SAND2010-2695C

High-Power Ion Beam Deposition of Nanocomposite, Multilayer and Single-layer Metal Coatings: Synthesis and Characterization*

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37th International Conference on Metallurgical Coatings and Thin Films (ICMCTF 2010)
San Diego, CA USA
April 26 - 30, 2010

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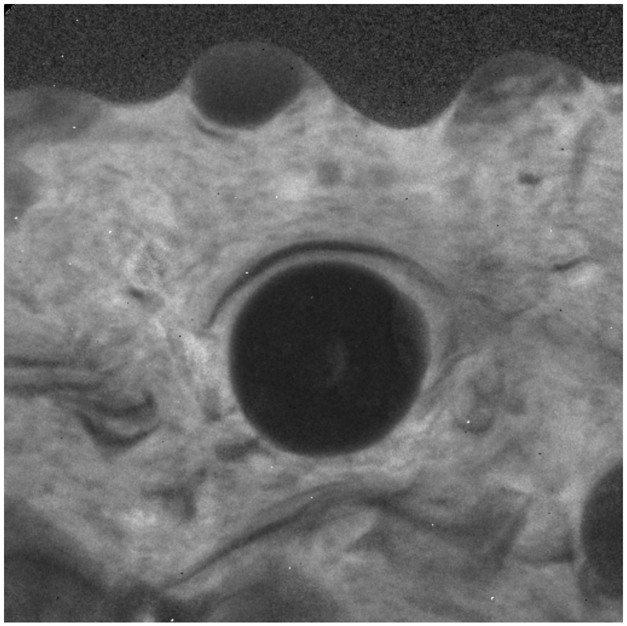
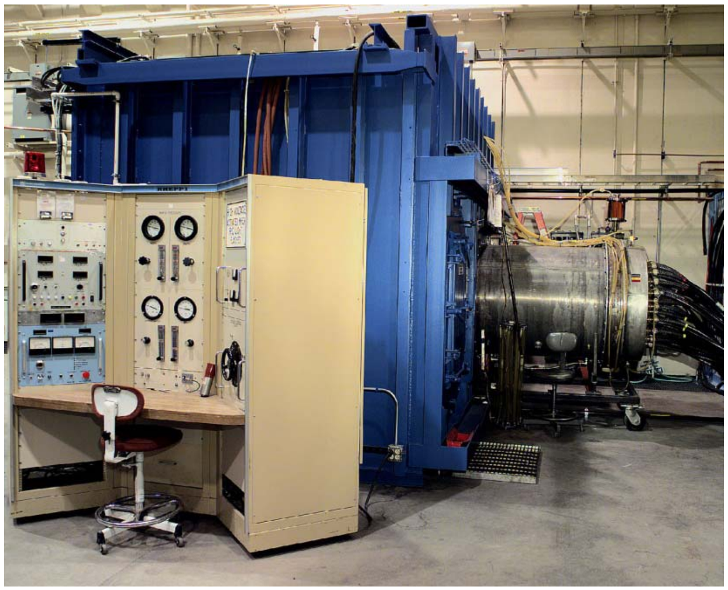
Outline



MoS$_2$-Ti Nanocomposite Layer

- Thin-films of multi-layer metals, nanocomposites catalyzed by sulphur (e.g. MoS$_2$, WS$_2$), single-metal layers
- Deposition Method: RHEPP-1 high-power ion beam
- Deposition description
- Experiment Discussion
  - MoS$_2$ with metal additions can lead to low friction/low wear in 50% RH conditions
  - Pure metal thin films: low friction, low wear IF nano-crystalline structure is maintained.
- Post Diagnostic analysis
  - Tribology – wear tracks from pin-on-disk
  - SEMs
  - FIB/XTEM
  - Spectral Imaging, XRD, SAD

The RHEPP-1 Facility at Sandia generates intense pulsed ion beams for thin-film formation

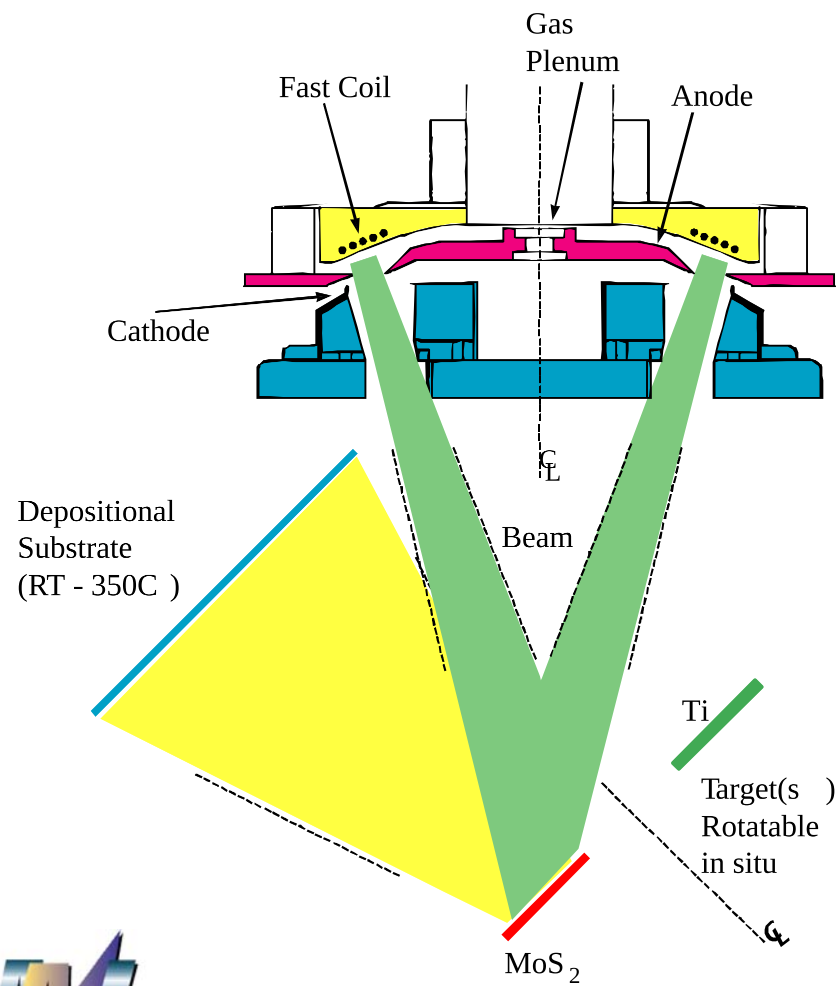


Marx tank with pulse-forming line

Vacuum tank with treatment area

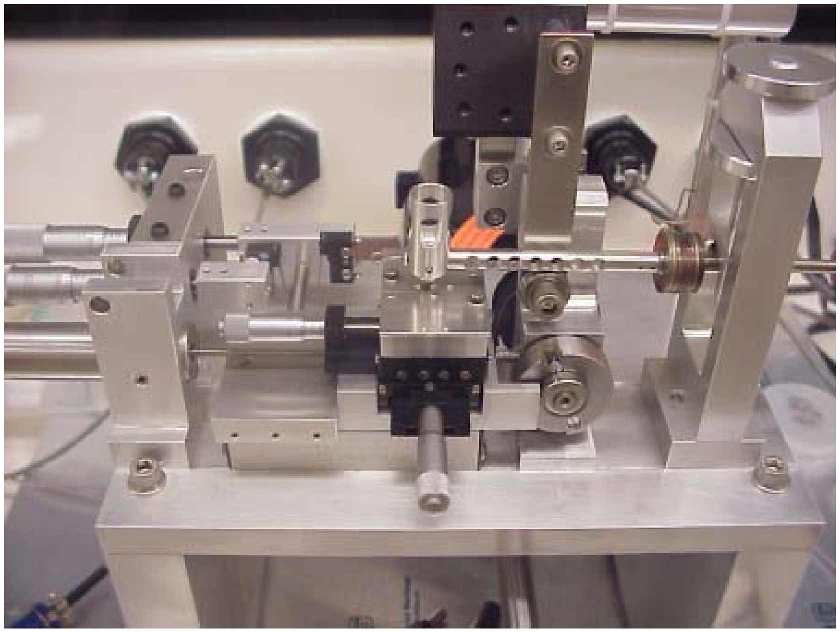
- **500-800 kV**
- **Up to 300 A/cm^2**
- **Nitrogen beam used here**
- **Overall treatment area ~ 150 cm^2**
- **Diode vacuum ~ 10^{-5} Torr**

An intense ion beam is used to ablate alternating targets to form multilayer thin films

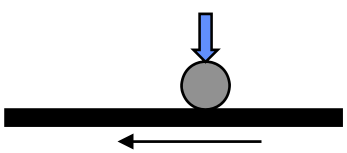


- Alternating targets (MoS_2 and Ti are shown) or single targets are rotated into target position for beam ablation
- Process resembles Pulsed Laser Deposition, but 50 cm^2 ablation spot size on target increases deposition per pulse by 2 orders of magnitude
- Nitrogen beam forms ablation plume normal to target surface. Distance target-substrate ~ 35 cm
- Film thickness/pulse from 10 to 5000 Å
- Depositional substrate heatable to 350°C

Tribological measurements were made in controlled environments



Linear Wear Tester
(Ball-on-Flat configuration, unidirectional)



Counterfaces: Si_3N_4 Ball (3.175 mm dia)

Normal Loads: 0.95 GPa (100 grams), 10 grams for most recent testing

Environments: Dry Nitrogen, Dry Nitrogen and Air with 50 %RH

Environmental Control

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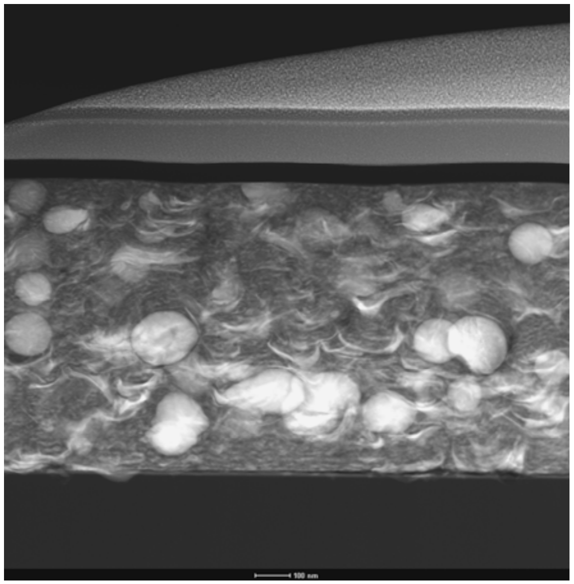
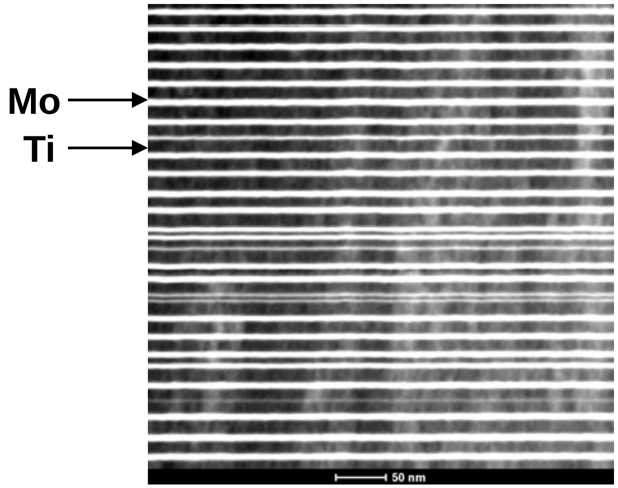
We have formed three types of films

MoS_2-Ti multilayer
108 Pulsed Layers



100 nm single-crystal Mo spheres disrupt multi-layer structure

Bi-Metal layers
(Mo-Ti, Mo-Ir, Mo-W)



TEM of a FIB prepared cross-section

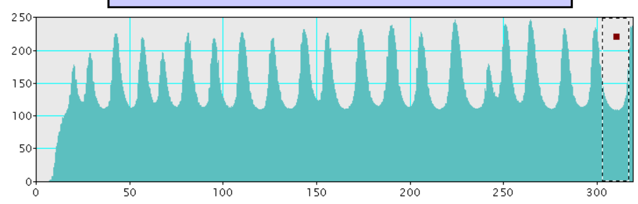
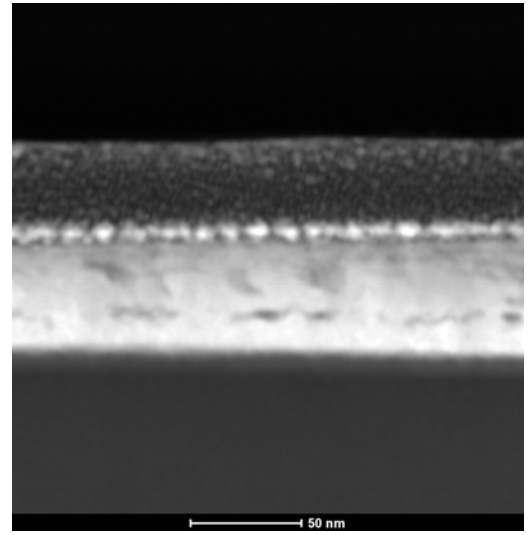


Image contrast plot

Single Metal layers
(Mo, Rh, Ni)



Shown: XTEM, 50 nm pure Rh layer

Mo: BCC
Rh: CCP
Ni: CCP

Per pulse layer thickness is controlled by:

- **the intrinsic ablation propensity of the material**
- **distance from substrate to target**
- **NOTE: Ti microstructure (above) continues PAST Mo interlayer**

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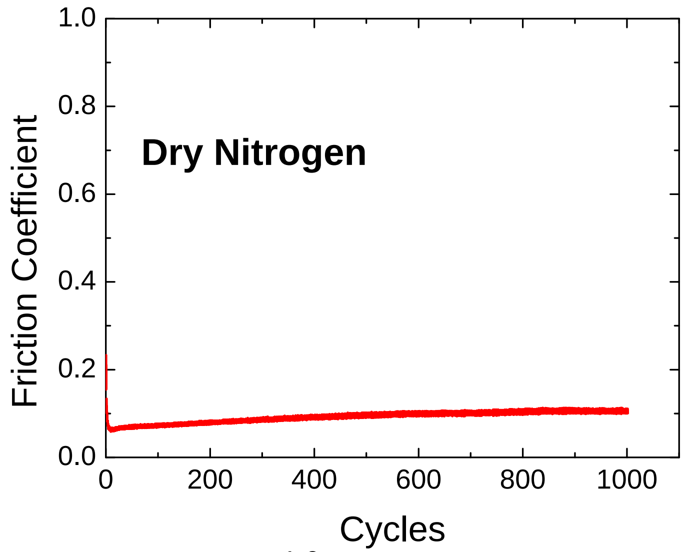
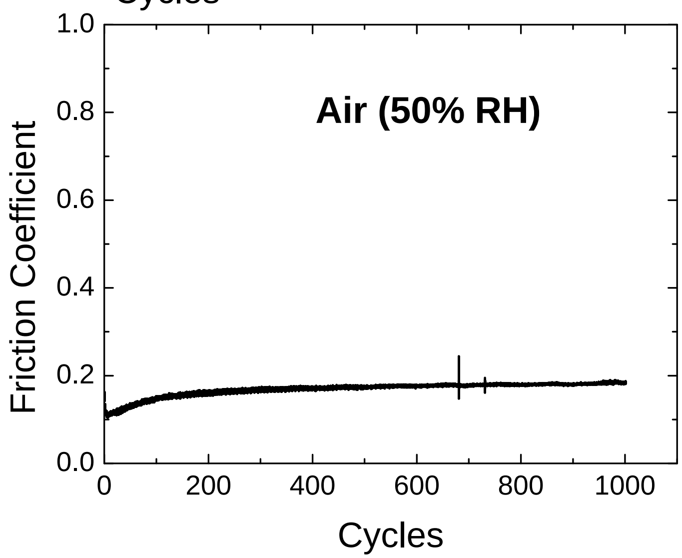
Motivation for MoS_2-Ti Film layer: low friction coefficient in 50% RH. Resulting films also have low wear

MoS_2-Ti 1:2 36 cm 300ºC head-on
108 Pulsed Layers

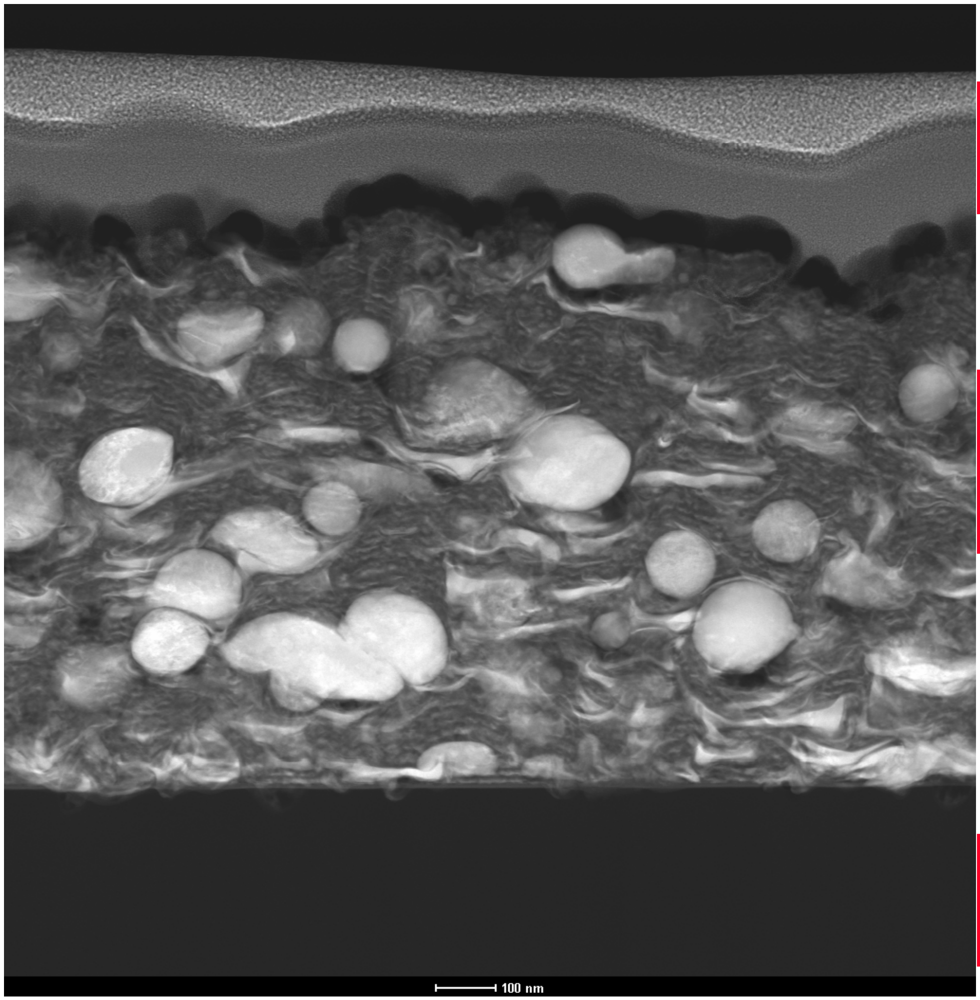




- **1000-cycle ball-on-flat geometry in both Dry Nitrogen and Air (50% RH)**
- **Friction coefficient < 0.10 in Dry Nitrogen**
- **Slight Increase to 0.15 in 50% RH Air**
- **Run-in wear-through about 50 nm out of ~ 1000 nm as-deposited**
- **Requires 300°C in-situ substrate heating, 1:2 MoS_2-Ti layer ratio.**

MoS2-Ti 1:2 300C

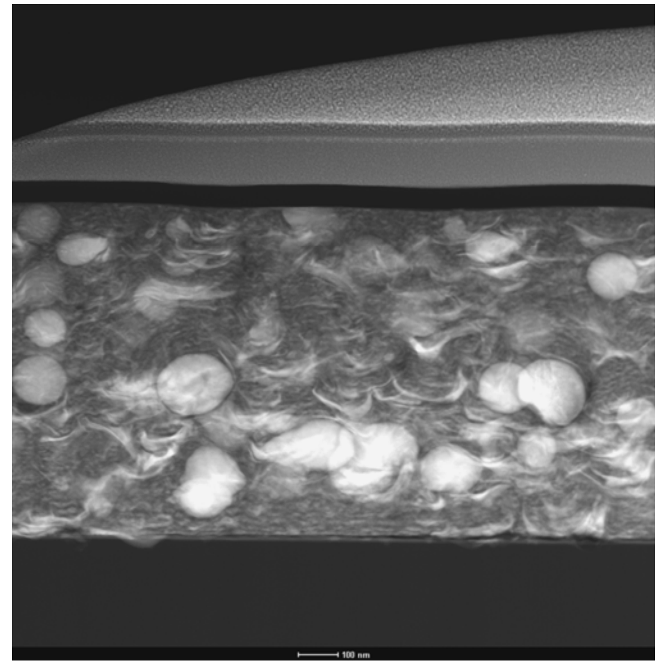
FIB/XTEMs: (left) as deposited, (right) under wear track: Self-Assembled array of 100 nm Mo spheres



C/Pt cover

100 nm Mo spheres

Si substrate



- 10 nm multi-layer (108 layers) disrupted by Mo single-crystal spheres
- Ti appears to be nano-crystalline
- Si_3N_4 ball smoothes off top roughness

Deposition rate: MoS_2 ~ 30 nm/pulse, Ti ~ 7.5 nm/pulse

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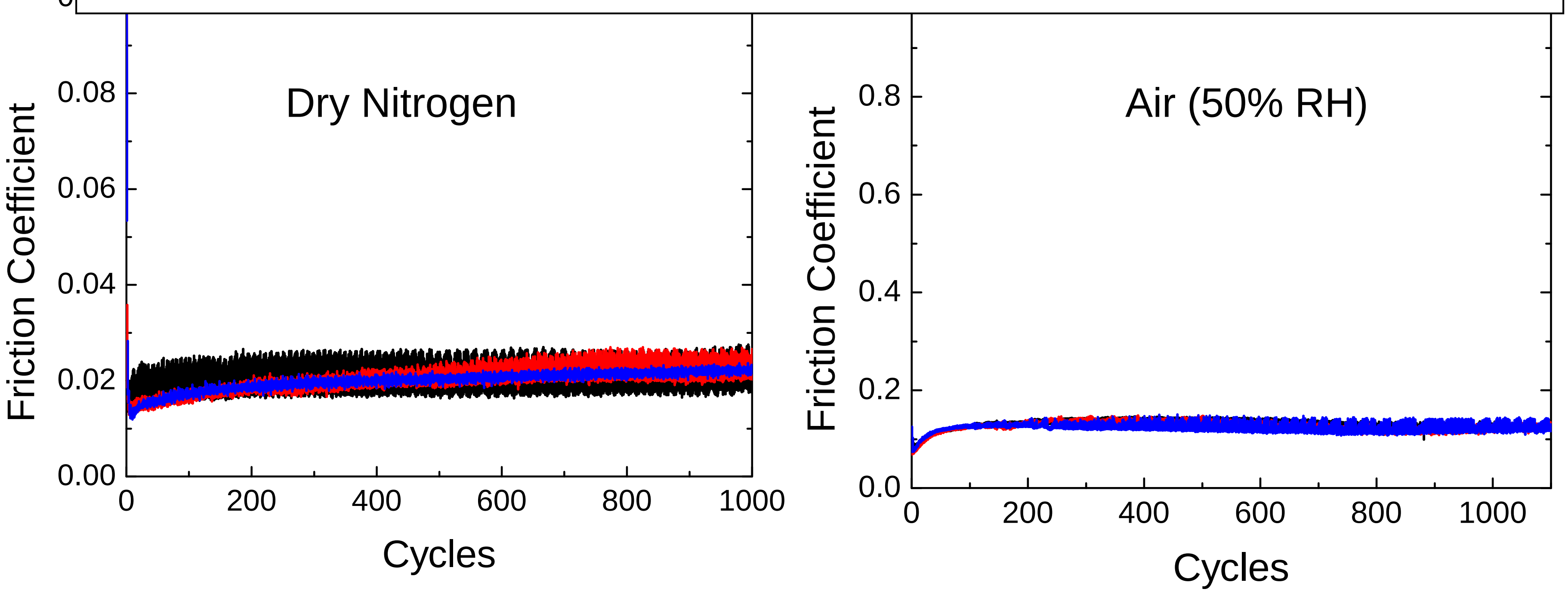
Friction Behavior of MoS_2-V Films better in dry and 50%RH than MoS_2-Ti films



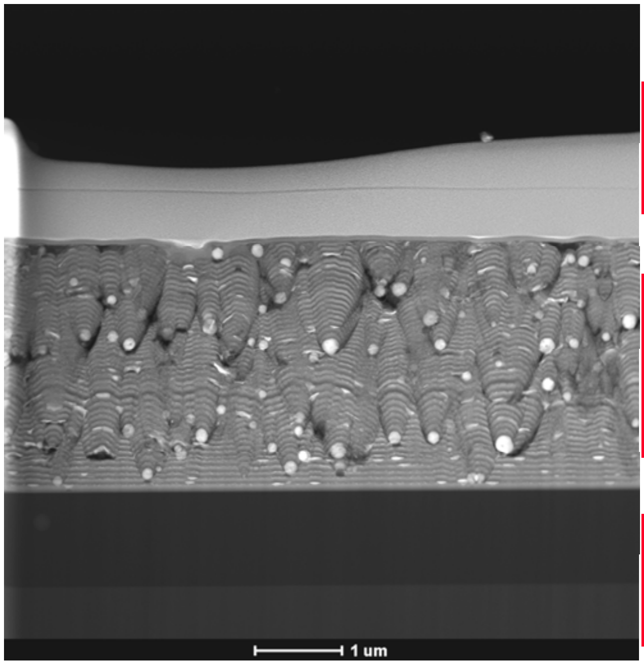
Average COF: 0.019 ± 0.007

Average COF: 0.125 ± 0.027

Counterface: Si_3N_4 Ball
Contact Stress: 1.1 GPa

MoS2-V 1:2 300C

FIB/XTEMs: Structure with V similar to Ti

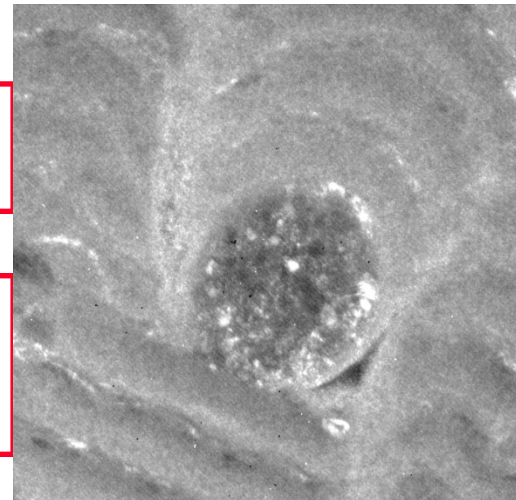


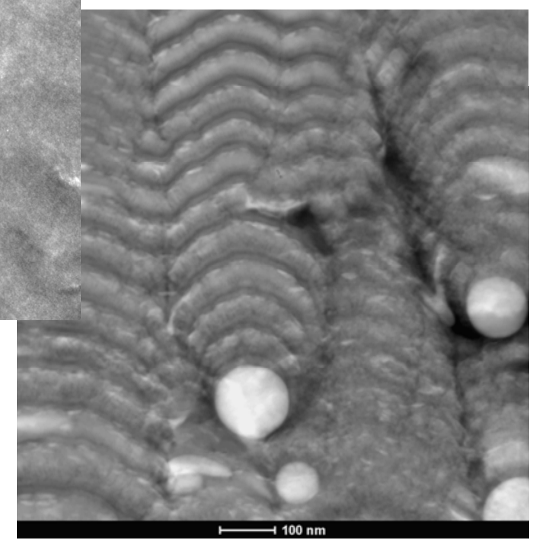
C/Pt cover

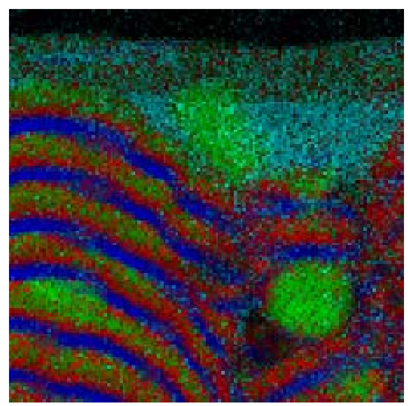
100 nm Mo spheres

Si substrate

Composite Spectral Image





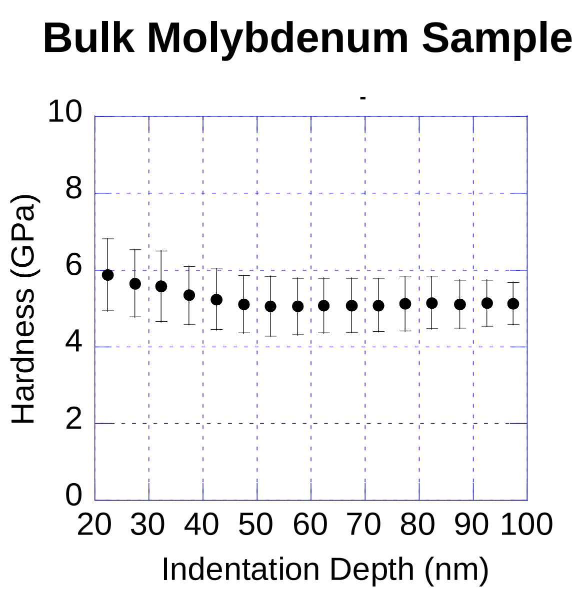


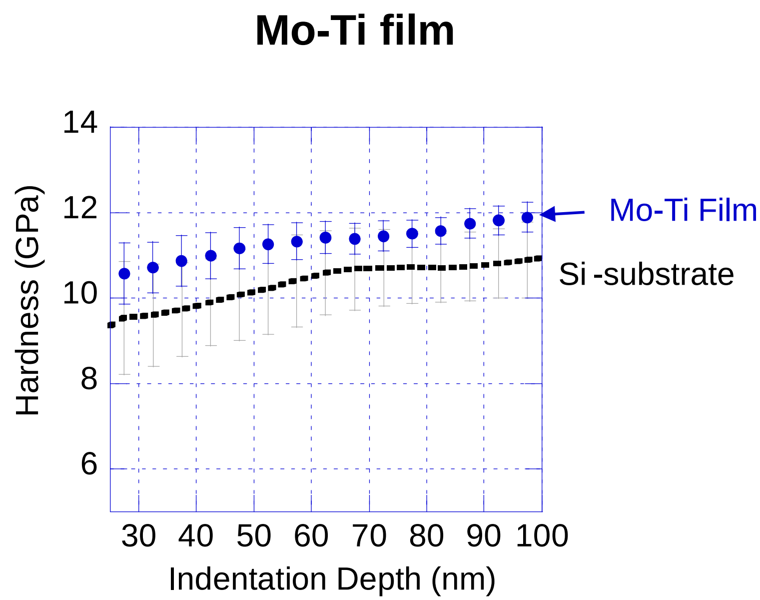
- **Similar 10 nm multi-layer (108 layers) disrupted by Mo single-crystal spheres**

Red = Mo-S
Green = Mo
Blue = V
Cyan = Mo-O

Deposition rate: MoS_2 ~ 300Å/pulse, Ti ~ 60Å/pulse

Bi-Metal film result: Mo-Ti film exhibits an increased hardness vs. base materials





- **Hardness of commercially pure Ti: 2-3 GPa**
- **Extremely fine microstructure contributes to high hardness in Mo-Ti film**

Instrumented indentation performed with a Berkovich tip using Nanoindenter XP with CSM option

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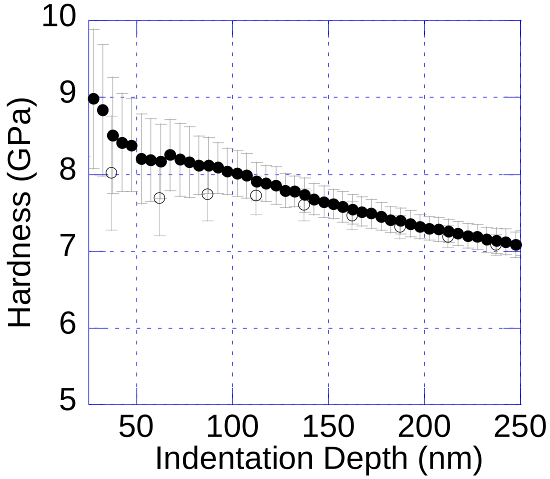
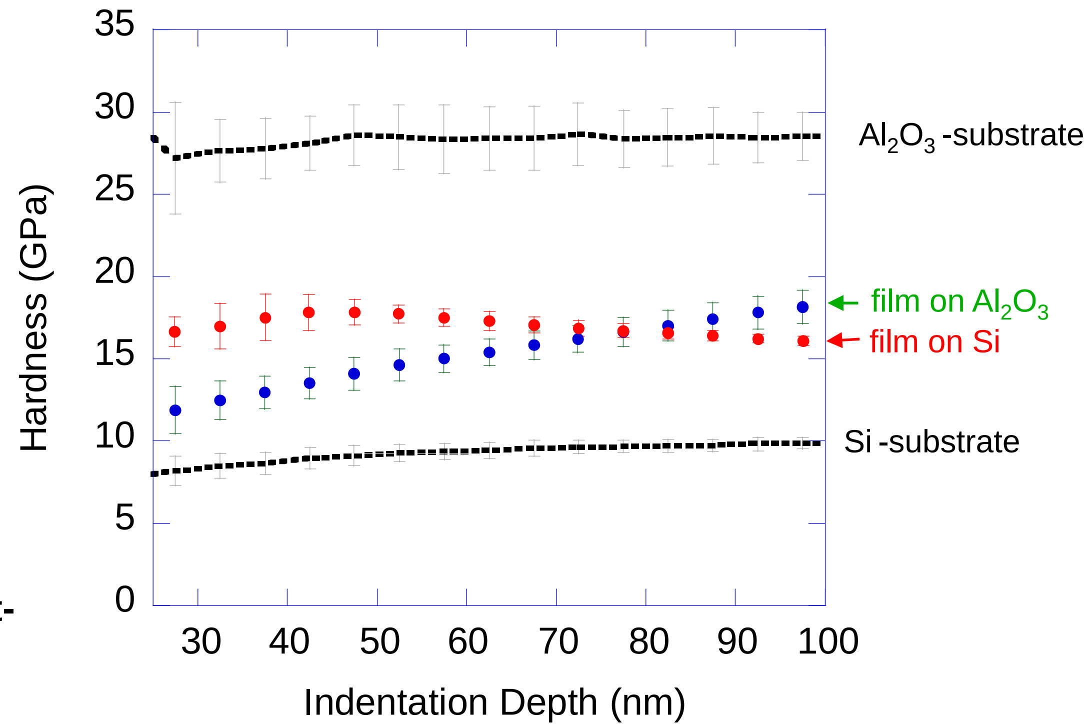
Mo-Ir film (big Modulus difference) exhibits a significant increased hardness vs. base materials

Bulk Iridium Target



Mo-Ir Thin-Film



- **Mo-Ir: In-situ 315°C deposition hardest. Post-anneal *softens* film**
- **Mo-W: 560°C post-anneal *raises* multilayer hardness gain from modest to significant**
- **Films exhibit unexpected processing/properties trends**

- Mo-Ir films: significant increase in hardness vs.base materials
- Ir shows notable size scale effect

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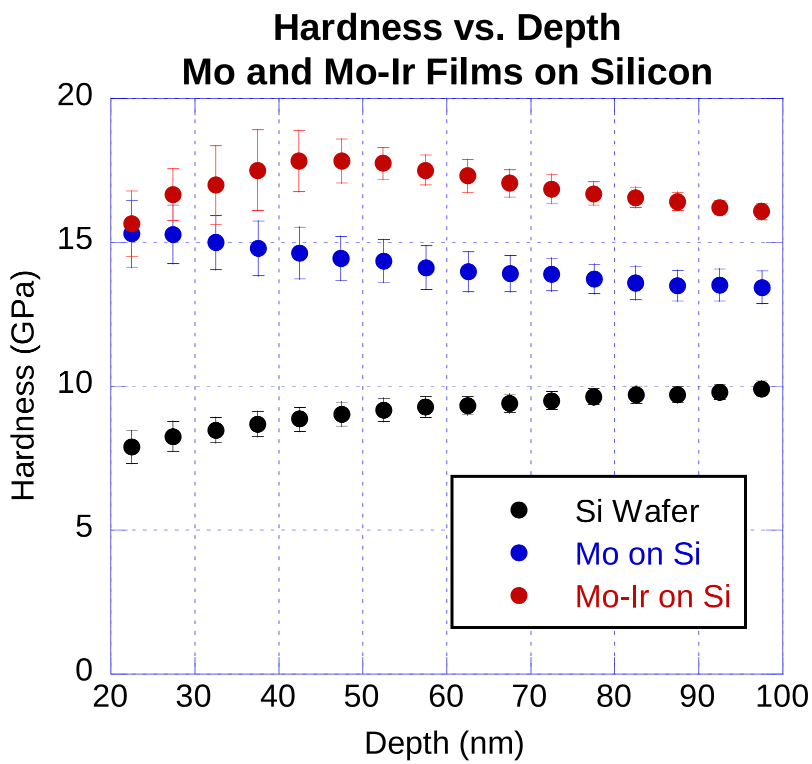
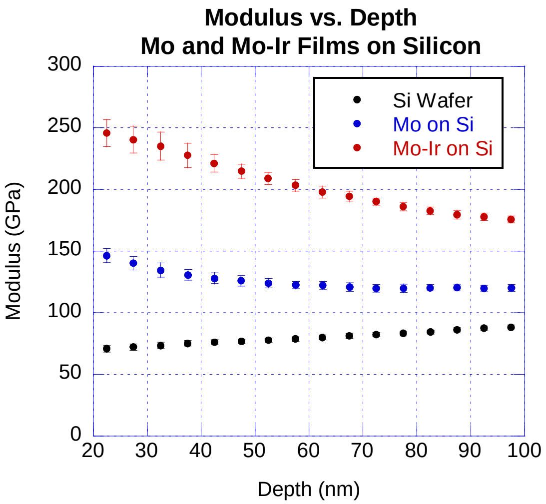
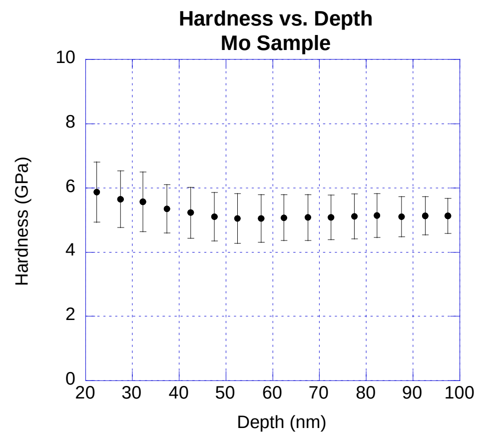
Unexpected result: Mo only on Si substrate: surprisingly hard





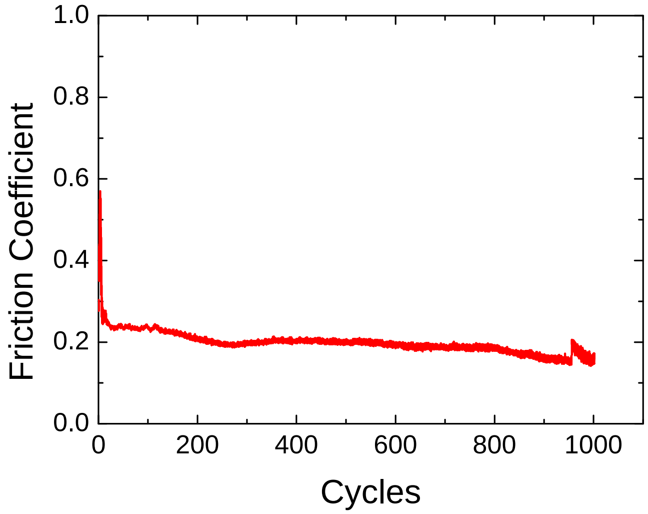
Bulk Mo Target



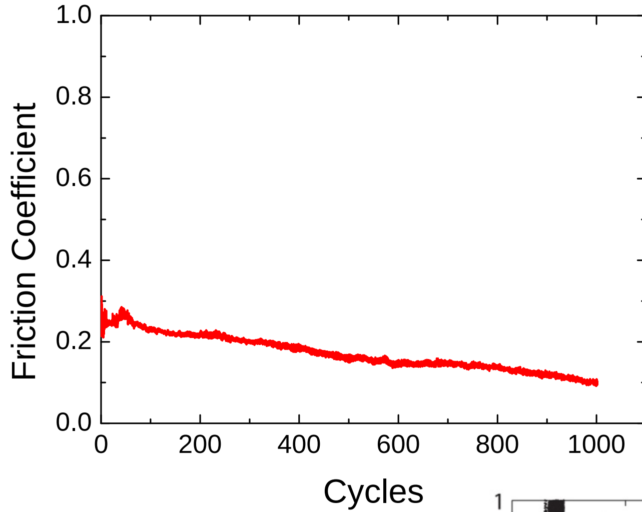
- **Mo film (BLUE Data) is surprisingly hard, may be due to very small grain size (TEM in process)**
- **Mo-Ir (RED data) film is very hard for a metal-metal film**

Unexpected result: Mo thin-films from RHEPP exhibit low friction coefficient

Mo 150 nm on Al_2O_3
460°C in-situ heated

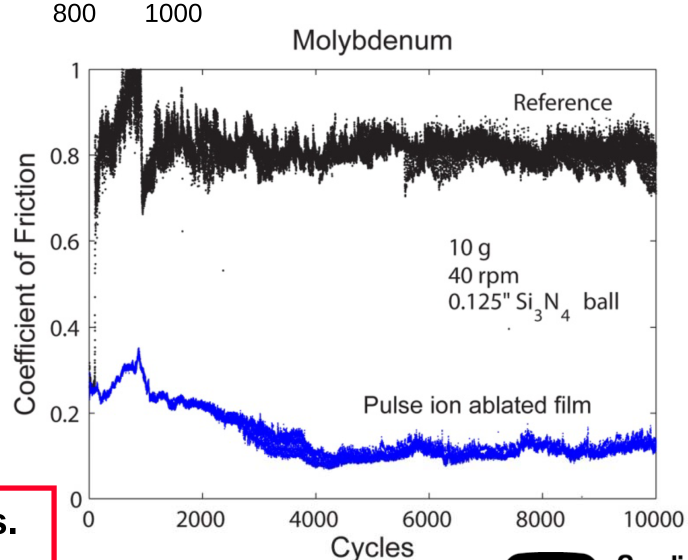


Mo 50 nm on Al_2O_3
460°C in-situ heated



Environment: Dry Nitrogen, 1/8 in diameter Si_3N_4 ball, normal load 100 mN (Rh same)

- **600 nm Mo film shows same performance**



Recent test to 10,000 cycles. Note high 'reference' (bulk Mo) friction

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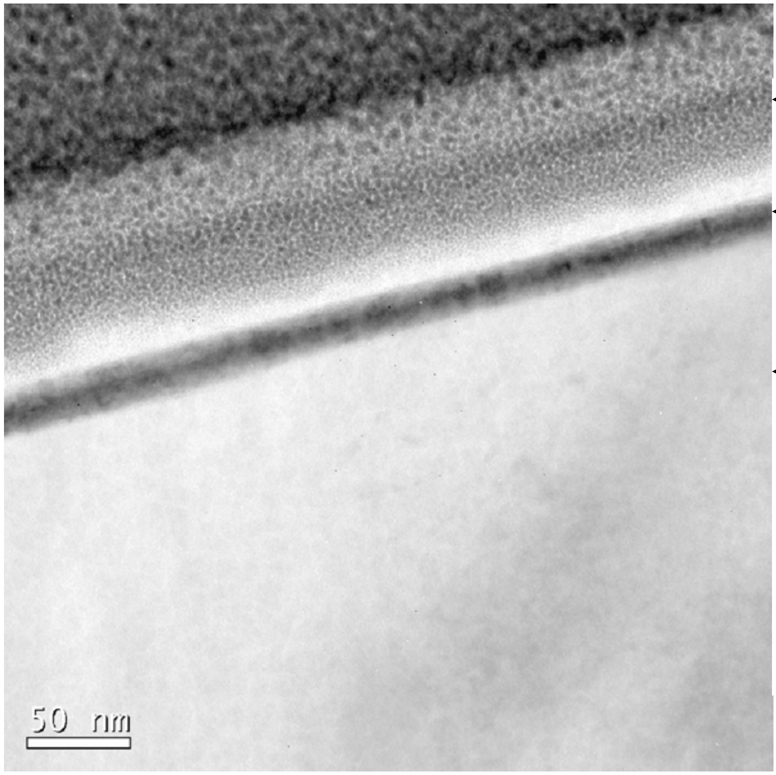
Suspect fine-grain Mo microstructure. Confirmed by XTEM.

Pt sample prep overcoat



50 nm Mo layer

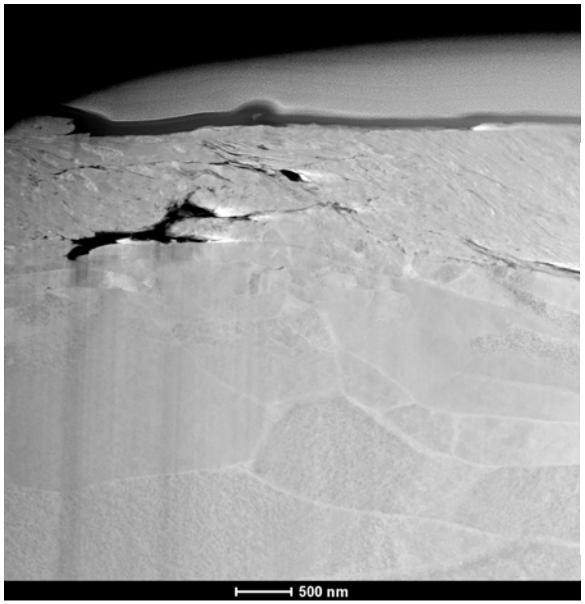
Ti adhesion layer

Al_2O_3 substrate

Bright-field XTEM image

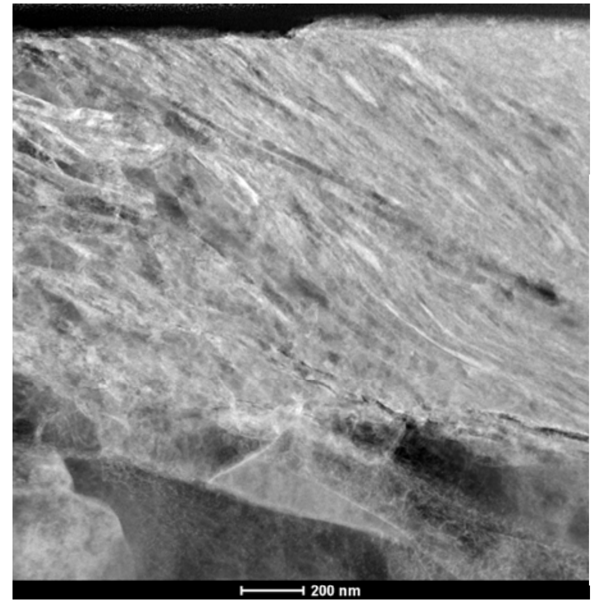
- **FIB cut taken under wear track from 1000 cycles**

Bulk Mo target - source material for film.
XTEM shows variegated grain change, mechanical shear failure

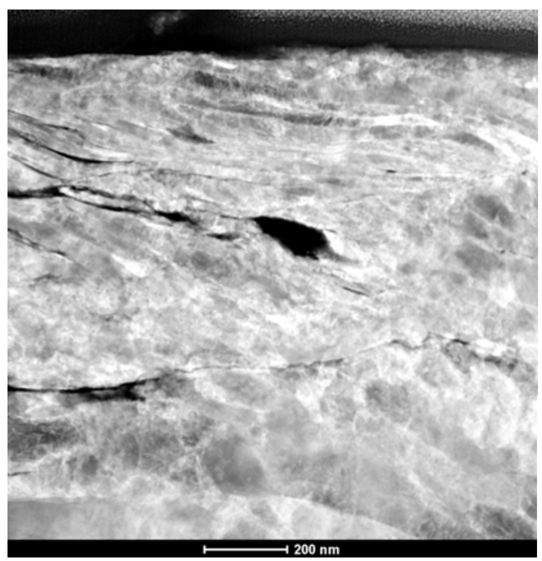


Surface

Counterface-induced elongated grains



- Mechanical shear failure layer ~ 1 µm thick



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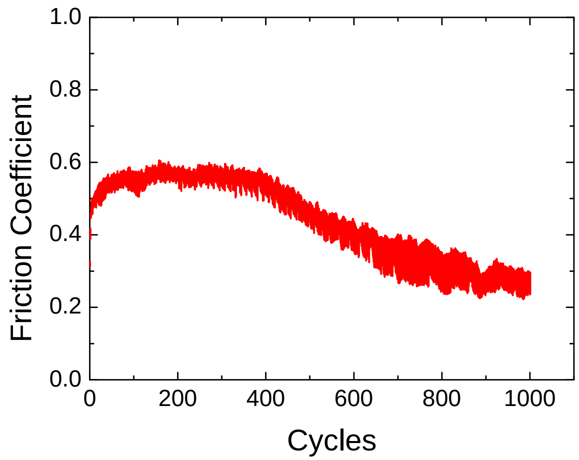
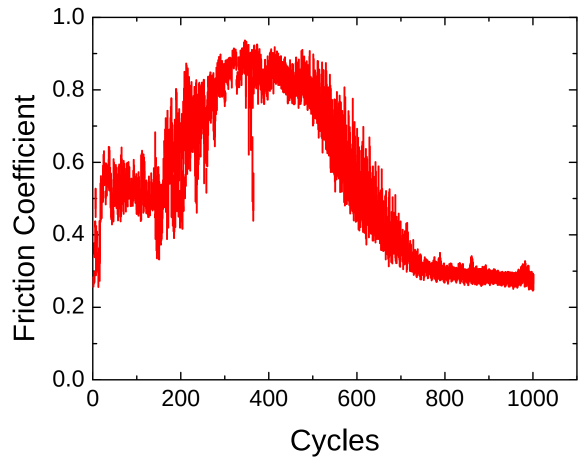
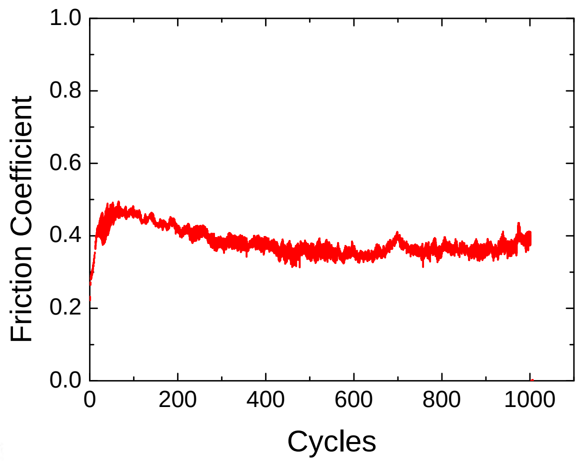
Comparison: Pure Rh thin-films from RHEPP-1 exhibit unremarkable friction coefficient



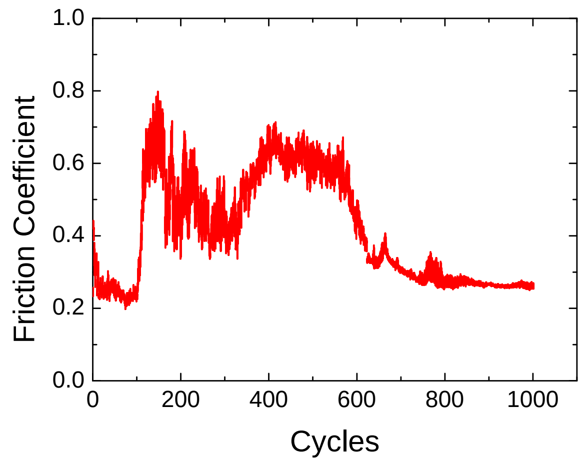
~ 200 nm Rh 480°C



~ 25 nm Rh RT



~ 200 nm Rh RT



~ 25 nm Rh 460°C

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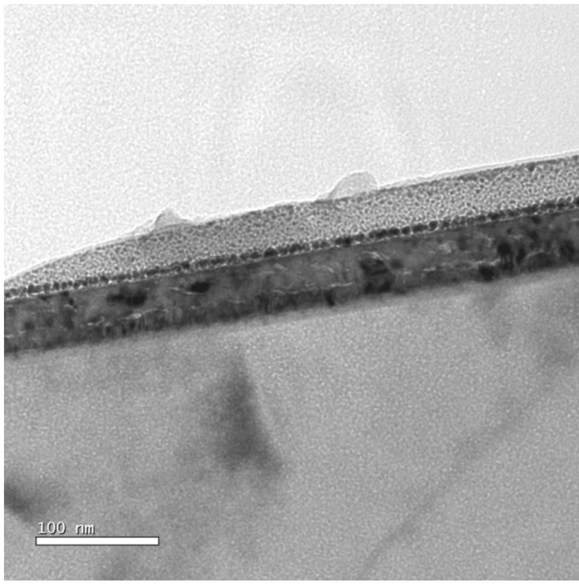
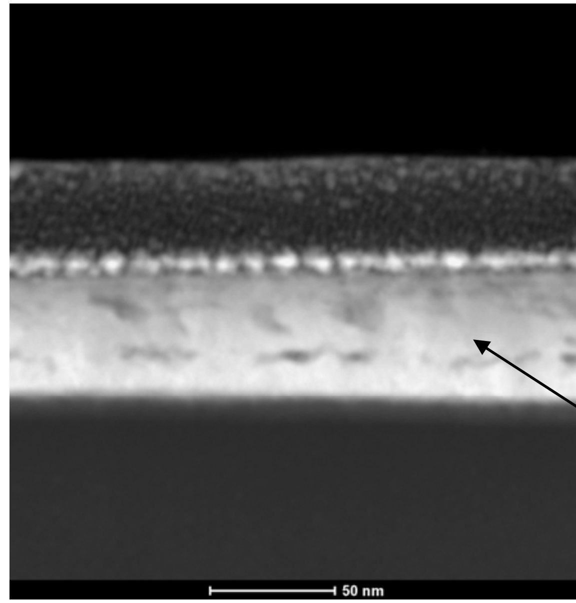
Rhodium film XTEMs. Porosity in layer, inhomogeneous grain growth, possible wear debris



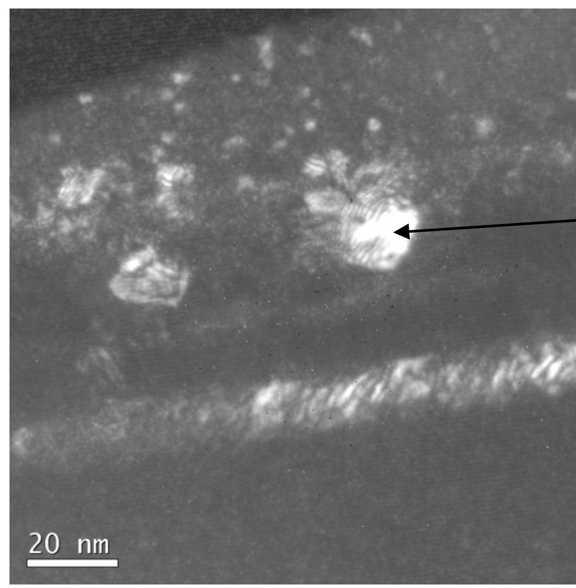
50 nm Rh layer

Al_2O_3 substrate



Wear Debris?

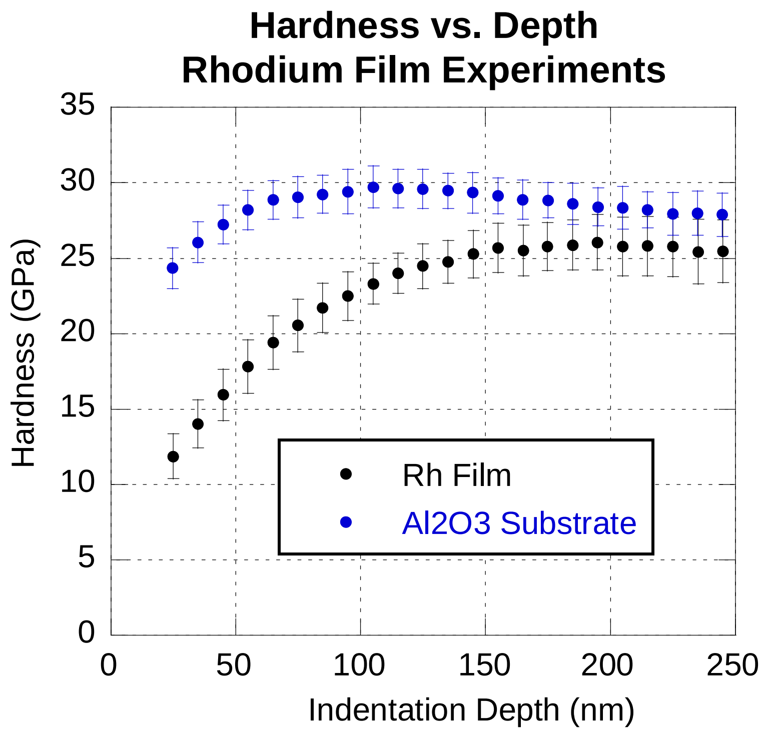
Appears not fully dense

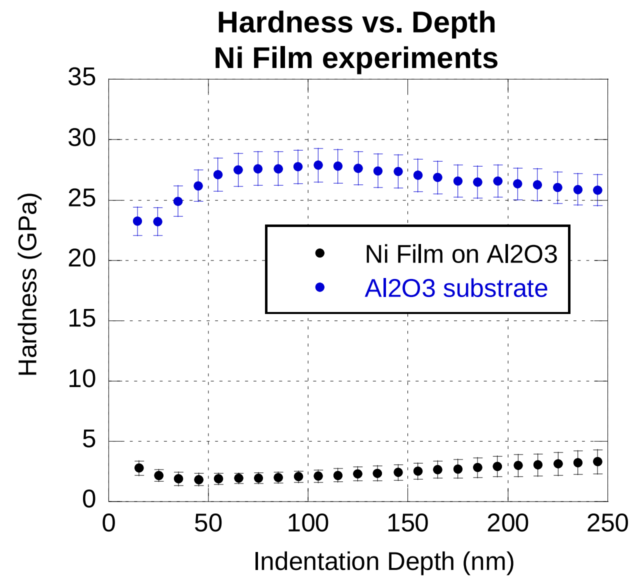


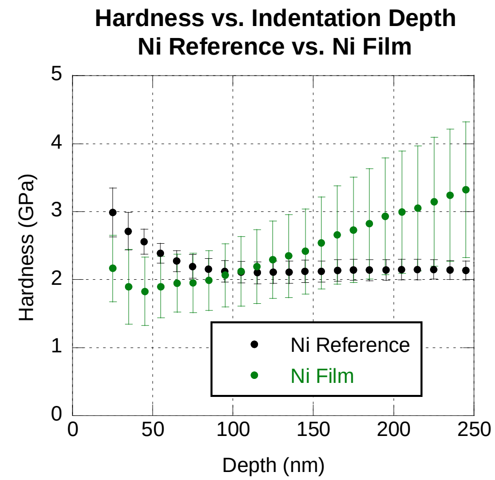
Spontaneous Grain growth

- FIB cut taken under wear track from 1000 cycles

Rhodium film hardness from nano-indentation: Not as hard as Mo film, but still 10 GPa.

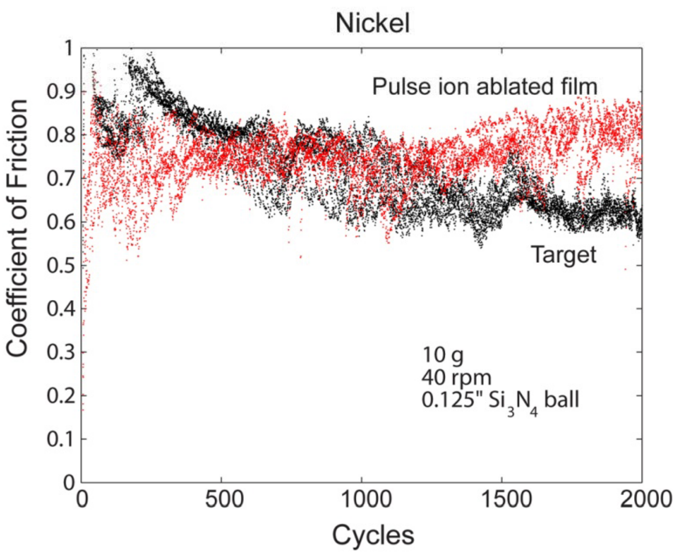


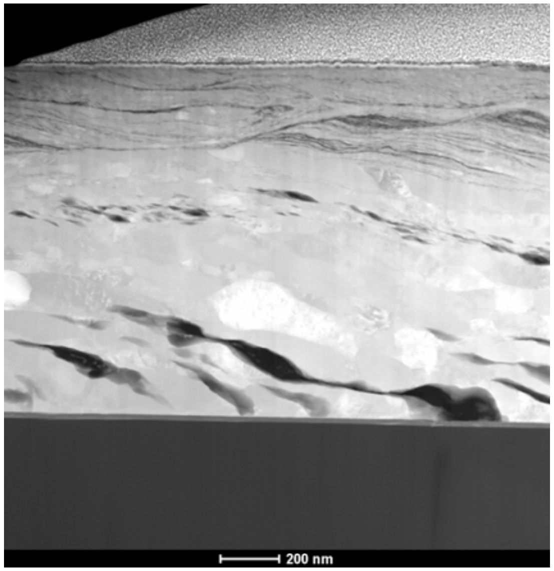


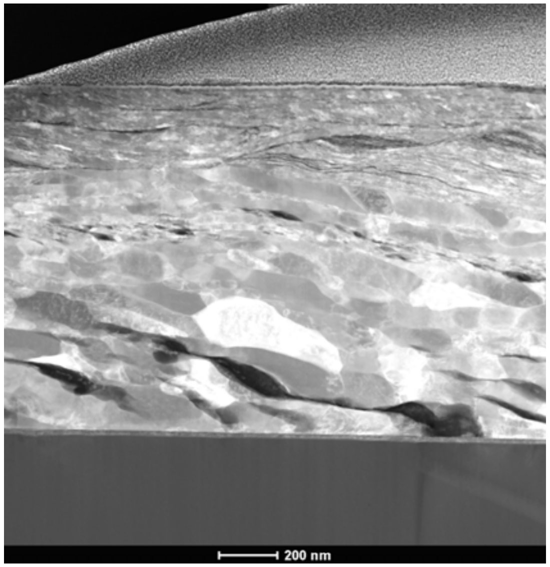


- **(RIGHT) 3rd film - Nickel. Both film and bulk target test soft (2 GPa)**

Both Ni film and target exhibit high friction coefficient. XTEM shows grain size increasing towards layer bottom, 'pancake' grain structures, mechanical failure throughout 1 μm thickness

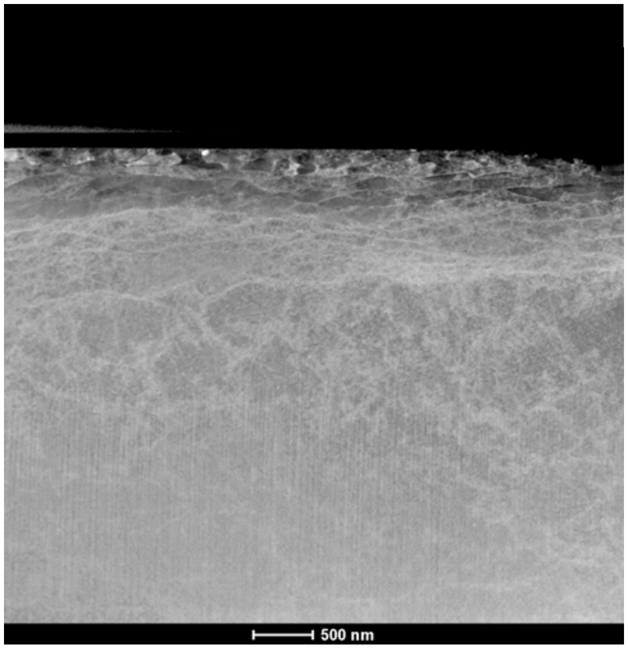




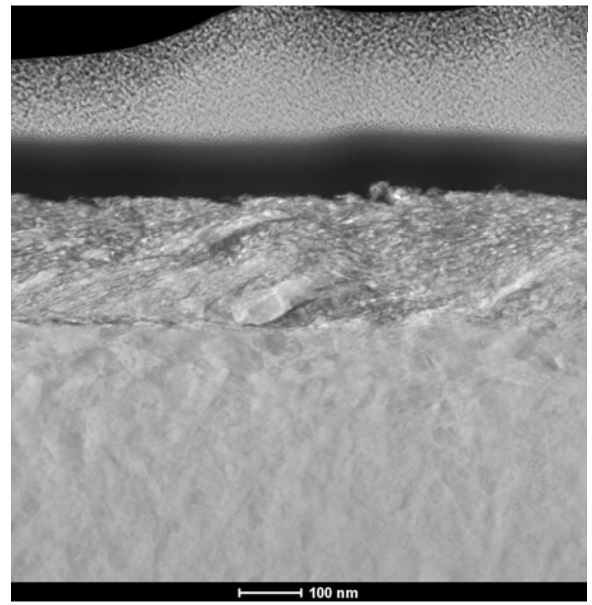


- **Hypothesis: high friction due to counterface 'plowing' through soft layer**

Previous tribology experiments with Nickel suggest grain evolution is inevitable, but Fe addition may be beneficial



- Single-crystal Ni evolves pancake grains near surface under tribological testing



- Ni w/ 20at% Fe: grain evolution, but low friction. Fe may stabilize grain boundaries

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Summary

- **Several research paths discussed here: nanocomposite MoS_2-Me2 films for low wear-low friction, bi-metal hard layers, single-element metal films.**
- **WS_2-Zr has replicated some aspects of MoS_2-X films. So Me1:S:Me2 films may form a class of self-assembled nanocomposite films with attractive properties.**
- **Bi-metal films: multi-layer films, hardness may be related to difference in shear modulus of two metals.**
- **Single metal films: nanocrystalline film microstructure (Mo) leads to hard, low-wear films with low friction coefficient. Key is keeping the grain size small. Hypothesis: Once grain enlargement reaches a critical level, layer properties deteriorate. This may be related to number of slip planes available. Fine-grain BCC material (e.g. Mo, W) has clear differences in mechanical behavior compared to large-grain material.**
- **Rh and Ni both CCP, but Rh is harder. Ni performance may be improved by adding Fe to stabilize grain boundaries.**
- **This is a Work in Progress.**