spheres a result of the dissociation process rather than precipitate formation**

The Influence of Temperature on Phase Evolution



<u>High vacuum</u> condition film exhibited…

- **Conspicuous grain contrast evident at 900ºC with grain sizes >100 nm**
  - **SAD pattern confirmed nanocrystalline state**
  - ***Grains more than double the size than the low vacuum film***
- **Little change in BF image at 1000ºC, but severe film dissociation occurred at 1100ºC**

Phase analysis revealed…

- **Orthorhombic $Ta_2O_{2.2}$ at 900ºC whereas the hexagonal $Ta_{1.52}O_{3.12}$ appeared at 1000ºC**
  - ***Latter not previously observed***
- **Film instabilities at 1100ºC accompanied by the appearance of tetragonal TaO_2**
- **Dark spheres a result of the dissociation process rather than precipitate formation**

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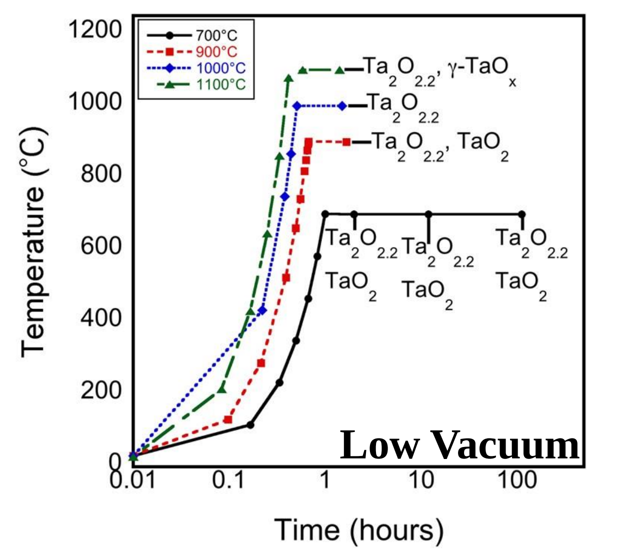
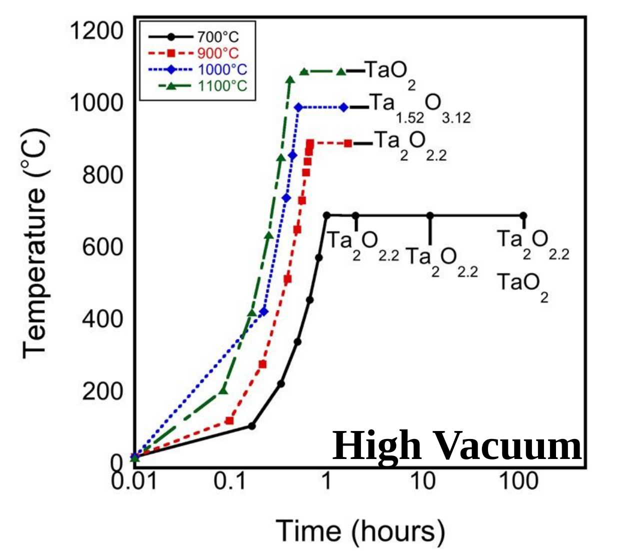
Phase Transformation Sequence





$$Ta - O_{solid\ solution} \rightarrow TaO_y \rightarrow TaO_z \rightarrow Monoclinic\ Ta_2O_5$$

Orthorhombic (TaO_y) Tetragonal (TaO_z)

Under low vacuum with greater oxygen levels…

- $Ta_2O_{2.2}$ was the most widely observed phase
  - The orthorhombic γ-TaO_x phase also appeared
- TaO_2 appeared along with $Ta_2O_{2.2}$ at most temperatures

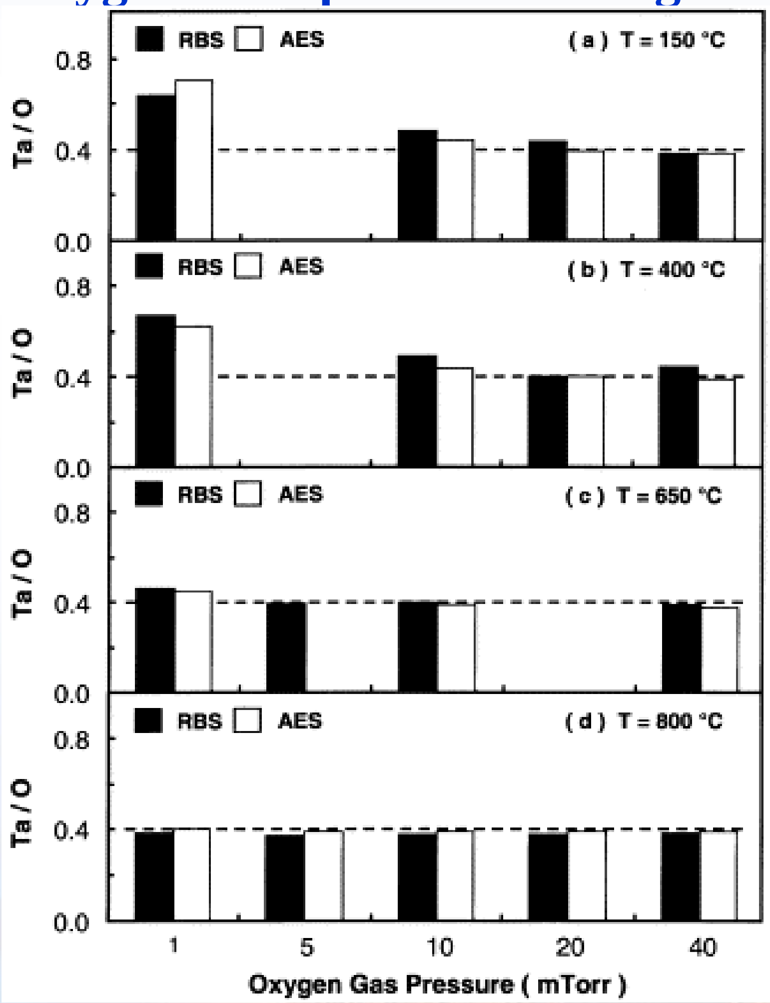
Reducing the oxygen content via high vacuum…

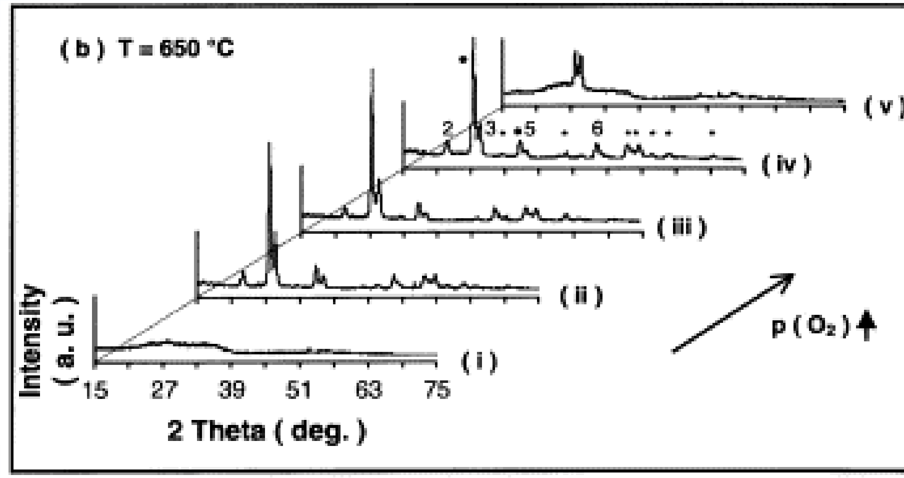
- $Ta_2O_{2.2}$ most prevalent at lower temperatures
- TaO_2 formation delayed to higher temperatures and longer annealing times
  - Suggests additional oxygen incorporated during annealing promoted the transformation to TaO_2

Intermediate metastable phases present in the PLD films support the above transformation sequence

Why are We Stuck with Metastable TaO_x Phases?

Oxygen Incorporation during PLD ⟹ Influence on Film's Crystal Structure





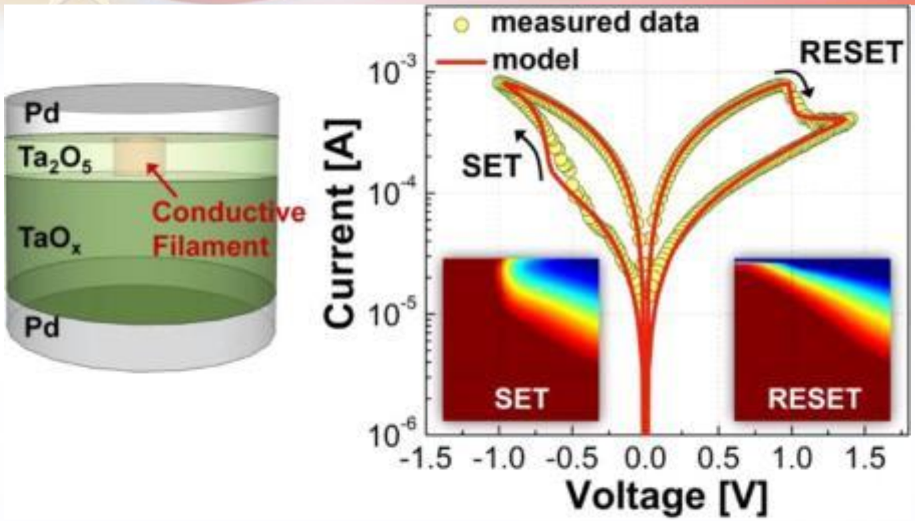
Boughaba et al., Thin Solid Films, 2000

The stable Ta_2O_5 phase has been demonstrated at 3.2 at.% (phase diagram would require 4 at. %)

- Increasing the oxygen gas pressure drove the transformation sequence forward (TaO_2 phase)
- However, insufficient oxygen levels to promote the evolution to the stable monoclinic Ta_2O_5

Convenient technique for achieving intermediate metastable phases of TaO_x

A Range of Applications for Tantalum Oxide

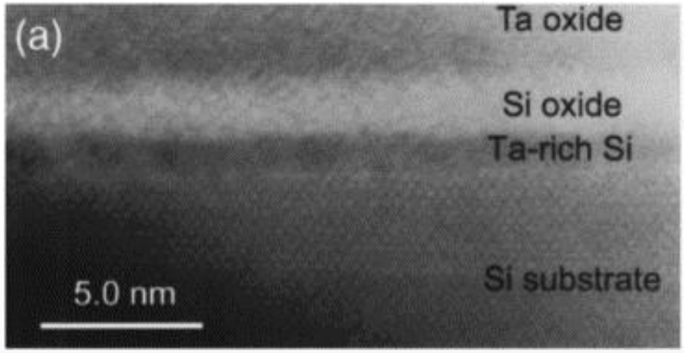


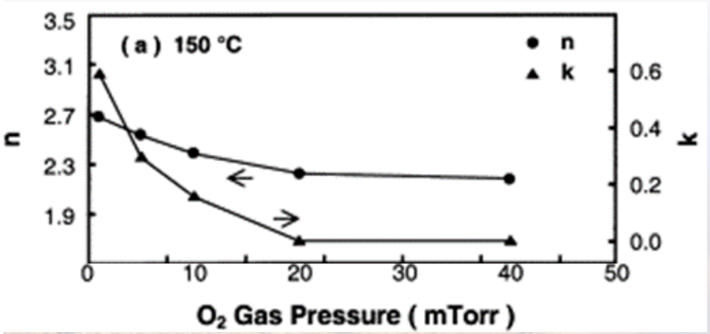
Schematic of the Pd/Ta_2O_5/TaO_x/Pd bilayer memristor device

Kim, et al., ACS Nano, 8 (3), 2014

Tailoring other properties

- Tantalum exhibits over 25 different metastable oxide phases
- Device performance can be optimized by exploiting different phases





Boughaba et al., Thin Solid Films, 2000

Memristor applications

- A memristor can “remembers” its most recent resistance through power downs/ups
- Tantalum-oxide-based memristors have shown excellent switching performance between two discrete resistance levels
- Applications in nanoelectronics, logic, and neuromorphic/neuromemristive architectures

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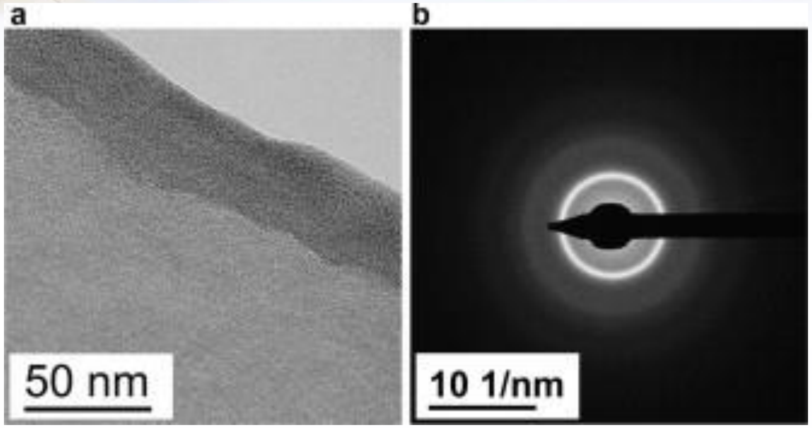
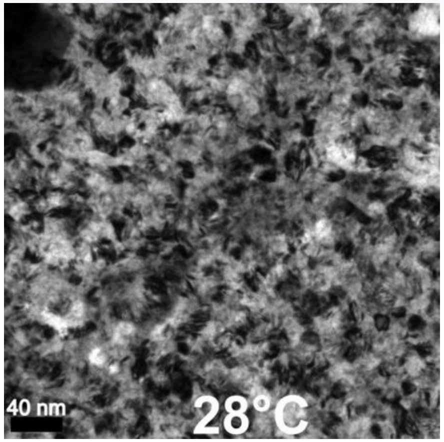
Synthesis of Ta and TaO_x Films



Bright field TEM image of as-deposited amorphous Ta film

Janish, et al., Scripta Materialia, 96 (2015)



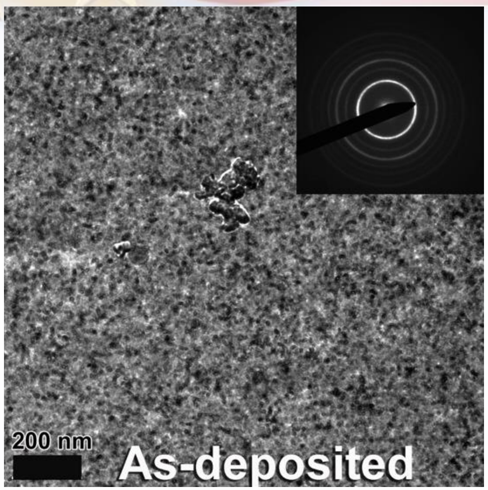
Bright field image of room temperature nanocrystalline Ta film deposited using PLD

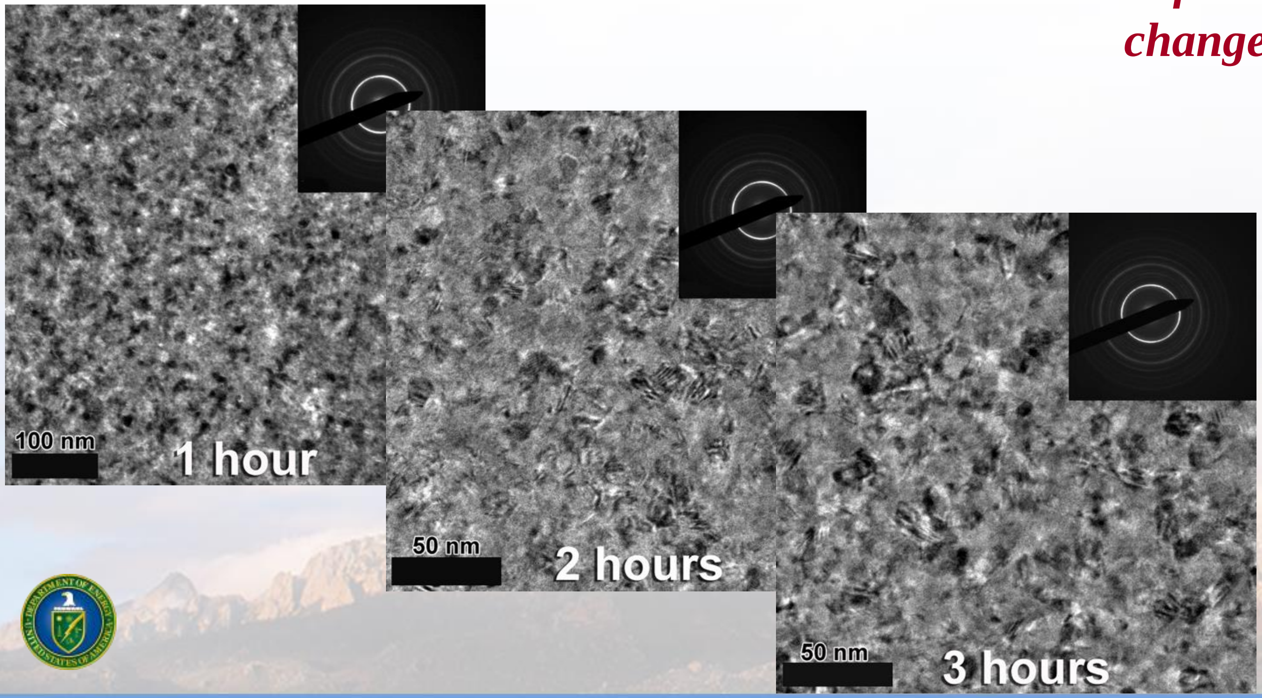
- **Room temperature pulsed-laser deposition (PLD) can produce amorphous Ta thin films**
  - Due to tantalum's high affinity for oxygen, it is extremely difficult to avoid the incorporation of oxygen into the films during deposition
- **Some preliminary work by the group at Sandia demonstrated nanocrystalline Ta via PLD**

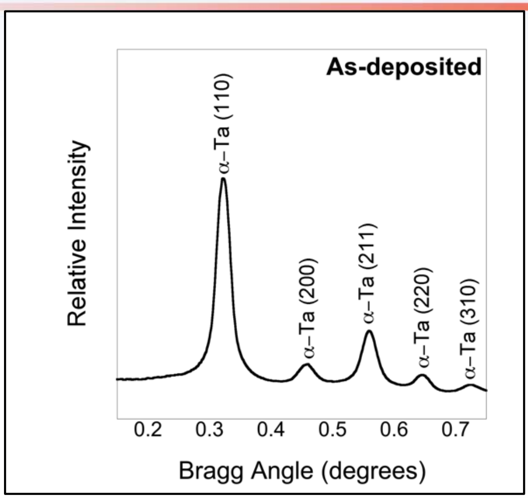
Research Objectives

1. Synthesize amorphous tantalum thin films and map out the phase transformation sequence through devitrification… metallic vs. oxide, nanocrystalline stable?
2. **Investigate the thermal stability of nanocrystalline tantalum and identify strategies for stabilizing nanocrystalline structures**

In Situ Annealing of Nanocrystalline Ta







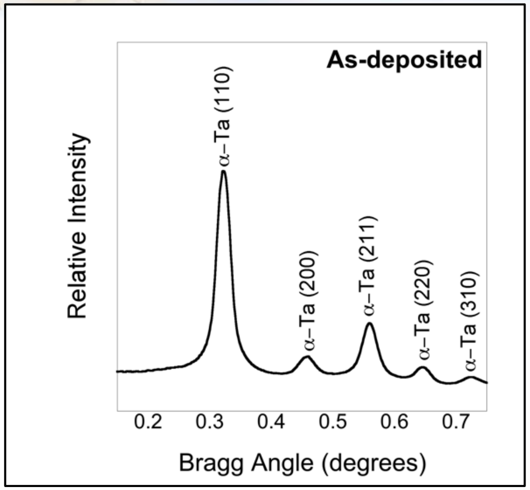
PLD Nanocrystalline Ta

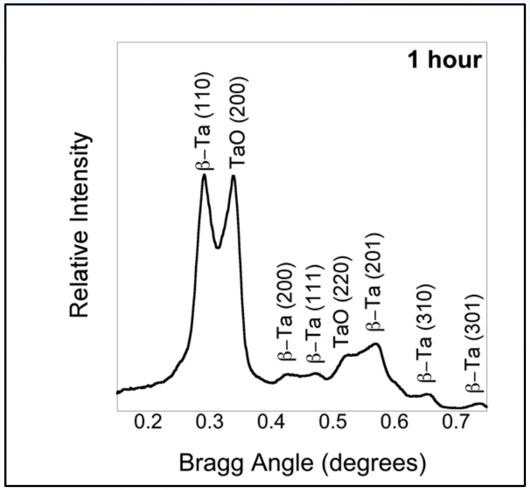
- **BF and SAD analysis confirm the nanocrystalline state**
- **Average grain size around 18 nm**
- **Integrated radial intensity profile exhibited single phase α-BCC Ta**

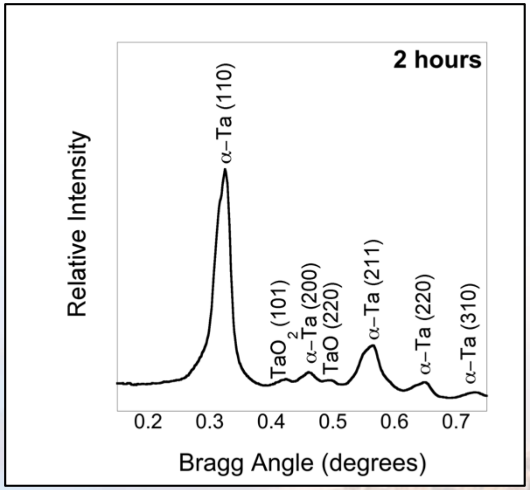
➔ ***After 3 hours at 800ºC, virtually no change in the as-deposited grain size***

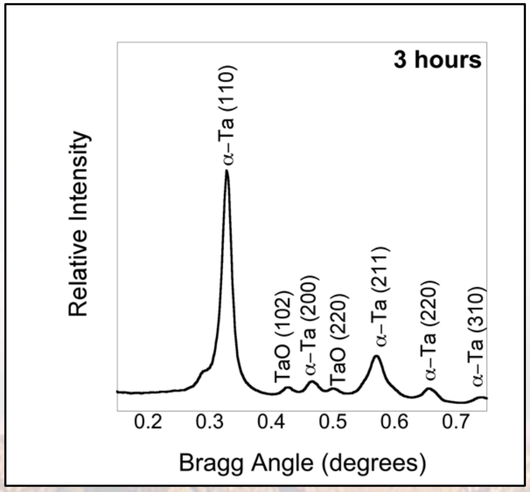
Anneal Time (at 800°C)	Average Grain Size
0 hours	17.51 nm
1 hour	16.90 nm
2 hours	18.85 nm
3 hours	22.14 nm

Quantitative Analysis of SAD Patterns









Phase Analysis

- As-deposited: α- BCC Ta
- 2 hours at 800° C : α- BCC Ta
- 3 hours at 800° C : α- BCC Ta

What happened at 800° C after only 1 hour of annealing?

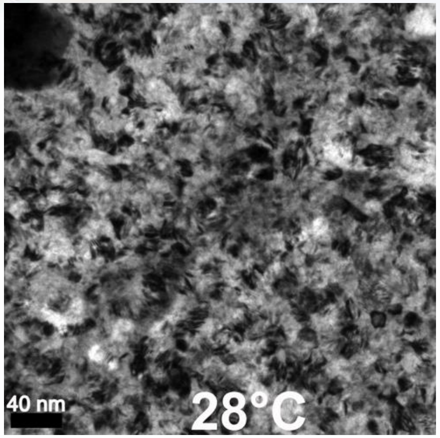
- α → β Ta phase transition
  - β is the tetragonal phase of Ta
- Accompanied by the appearance of the TaO phase
- No precipitates detected in the BF
- Transformation back to α-Ta after 2 hours of annealing

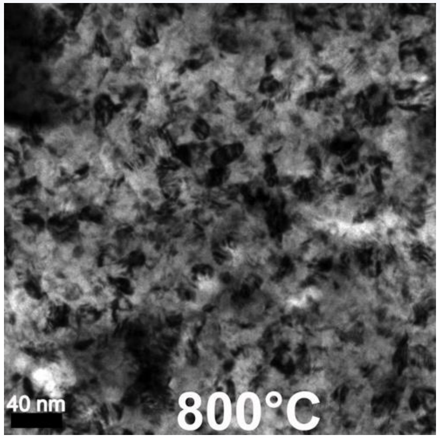
Does this make sense?

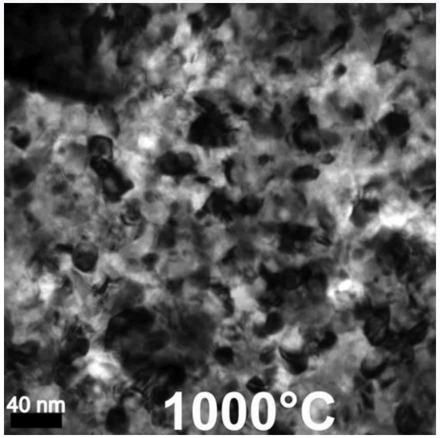
- The β → α transition occurs over the temperature range 755-775° C
- Sample temperature at the top end of this range

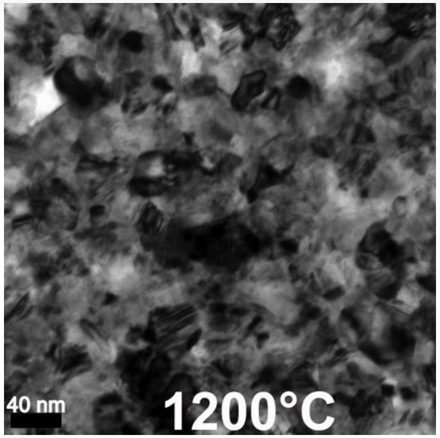
[1] Read & Altman, Applied Physics Letters 7 (1965)
[2] Read & Hensler, Thin Solid Films 10 (1972)

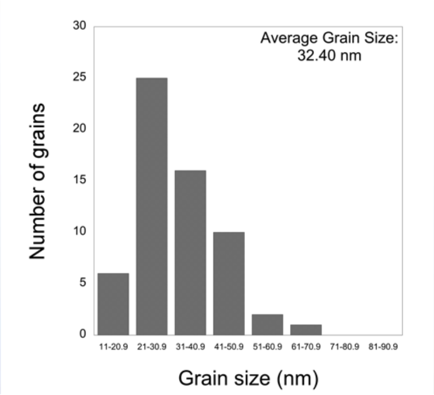
In Situ Anneal of Nanocrystalline Ta

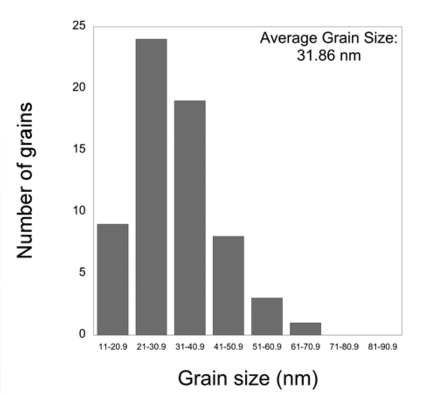


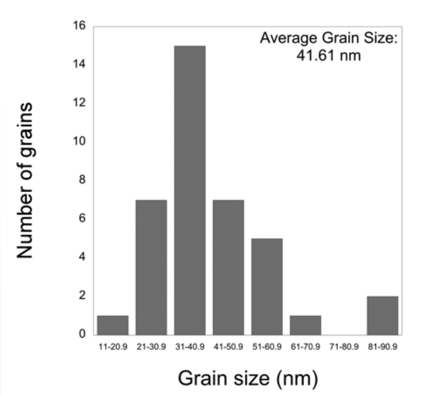


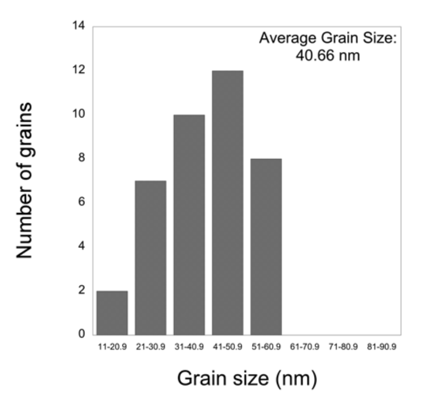












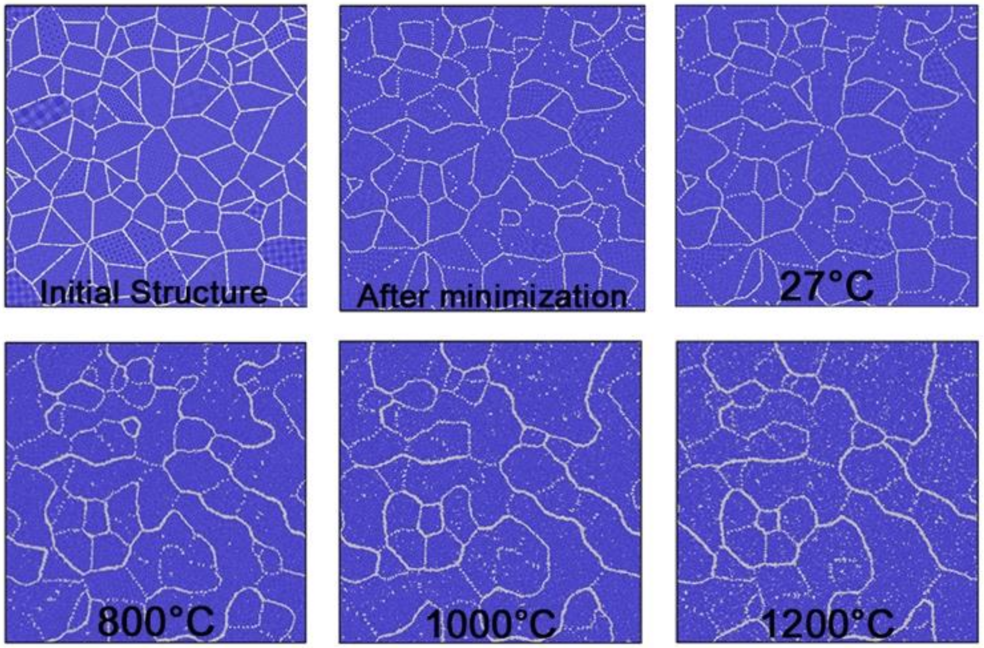
In situ annealing up to 1200°C

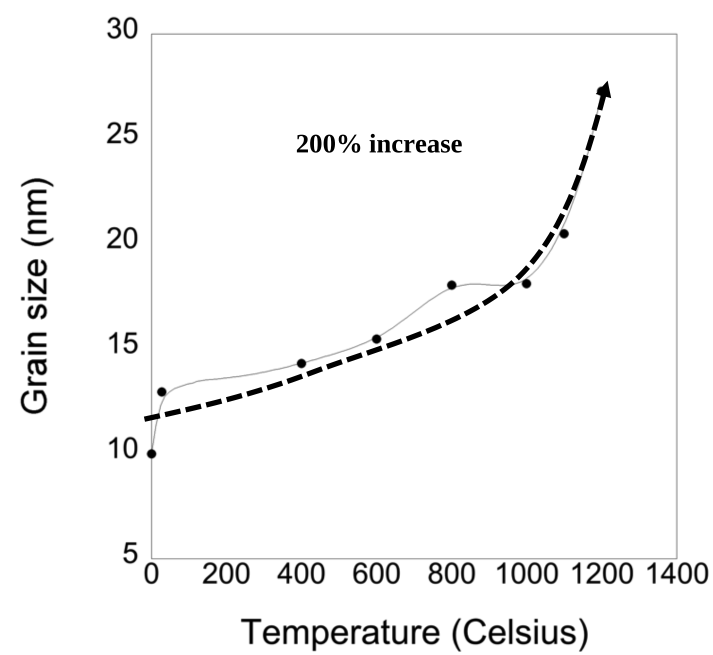
- **At 25% of the melting point (800°C), grain growth was completely absent**
- **Increasing the temperature to 1000°C produced a 25% increase in grain size to 40 nm**
- **A further increase to <u>40% of the melting point</u> produced no additional grain growth**

Do we expect considerable grain growth?

- **MD simulations were used to study grain growth during annealing in a pure Ta film**
- **A 200% change in grain size was observed during a 15 ns simulated anneal with abnormal grain growth**
- **Indicates pure nanocrystalline Ta should exhibit more extensive grain growth**

Anneal Temperature	Average Grain Size
0°C	10.00 nm
27°C	12.956 nm
800°C	18.047 nm
1000°C	18.105 nm
1200°C	27.267 nm





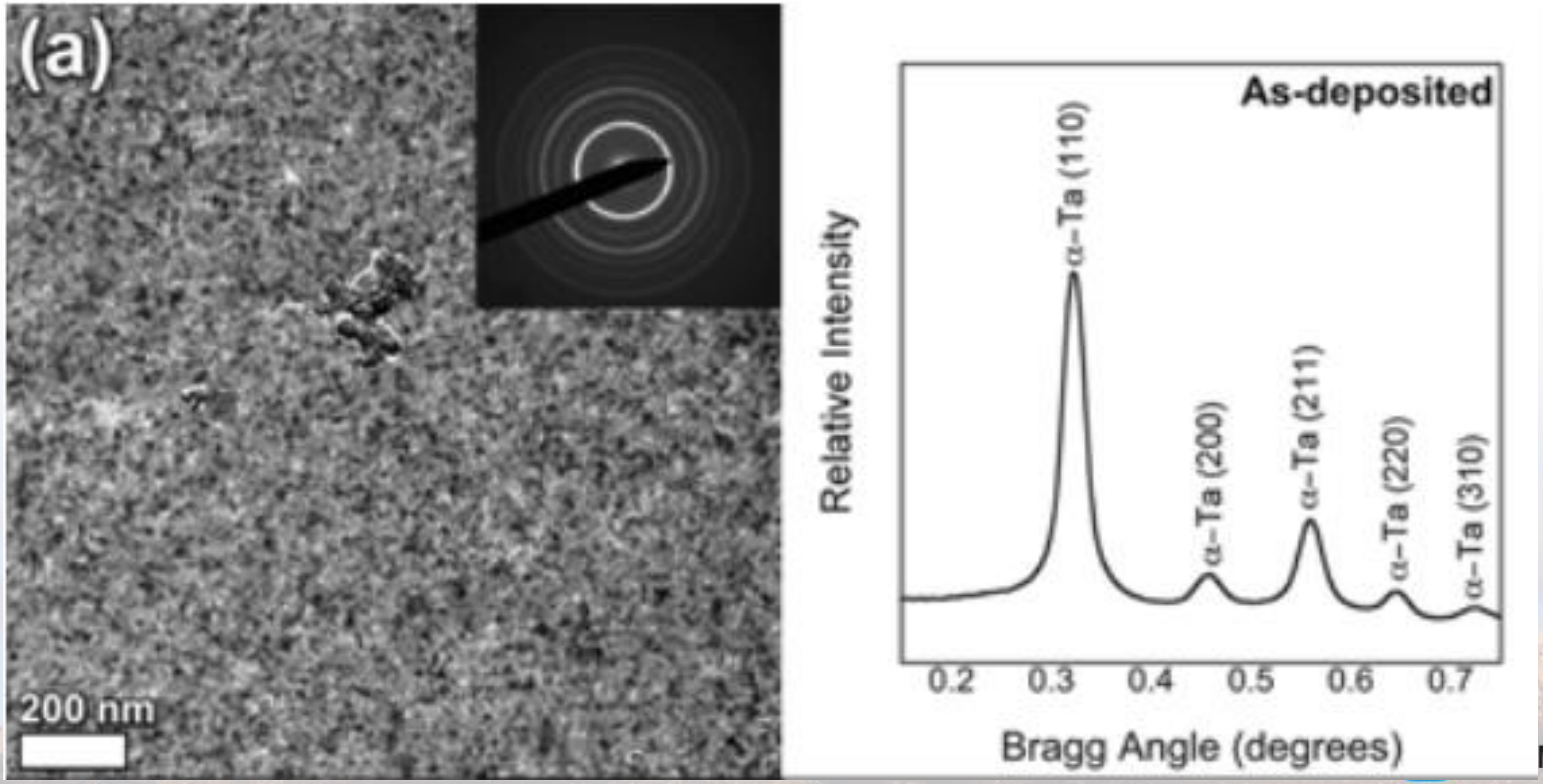
In-situ Anneal of Nanocrystalline Films

<u>**Examine microstructural stability at elevated temperatures:**</u>

- **Isothermal annealing near α-to-β transition temperature**
- **Effect of temperature up to 40% of Ta melting temperature**

<u>**As-deposited nanocrystalline films:**</u>

- **Equiaxed nanocrystalline structure (18 nm average grain size)**
- **Single phase α-Ta and no Ta oxide peaks**



Isothermal Anneal at 800C

1 hour anneal:

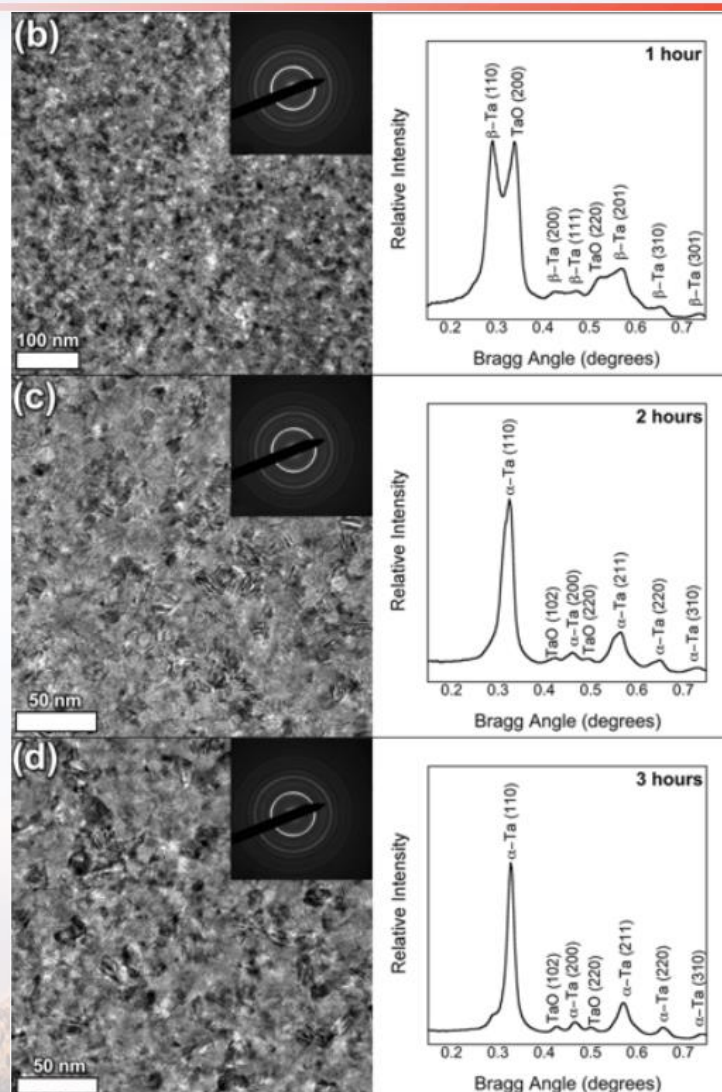
- α-to-β transition
- No discernible changes in structure or grain size
- Appearance of metastable TaO phase

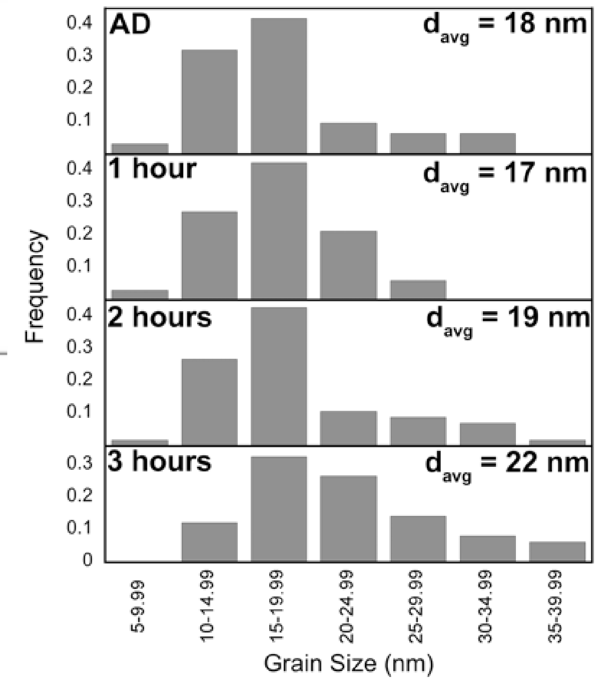
2 hour anneal:

- β-to-α transition
- Reduction in TaO peak intensity

3 hour anneal:

- No phase transition
- Coarsening of nanostructure – increase in average grain size to 22nm

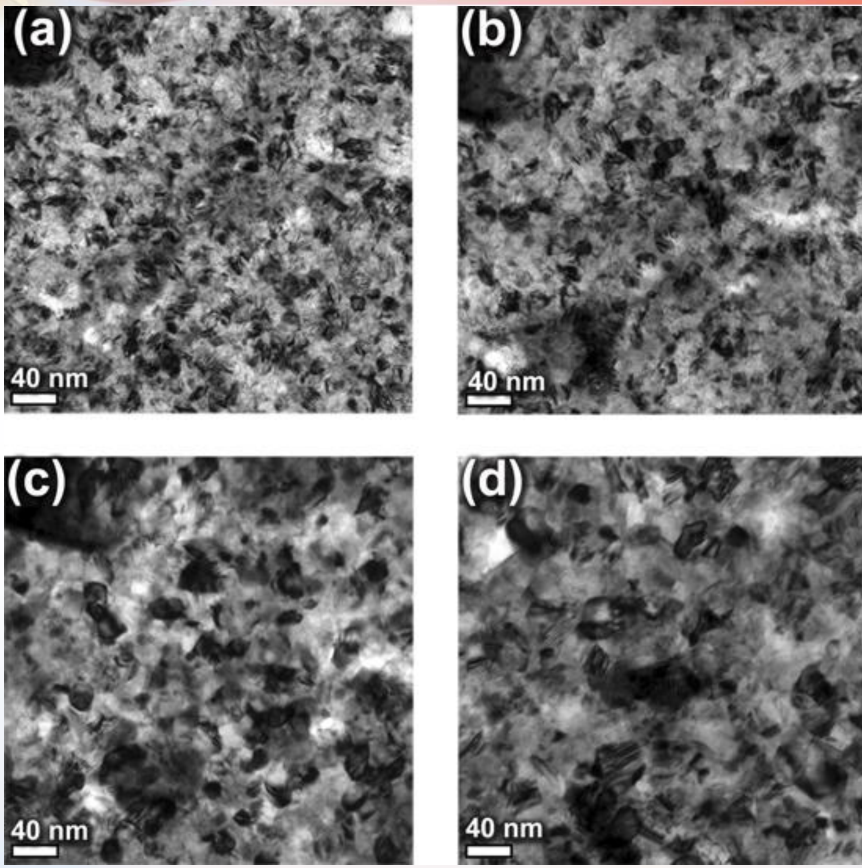


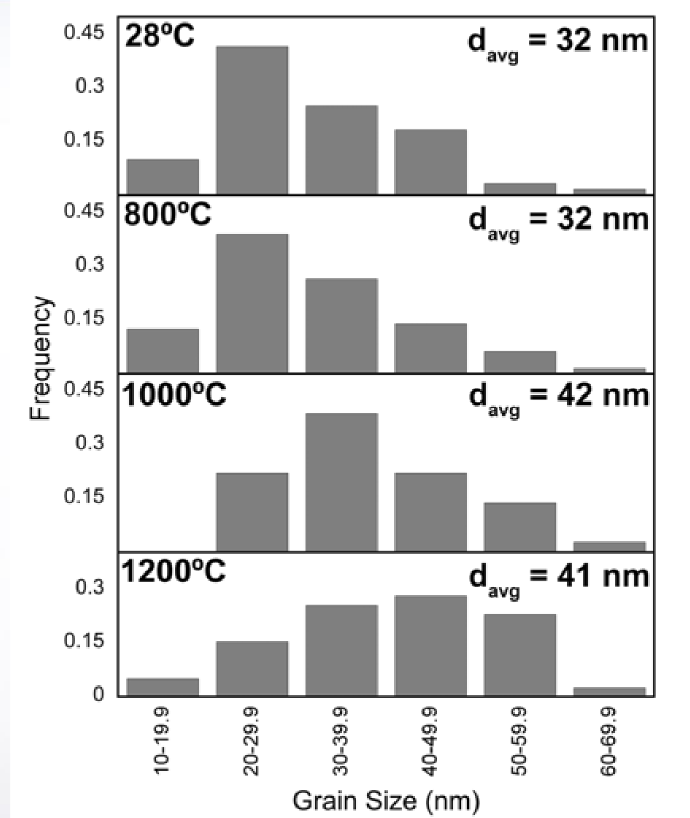


Grain growth at 800C in nanocrystalline Ta minimal and not influenced by α-to-β transition

Sandia National Laboratories

In-situ annealing to 1200C





b) Up to 800C:

- No discernible changes in structure or grain size

c) Up to 1000C:

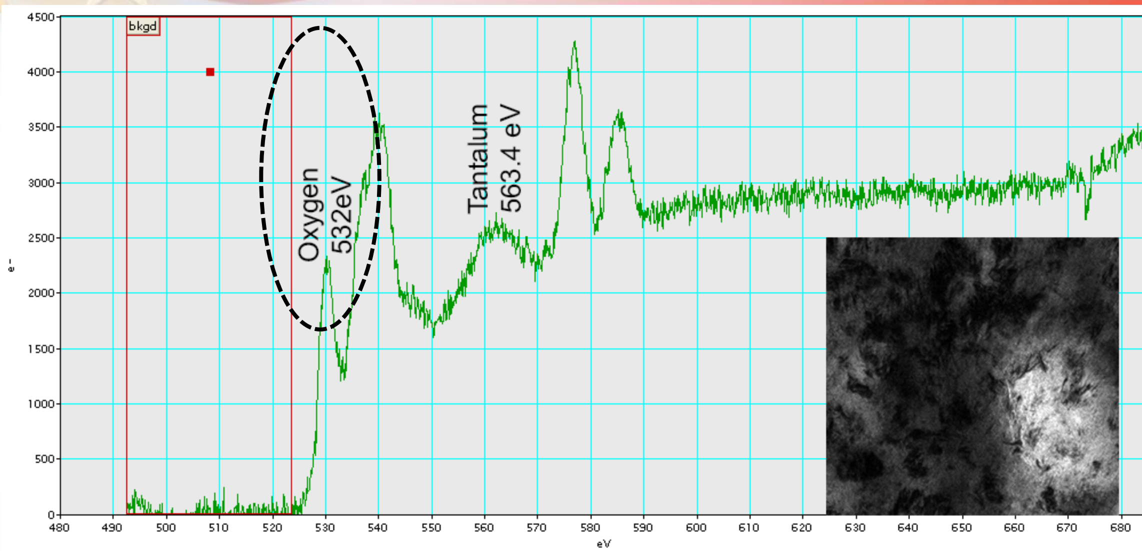
- Onset of grain growth

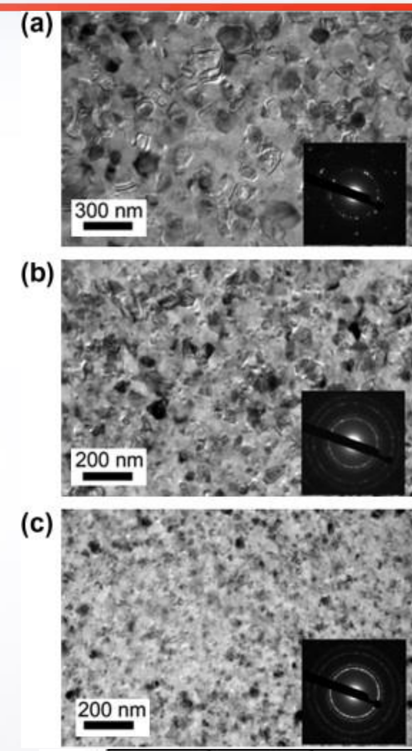
d) Up to 1200C:

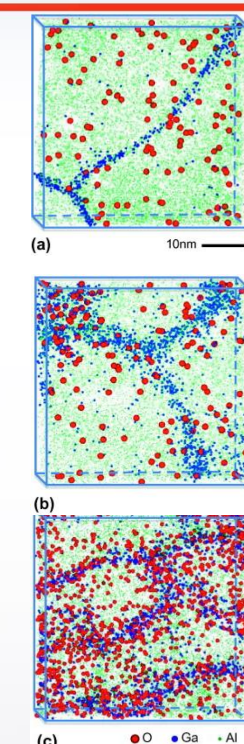
- No distinguishable change in grain structure

PLD fabricated Ta films exhibit unprecedented thermal stability at 40% of melting temperature

Impurity-induced Nanostructure stabilization



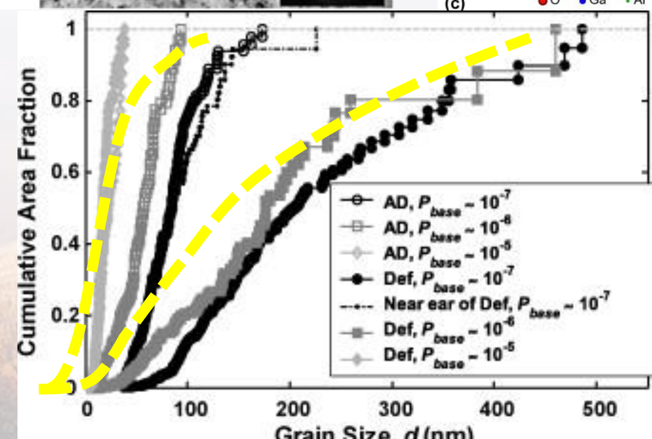




<u>EELS conducted to determine impurity content</u>

- **Oxygen impurities were confirmed in the as-deposited nanocrystalline Ta films**
- **Stabilization of "pure" nanocrystalline films has previously been attributed to oxygen enrichment at the grain boundaries in Al**

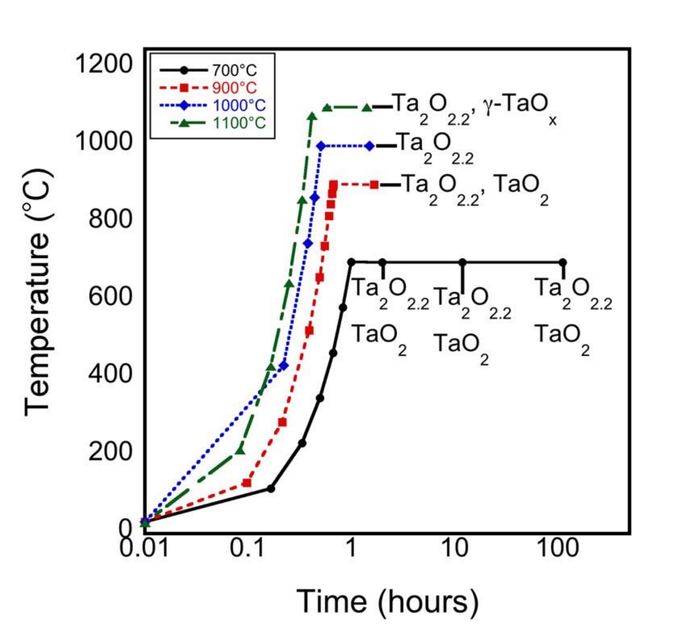
Demonstrates that a small amount of the "right" impurities can promote the stabilization of nanoscale grains

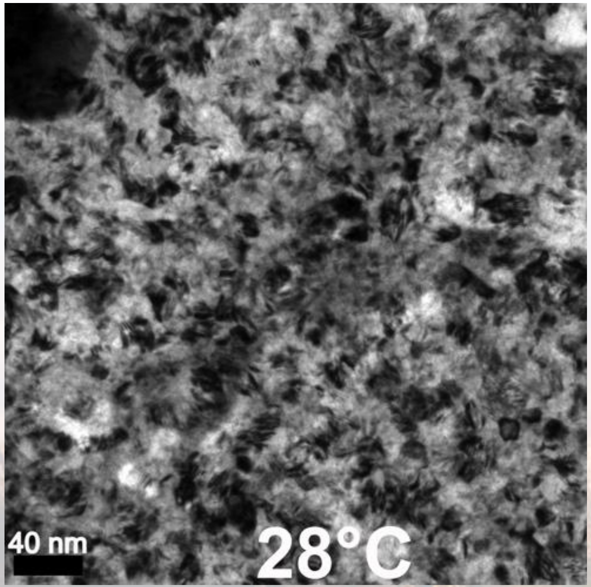


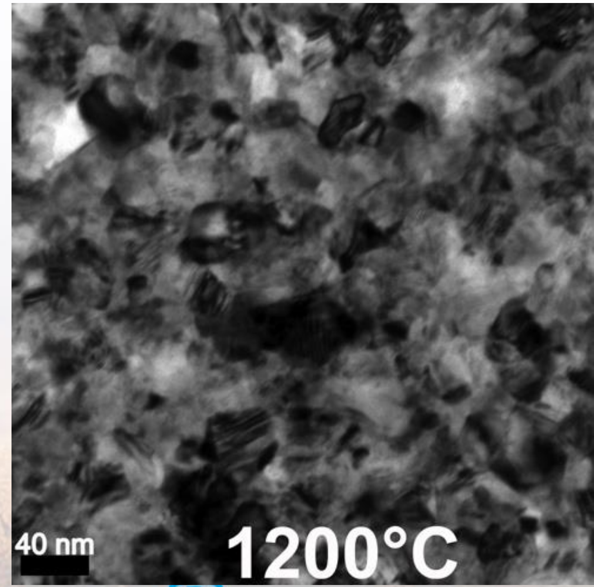
Tang et al., Acta Materialia 60(2012)

Thin film tantalum is a complex material…

- Amorphous tantalum films crystallized over a wide range of temperatures to form a series of metastable nanocrystalline tantalum oxides
- The absence of the stable monoclinic Ta_2O_5 phase of tantalum oxide was attributed to an insufficient amount of oxygen in the PLD films
- Thicker films were nanocrystalline BCC α-tantalum with an average grain size of 20 nm
- The "pure" nanocrystalline films exhibited unprecedented thermal stability at 40% of T_{melt}
- Enhanced thermal stability attributed to impurity induced nanostructural stabilization



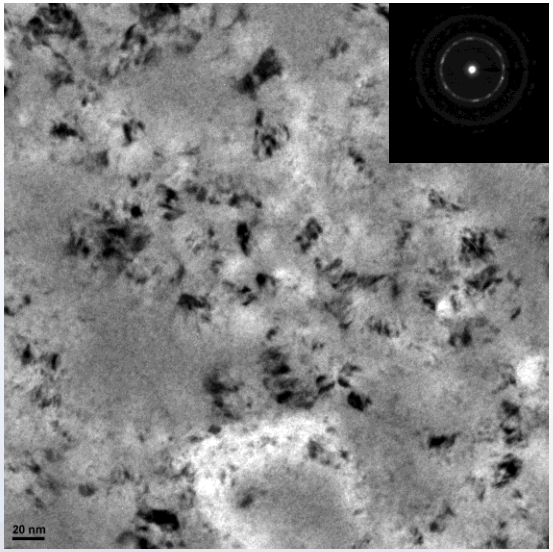




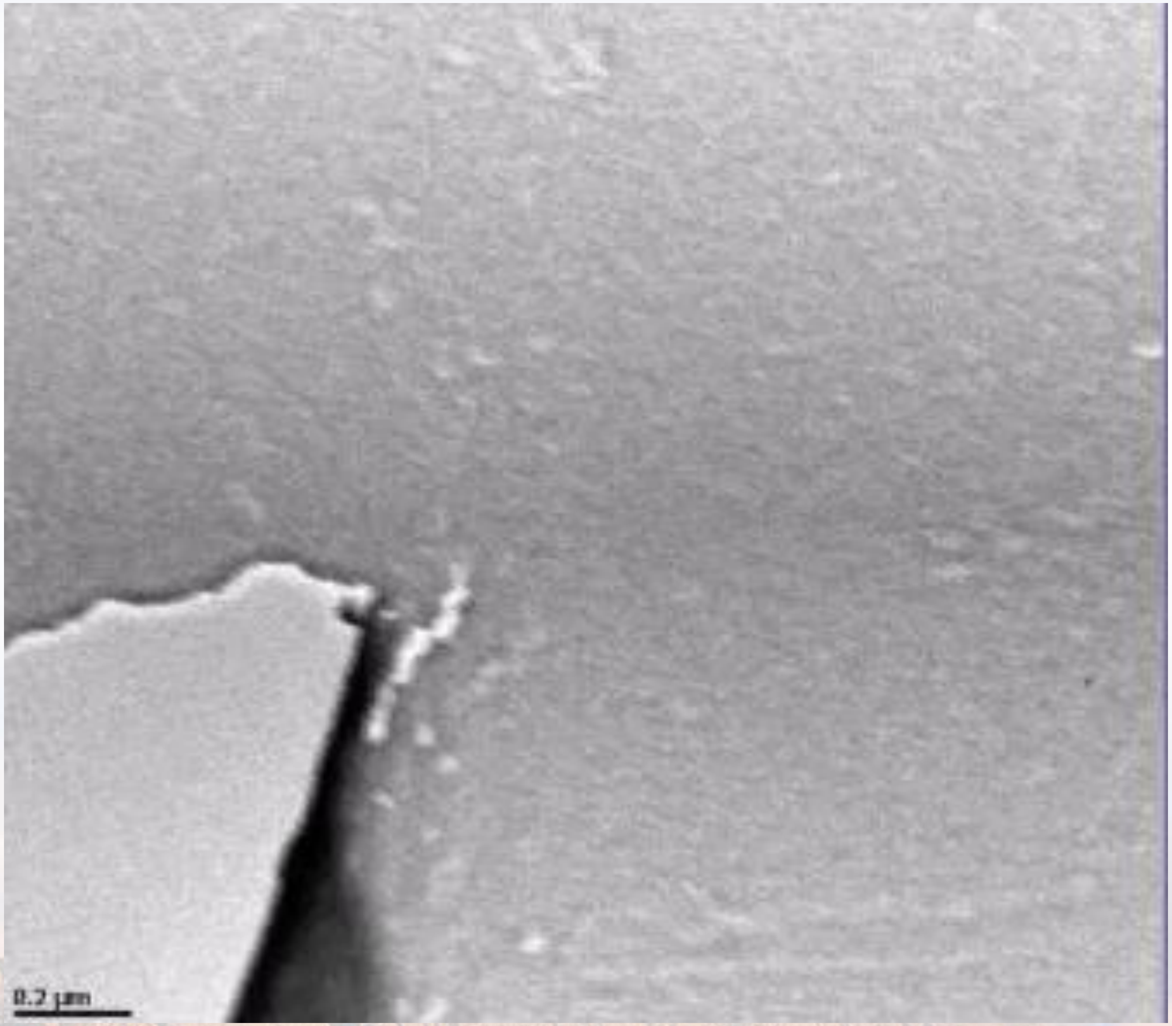
In-situ Straining of Amorphous Ta films

- **in-situ straining holder**
- **Room Temperature**
- **Phillips CM-30 at 300kV**
- **80nm thin film**

Gatan Straining Holder



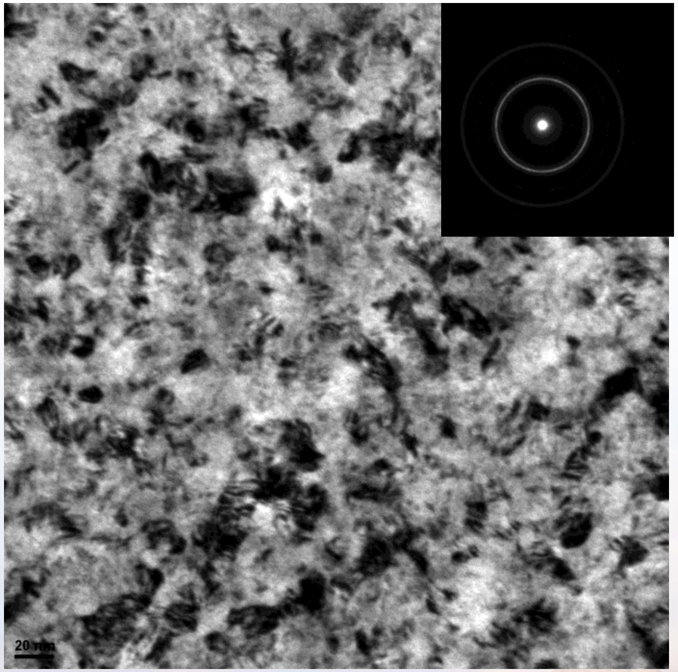
Amorphous Ta film prior to straining and electron diffraction pattern



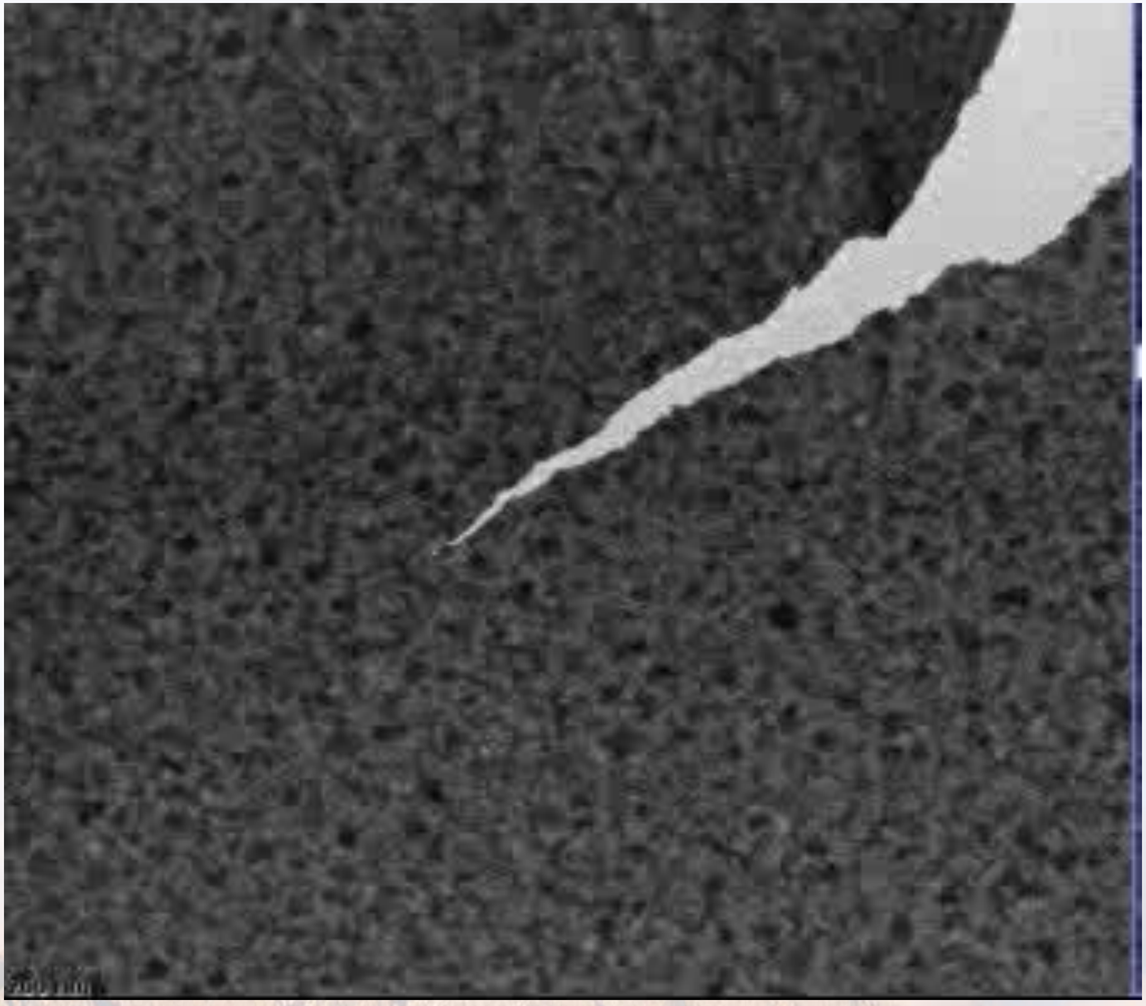
- **Brittle fracture up to 181 μm displacement**
- **Crack propagation sudden; no sign of elastic strain**

In-situ Straining of Nanocrystalline Ta films

- **Bulk in-situ straining holder**
- **Room Temperature**
- **Phillips CM-30 at 300kV**
- **150 nm thin film**

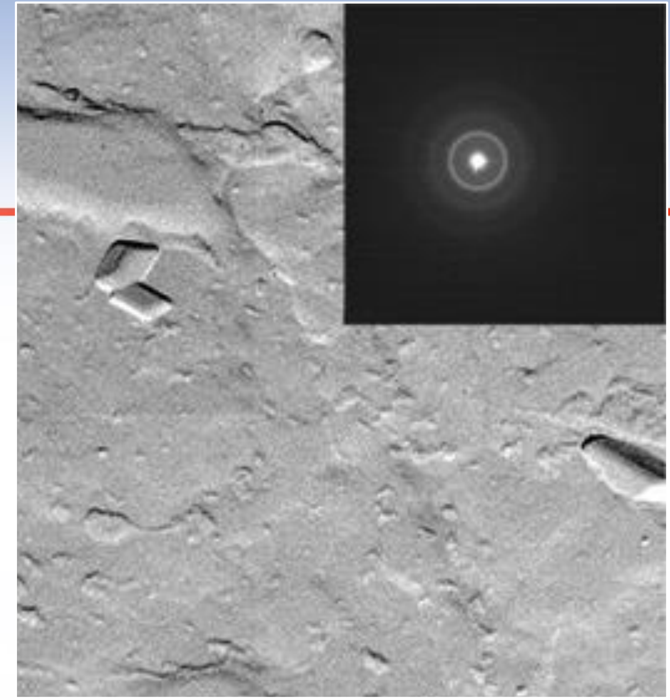


Nanocrystalline Ta film prior to straining and electron diffraction pattern



Brittle fracture – slower crack growth than the amorphous Ta films

Summary



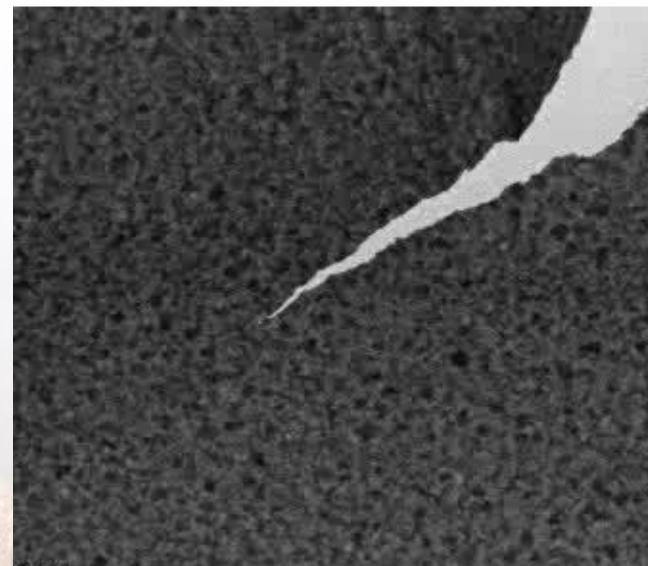
Thermal stability of PLD Ta films

I. **Amorphous**
   I. Low and high vacuum PLD samples resulted in crystallization with annealing up to 1200ºC
   II. Metastable tantalum oxides present after annealing

II. **Nanocrystalline**
   I. Phase transition seen during 1 hr anneal at α-to-β transition temperature; reversal during 2^{nd} hour
   II. Grain growth seen during 3 hour anneal near transition temperature
   III. Grain growth present around 1000ºC during in-situ ramp

Mechanical stability of PLD Ta films

I. Amorphous and nanocrystalline films both presented brittle fracture
II. Nanocrystalline films showed higher resistance than amorphous



Acknowledgements

- **Michael Marshall and Stuart Van Deusen (SNL)**
- **Wenbo Wang for his contributions to the molecular dynamic simulation studies**
- **Eric Stach of the Center for Functional Nanomaterials at BNL**

This work was supported by the US Department of Energy, Office of Basic Energy Sciences. Or other funding source. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.