Engineered Metallic
Nanostructures Laboratory

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In Situ Analysis of Microstructural Evolution during the Heat Treatment of Nanocrystalline and Amorphous Tantalum Films

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Background & Motivation

According to the World Nuclear Association and the International Energy Agency (IEA), the worlds electricity demands will increase by at least 80%. This demand requires new reactors to be built [1].

- Next generation nuclear reactor materials conform to a new set of requirements which focus on improved strength and radiation tolerance, increased lifetimes, and higher operating temperature conditions [2-5].
- New materials are needed to meet these demanding requirements, and nanocrystalline refractory metals, have demonstrated promising results [2,4]. Tantalum is considered here due to its applicability for extreme temperature environments [6].

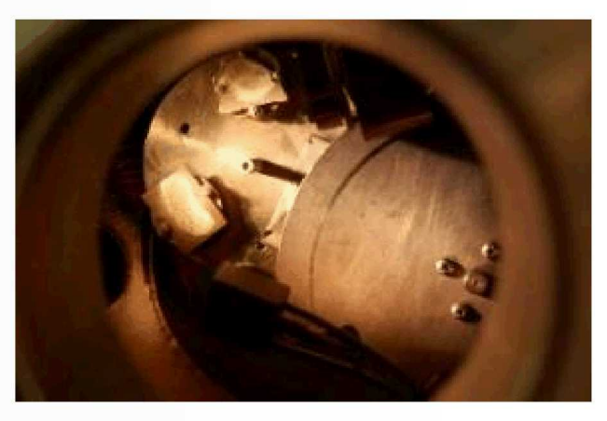
The focus of this study was to examine the thermal stability of nanocrystalline and amorphous Ta thin films synthesized by pulsed laser deposition.

- This research implemented *in situ* transmission electron microscopy (TEM) techniques to achieve precise probing of nanostructures and phase stability and characterization of microstructural evolution during heat treatment of nanocrystalline and amorphous tantalum thin films [7].
- By quantifying the structural stability of engineered nanocrystalline refractory metals at elevated temperatures, next generation reactor materials can be designed for future evaluation of other critical performance metrics such as radiation tolerance.

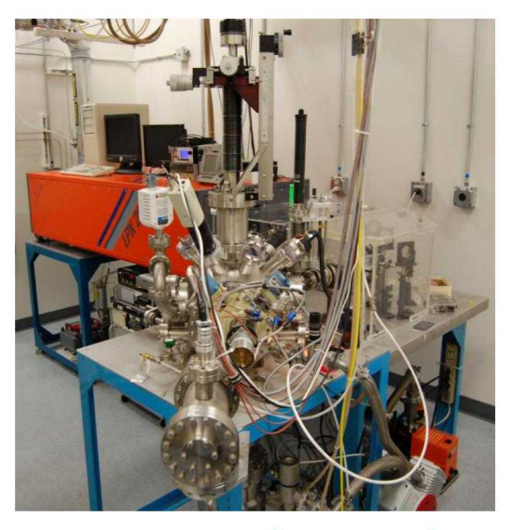
Sample Preparation using Pulsed Laser Deposition (PLD)

Nanocrystalline and amorphous thin Ta films were deposited at Sandia National Laboratories using Pulsed Laser Deposition with the following parameters:

- Nominally 100-150 nm thick Ta films deposited using a KrF excimer laser, λ = 248 nm
- System employed a raster system to limit the incorporation of impurities.
- Films were deposited on polished NaCl substrates and prepared for TEM investigations. using a float-off sample preparation technique upon dissolution of the substrate.



PLD target disc



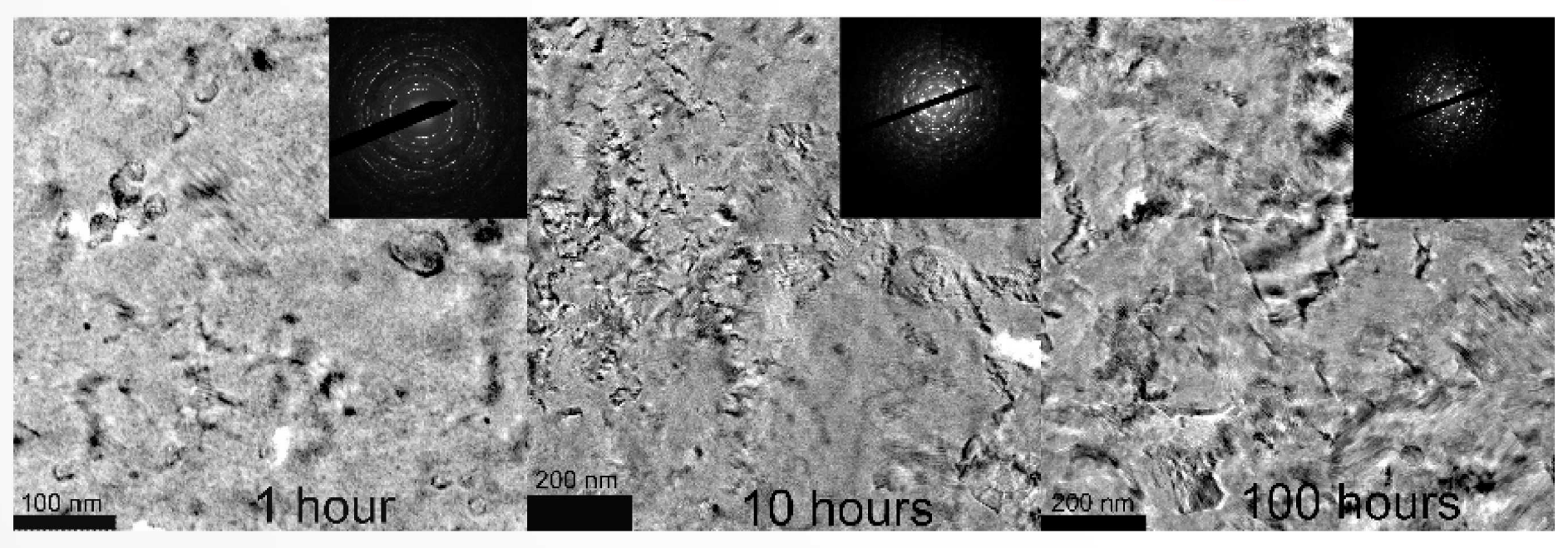
PLD system located at SNL

In situ heating holder

Experimentation & Analysis

- Anneals were performed *in situ* in a Philips CM-30 and JEOL JEM 2100F TEM using a Gatan heating holder operating between 700-1200°C. Extended anneals were performed *ex situ* using a Lindberg furnace and Omega controller. Electron energy loss spectroscopy (EELS) was performed using the JEOL JEM 2100F TEM
- Image analysis was accomplished using ImageJ and Adobe Photoshop. Phases were identified through integrated radial intensity plots.

Amorphous Tantalum

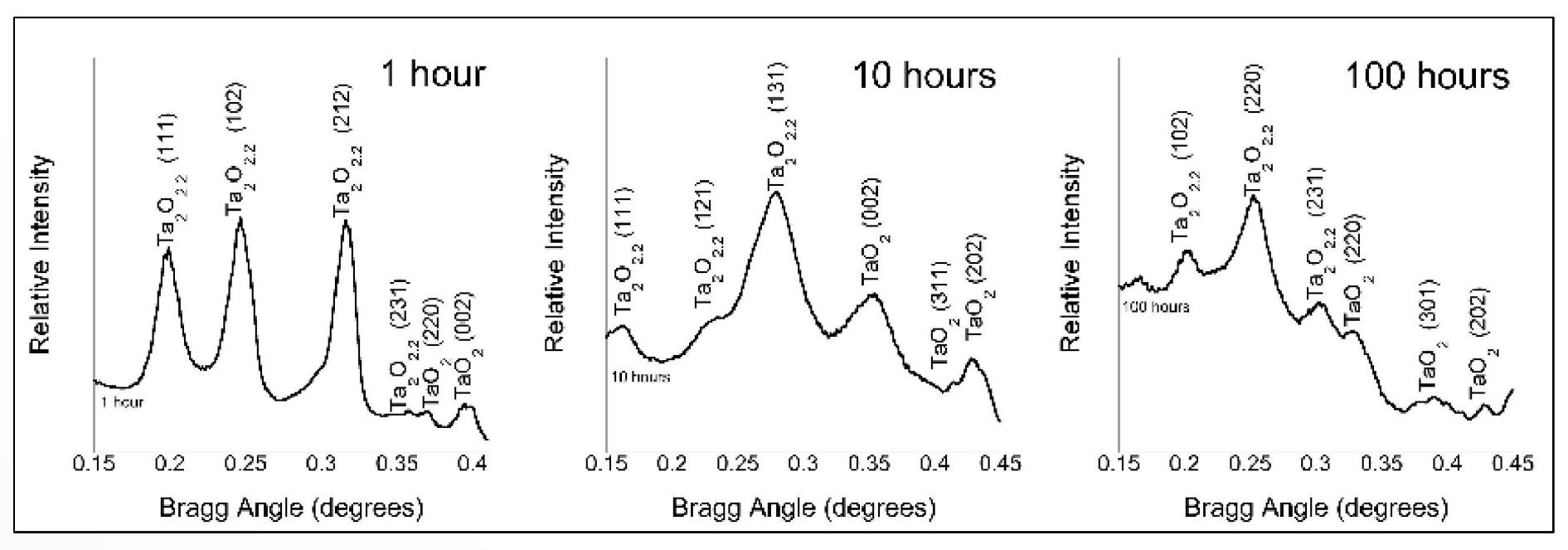


Bright field images of an amorphous Ta film annealed at 700°C revealed:

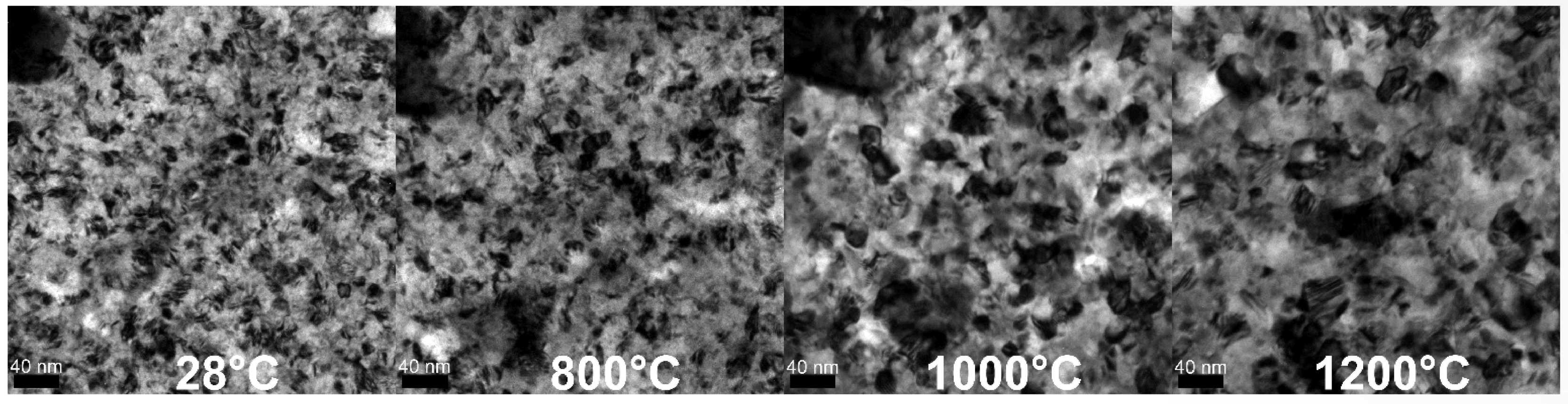
- 10-50nm grains after 1 hour of heat treatment
- Further annealing, up to 100 hours, produced coarse grains

Quantitative analysis of the electron diffraction patterns revealed:

- A nanocrystalline structure of metastable tantalum oxide.
- Increased annealing time showed conversion between metastable oxide structures.



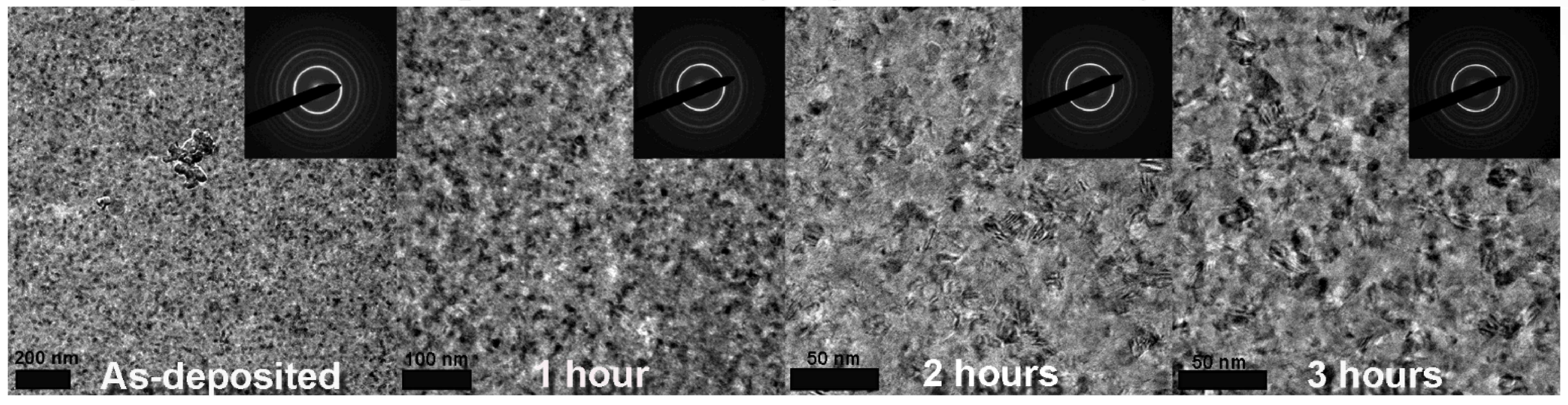
Nanocrystalline Tantalum



Temperature (°C)	Average Grain Size (nm)
28	32.40 nm
800	31.86 nm
1000	41.61 nm
1200	40.66 nm

***In situ* anneals from room temperature (28°C) to 1200°C of 150nm thick Ta films demonstrated:**

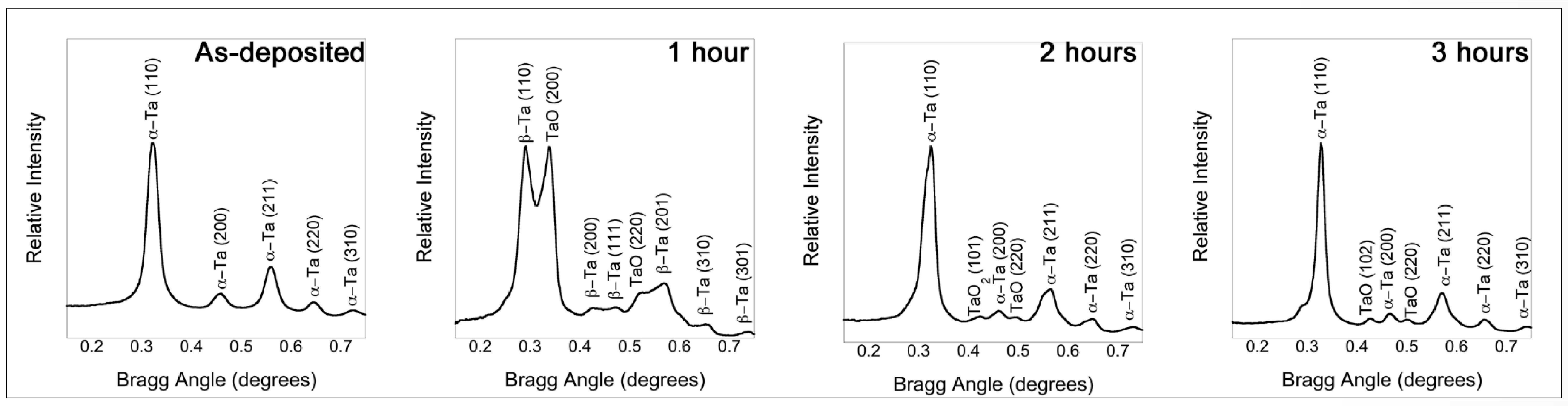
- Grain growth was completely absent up to 800°C, which represents roughly 25% of the melting point
- Even after annealing at 1200°C (40% of the melting point), the nanocrystalline film exhibited a 25% increase in grain size, which represents unusually high thermal stability for an elemental nanocrystalline metal.



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

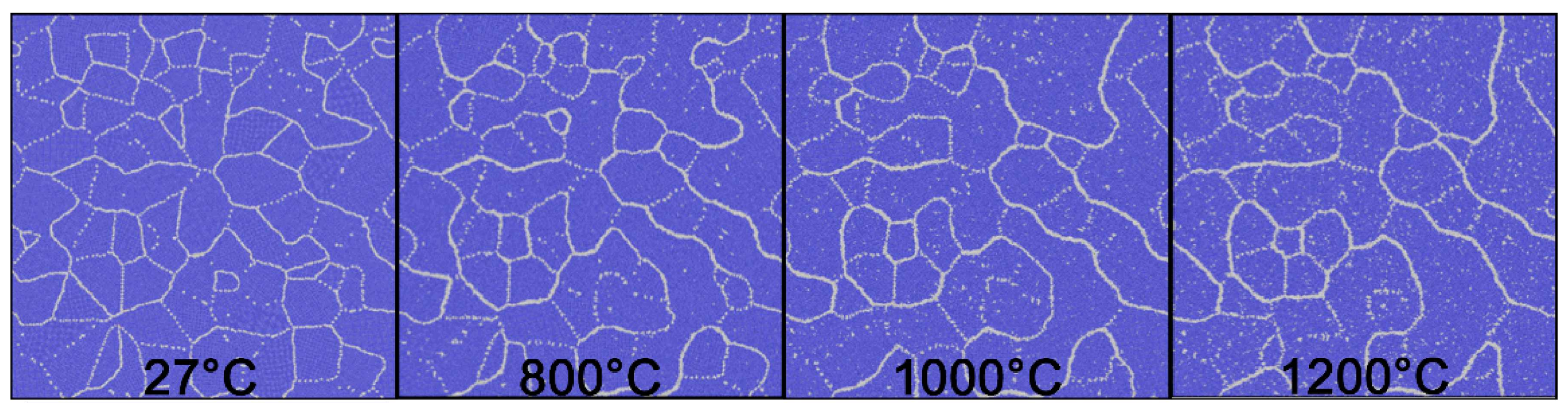
***In situ* isothermal anneals were conducted on the 100 nm-thick nanocrystalline Ta film and revealed:**

- Limited grain growth regardless of time with average grain size fluctuating between 17 and 23 nm.
- The subtle increase between 2 and 3 hours represented the only quantifiable change beyond measurement error.



Quantitative analysis of the electron diffraction patterns to produce radial intensity plots illustrated:

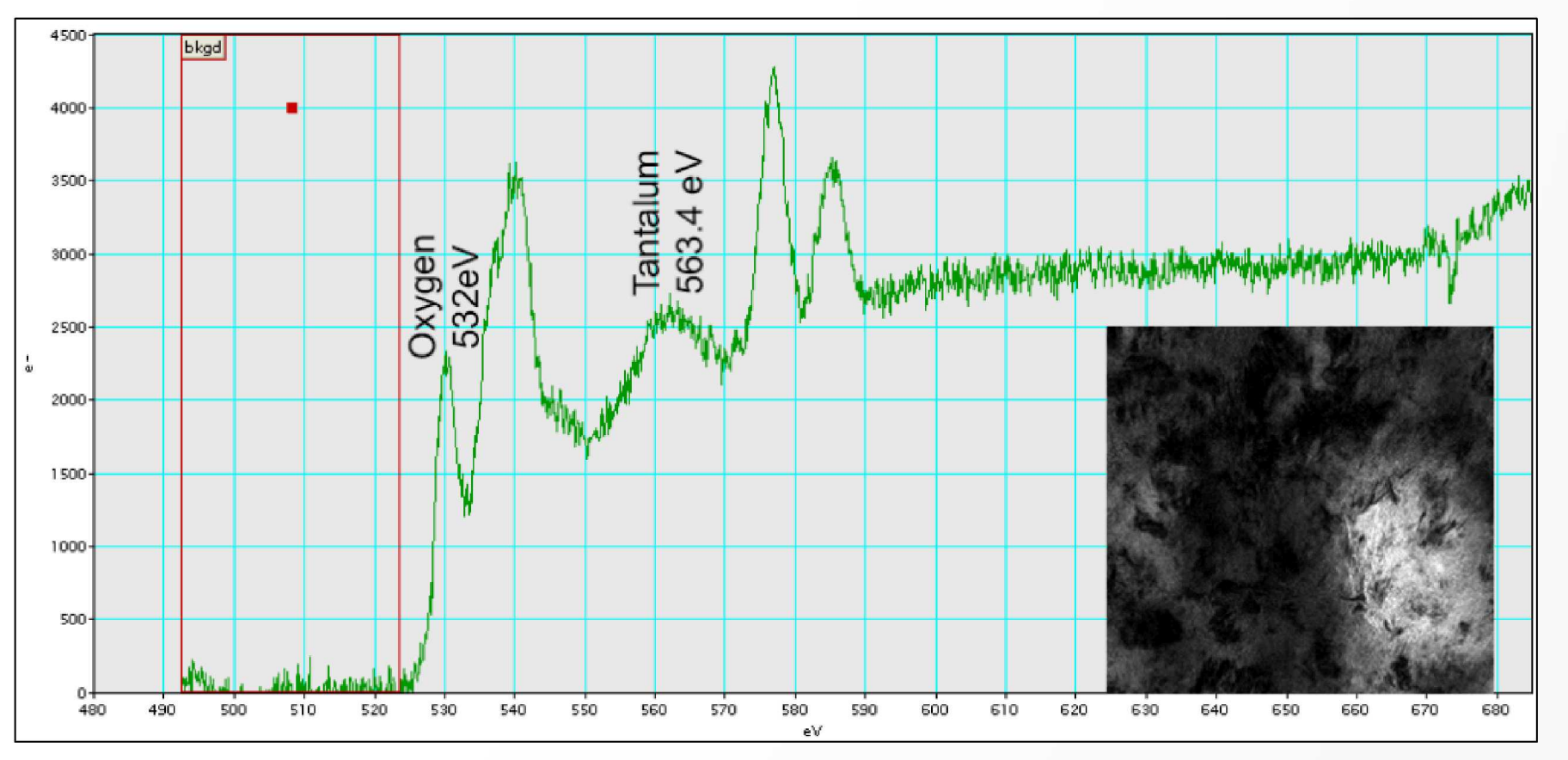
- Initially the film consisted only of the BCC α-Ta phase, which represents the equilibrium metallic phase of Ta.
- Upon annealing at approximately 800°C for 1 hour, an α → β transition was detected and accompanied by the formation of TaO; although no evidence of oxide precipitates was observed in the bright field image.
- The film transformed back to α-Ta after 2 hours of annealing, which was expected since the annealing temperature was very near the β → α transition temperature of 755-775°C [8].



Average Grain Size (nm)	Average Grain Size (nm)	Average Grain Size (nm)	Average Grain Size (nm)
12.956 nm	18.047 nm	18.105 nm	27.267 nm

Molecular dynamic simulations, performed to study the extent of grain growth during annealing, revealed:

- Relaxation for 15 ns at 1200°C demonstrated a 3-fold increase in grain size with abnormal grain growth resulting from the grain boundary misorientation distribution
- Simulations suggest that pure nanocrystalline Ta exhibits more extensive grain growth than observed in experiments



Impurity content of a 26 nm thick Ta film was analyzed using EELS and showed:

- Oxygen impurities were confirmed to be present in the as-deposited films
- Stabilization of "pure" nanocrystalline films has been attributed to oxygen enrichment at grain boundaries in Al [9].

Conclusions

- Nanocrystalline tantalum films exhibited exceptional thermal stability with virtually no grain growth observed at temperatures up to 800°C, representing 25% of its melting point. Microstructural evolution is in competition with the transformation between the equilibrium BCC α-phase and metastable tetragonal β-phase at this temperature, which completely hampered grain growth.
- Annealing of nanocrystalline tantalum films at temperatures up 1200°C produced only modest evolution of the microstructure with grain size increasing from 30 to 40 nm. This limited grain growth at 40% the melting point of tantalum is uncharacteristic of elemental nanocrystalline metals, as confirmed by molecular dynamics simulations of grain growth in pure nanocrystalline Ta.
- Stabilization of the film was attributed to the presence of oxygen impurities in the as-deposited films, which acted to stabilize the nanostructure as confirmed by electron diffraction analysis and EELS.

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