Rio Grande Symposium on Advanced Materials, Oct. 3, 2011

Synthesis of MoS_2-Au Films with Nano-Onion Like Structures

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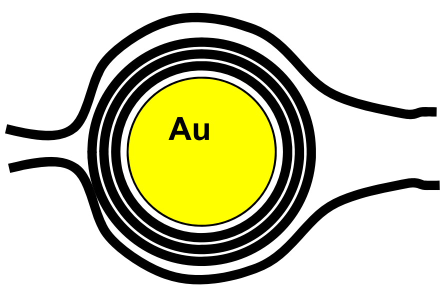

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Sandia National Laboratories

Lubrication on Sliding Surfaces

Reduce Friction, Wear, Debris

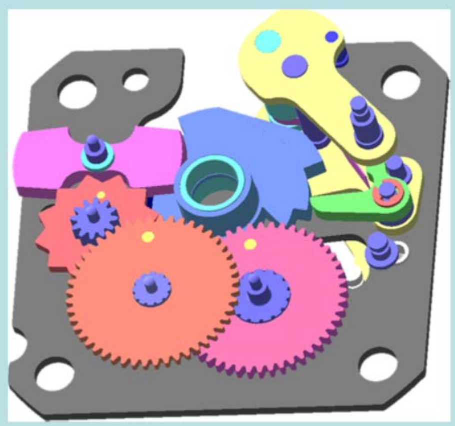
Lubrication Enhances Reliability & Safety

Liquid lubricants can't be used on:

- Satellites
- Electromechanical Switches
- Miniature Devices

Solid Lubricants:

- High temperatures
- Vacuum compatible
- High contact pressures

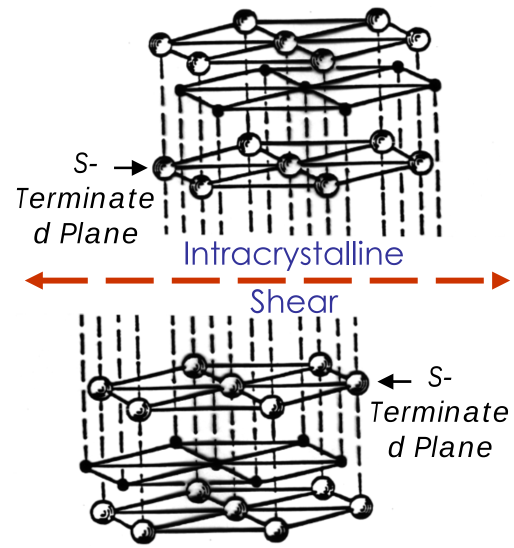


Moving Mechanical Assemblies

Solid lubricants

Commonly used materials

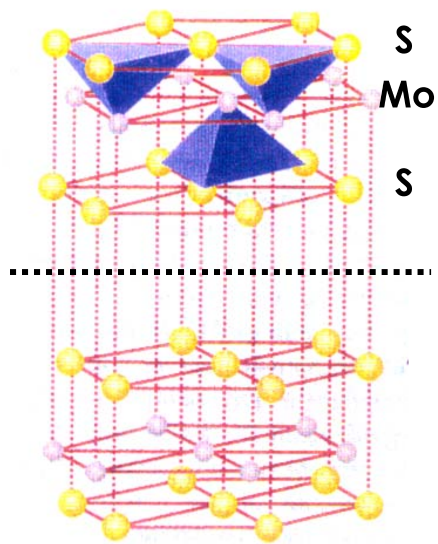
- Lamellar Solids
  - Transition metal dichalcogenides, graphite
- Diamond and Diamond-like Carbon
  - a-C:H, a-C:Si, UNCD
- Soft Metals
  - Pb, Ag, Au, In, Sn
- Glasses & Ceramics
- Polymers
  - PTFE, Polyimide



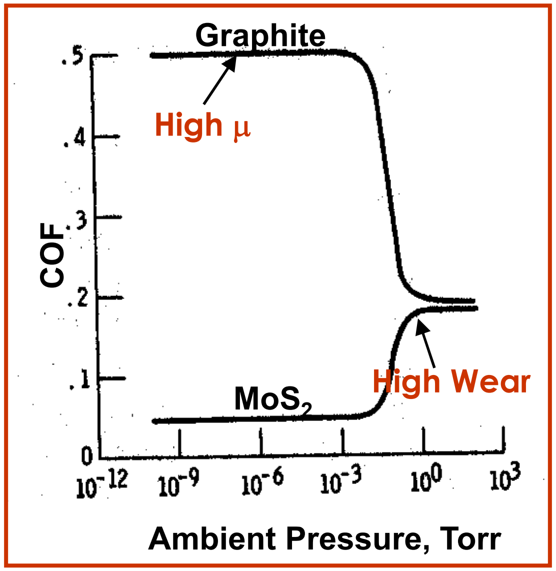
Environmental Dependence

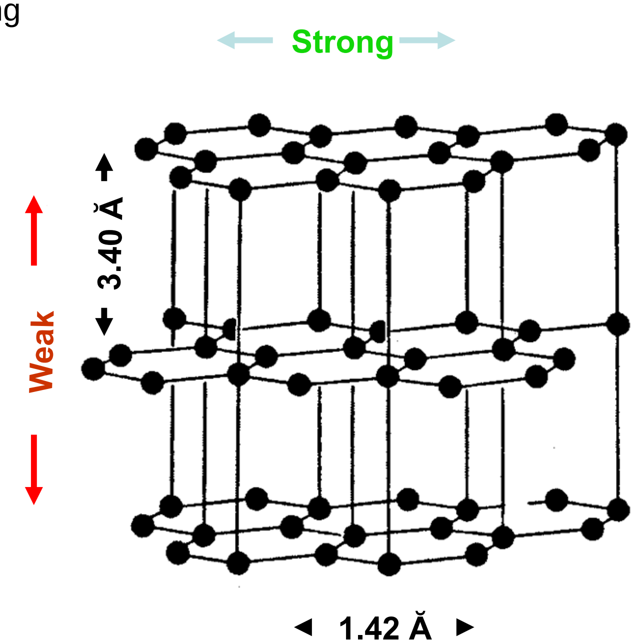
Lamellar Solid Lubricants Environmental operating conditions

MoS_2: Extremely low COF (0.01-0.05) and long wear life, **but only in dry environments**.



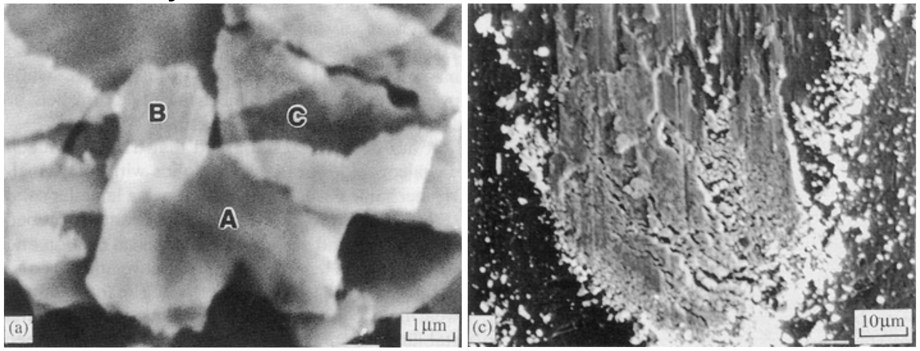
Mo/W Disulfide





Graphite

They form thin transfer films on the counterface

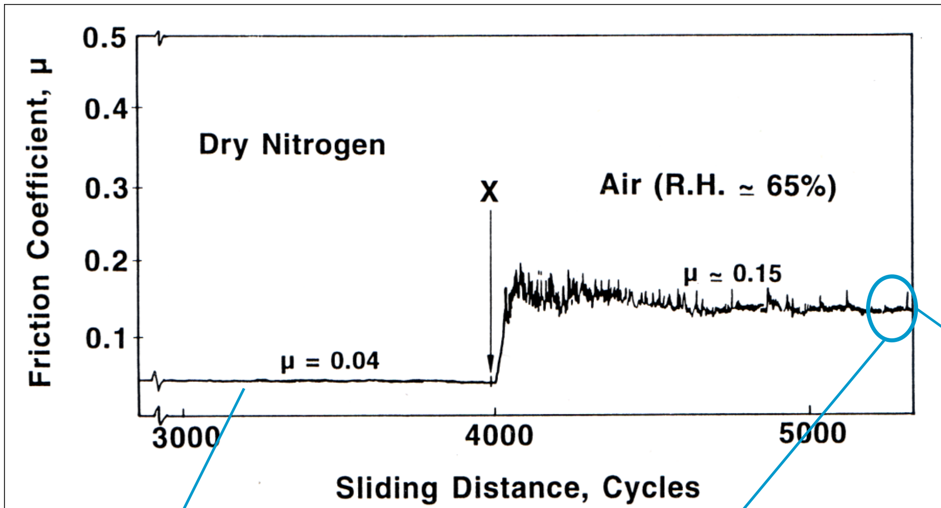


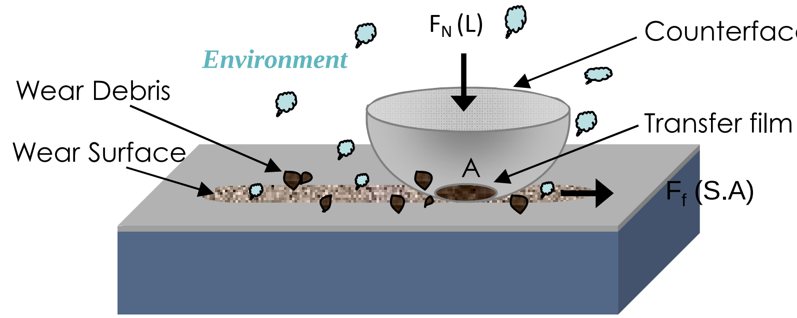
- Graphite needs moisture or adsorbed gases in the environment (>100 ppm) (they either act as intercalants, or passivate the dangling covalent bonds) to lubricate.
- In vacuum, graphite exhibits high friction and wear—a phenomenon known as "dusting", first observed in the late 1930's when graphite brushes in aircrafts experienced accelerated wear at high altitudes.

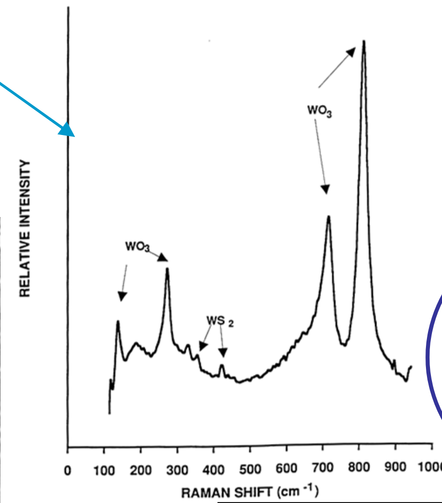
S. V. Prasad and J. S. Zabinski, J. Mater. Sci. Lett. 12 (1993) 1413-1415

Oxidation of WS_2 in humid air

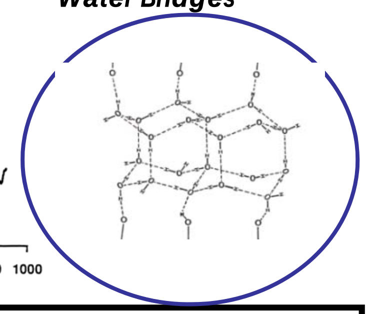
Metal dichalcogenides oxidize in humid environments

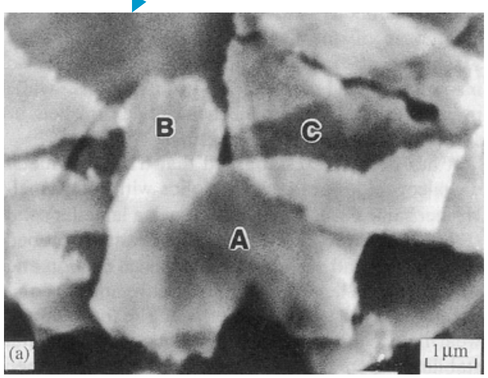


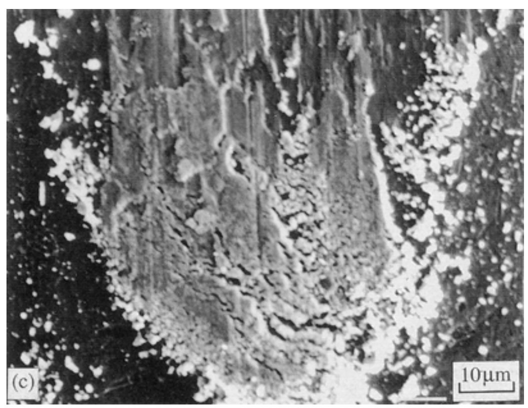




Hydrogen-Bonded Water Bridges

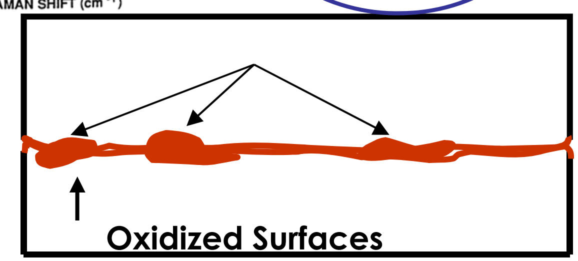






Transfer Film

SEM of Transfer Films (WS_2)



S. V. Prasad, J. S. Zabinski and N. T. McDevitt, Tribology Transactions, 38 (1995) 57-62

Doped MoS_2

Improved performance in humid environments

Doping MoS_2 has been shown to enhance durability in humid environments

MoS_2/titanium
-D. G. Teer, *Wear*, ***251, 1068 (2001).***
-X. Wang, D. G. Teer, et. Al. *Surface and Coatings Technology*, ***201, 5290 (2007).***

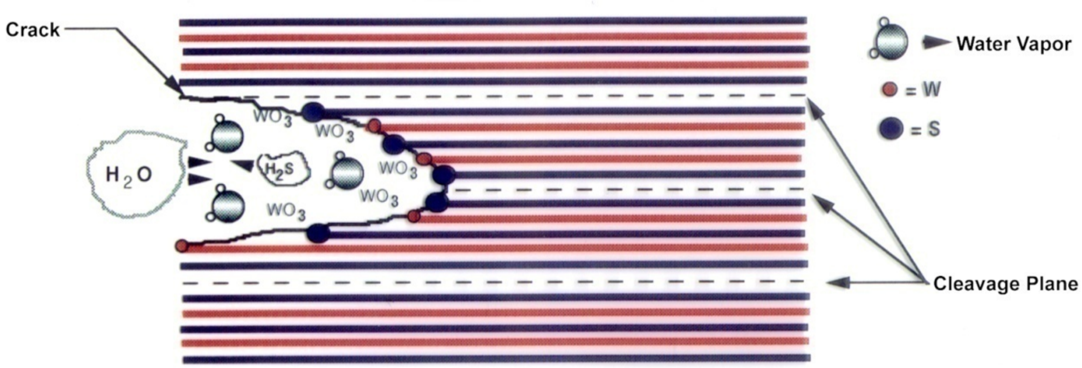
MoS_2/Sb_2O_3/Au
-T. W. Scharf, P. G. Kotula and S. V. Prasad, *Acta Materialia*, ***58, 4100 (2010).***

MoS_2/Au
-J. R. Lince, H. I. Kim, P. M. Adams, D. J. Dickrell and M. T. Dugger, *Thin Solid Films*, ***517, 5516 (2009).***

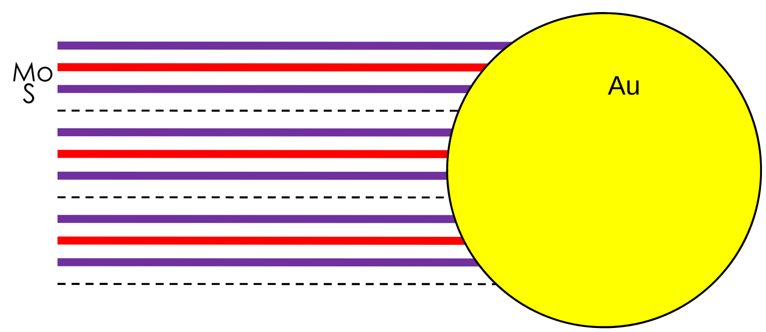
Mechanism not completely understood

Many of these doped coatings are brittle under high loads or impact

Our approach is to build novel structures that reduce the availability of edge planes, which easily oxidize, by the addition of an inert metal using a MoS_2/Au system



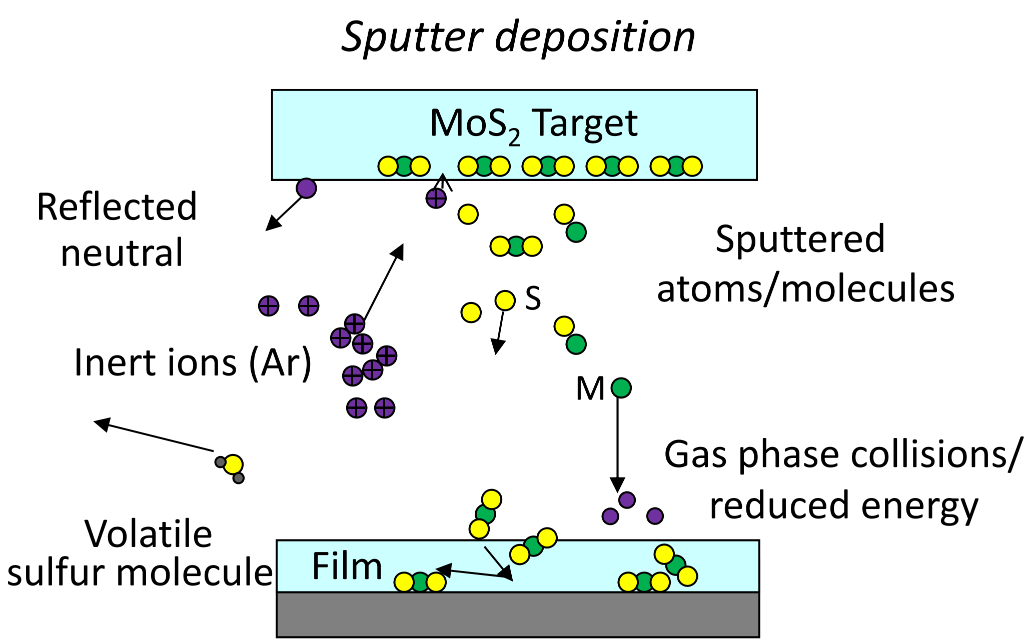
S. V. Prasad, J. S. Zabinski and N. T. McDevitt, Tribology Transactions, 38 (1995)



MoS_2 Coatings

Sputter Deposition selected as fabrication technique

- **Burnishing**
- **Resin Bonding**
- **Chemical Vapor Deposition**
  - *Plasma Enhanced Chemical Vapor Deposition (PECVD)*
  - *Atomic layer Deposition (ALD)*
- **Physical Vapor Deposition**



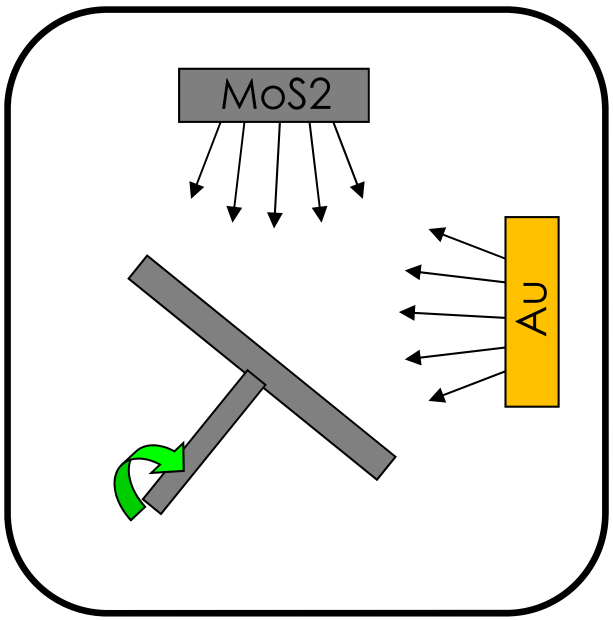
Argon gas ions are accelerated toward the (-) target/cathode resulting in the ejection of neutral target material

Sputtering offers:
Control over film properties and composition

PVD Co-Deposition

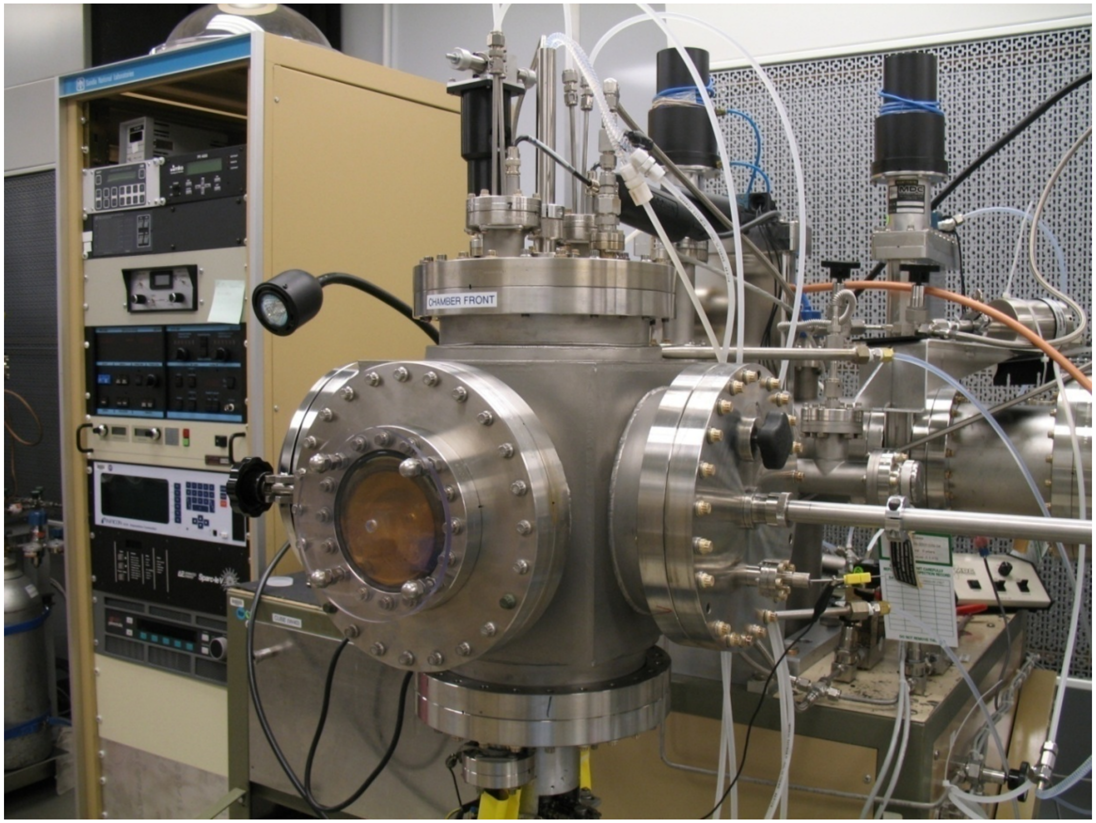
Two Targets at 90°

Sputter targets located at 90 ° to each other and ~45° to the substrate stage



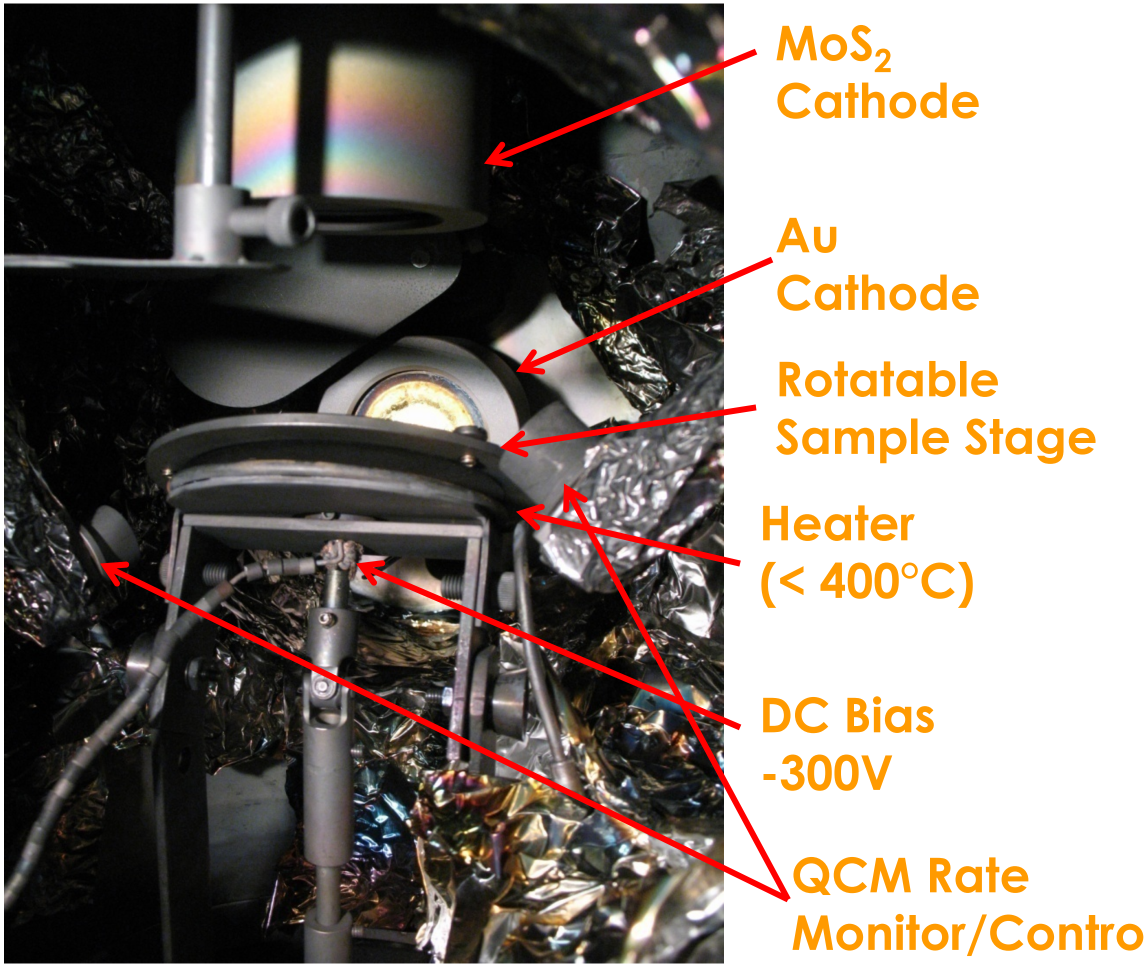
Independent rate control with stage rotation for uniformity

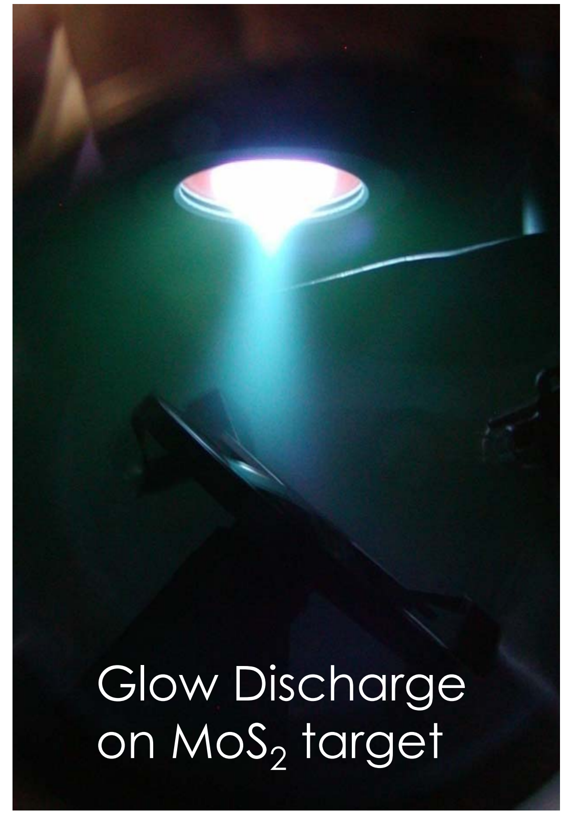
Experimental sputter co-deposition system used in this study



Co-Deposition Chamber

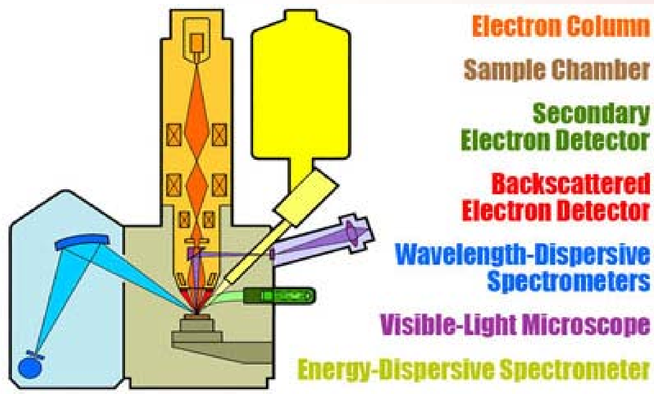
Heat, Bias and QCM rate control





Mo:S Stoichiometry

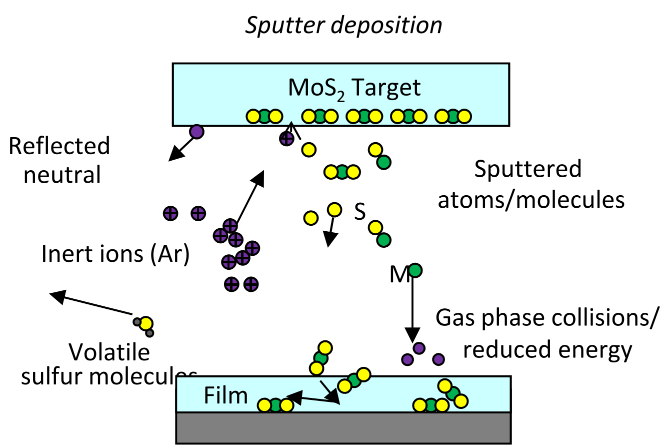
Electron Probe Micro Analysis (EPMA)

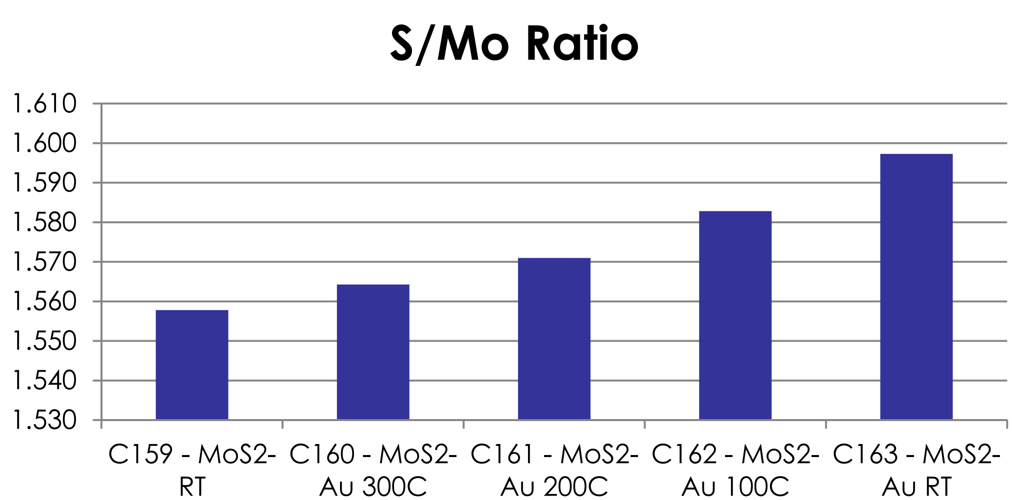


Run#	Desc	S/Mo ratio	wt% Au	vol% Au
C159	MoS2-RT	1.558	0.06%	0.02%
C160	MoS2-Au 300C	1.564	11.90%	3.03%
C161	MoS2-Au 200C	1.571	8.32%	2.13%
C162	MoS2-Au 100C	1.583	8.90%	2.28%
C163	MoS2-Au RT	1.597	9.83%	2.51%

Thin films are
Sulfur deficient ~$MoS_{1.57}$

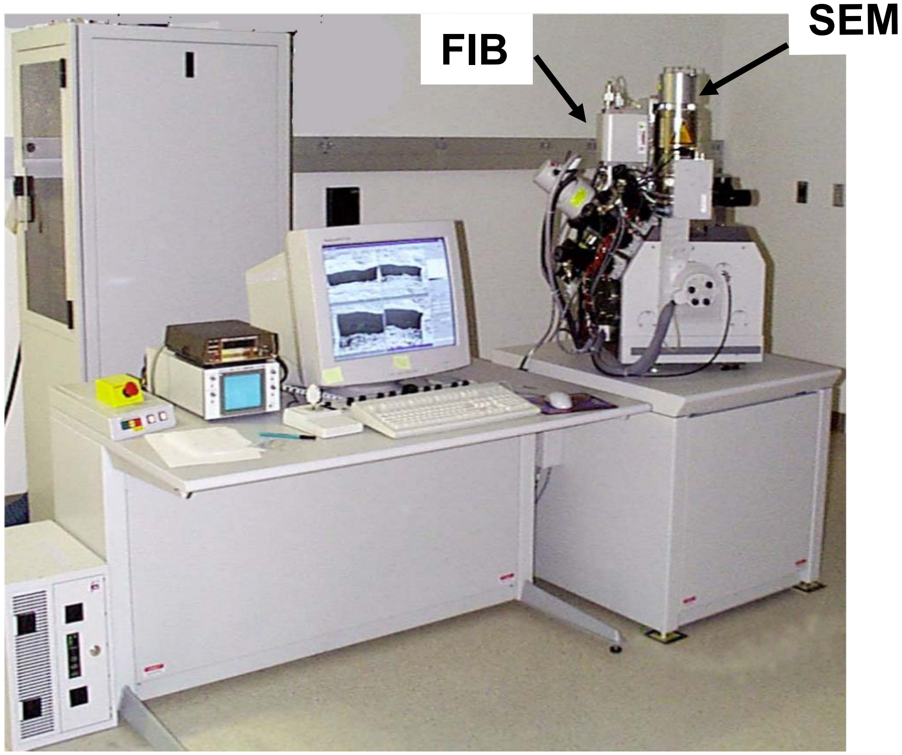
Slight dependence on run order
(residual sulfur background)

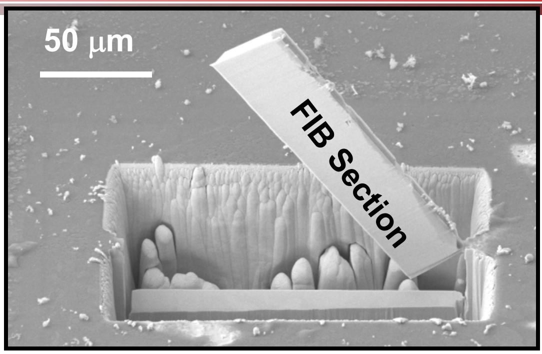


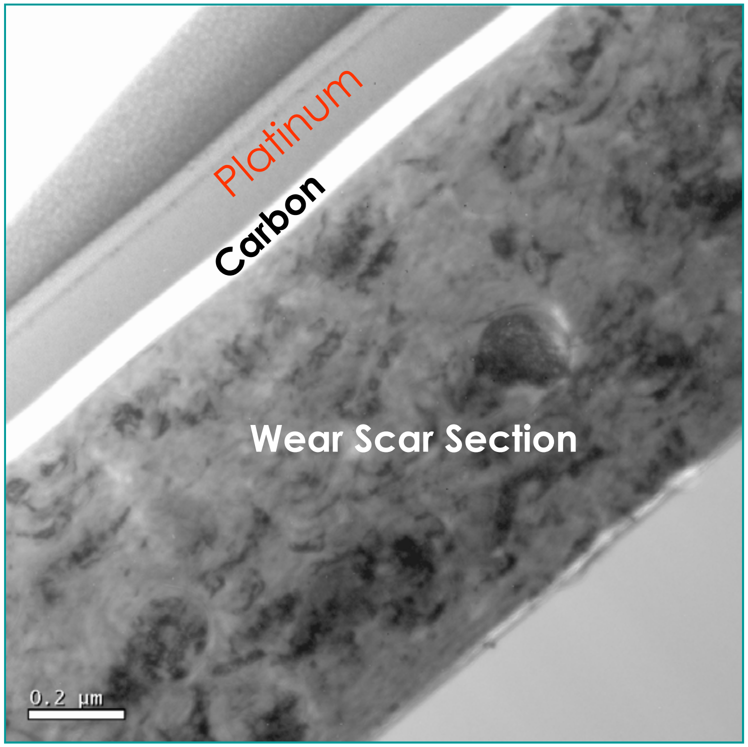


TEM sample preparation

FIB micromachining of sample cross-section





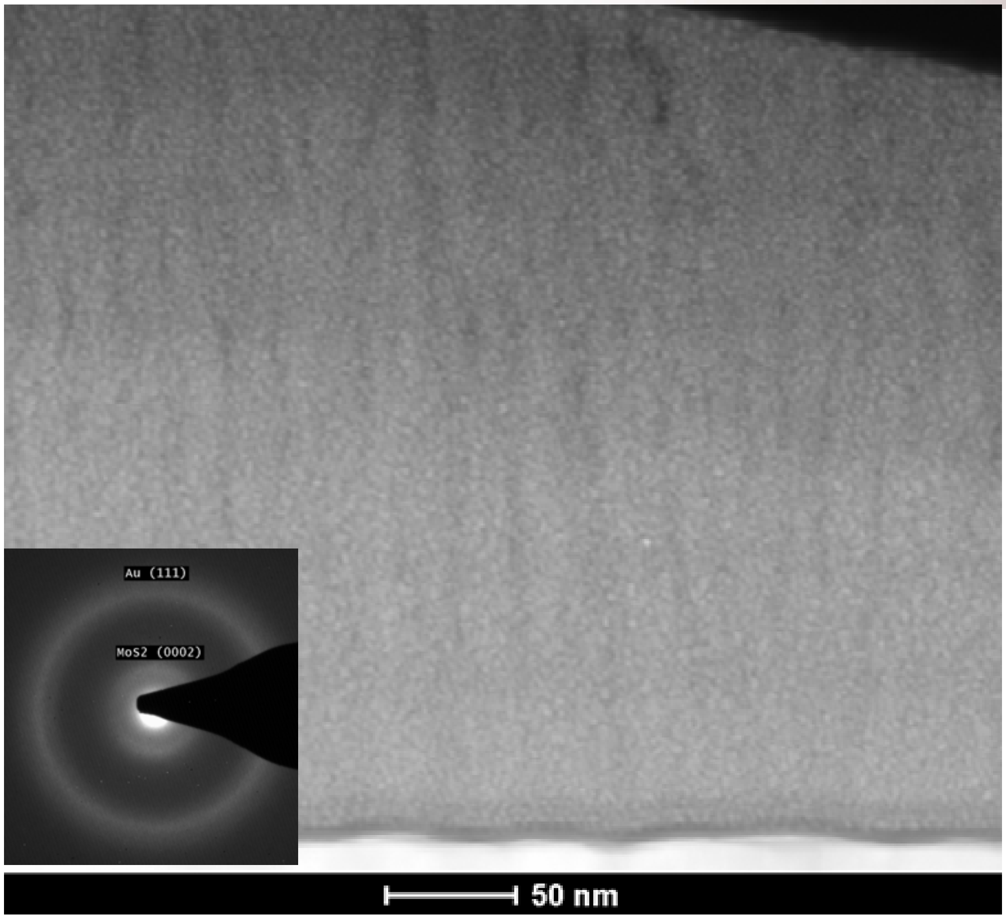


Dual-beam system from FEI: Both a FIB column and a SEM column are present on one sample chamber.

S. V. Prasad, J. R. Michael and T. R. Christensen, Scripta Materialia 48 (2003) 255-260

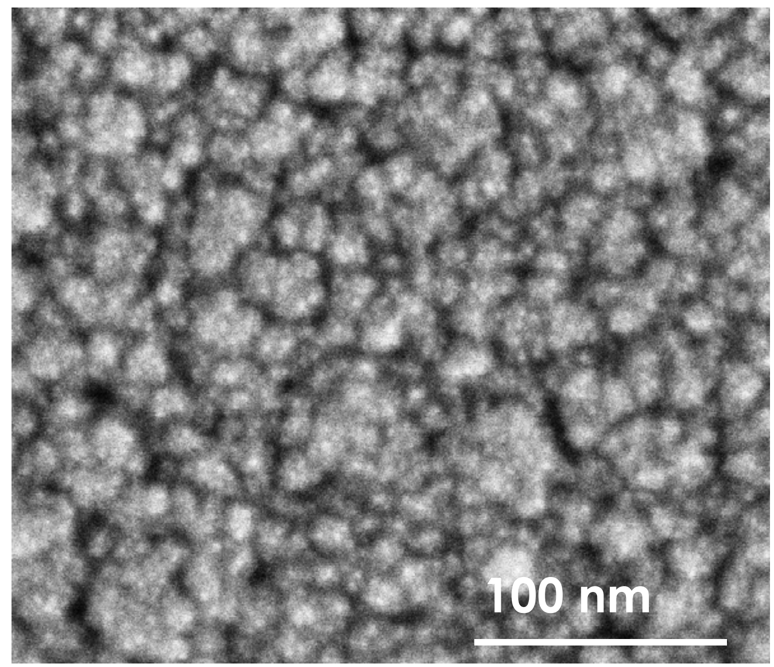
Co-Sputtered MoS_2-Au Films

RT deposition results in 2nm Au nanoparticles



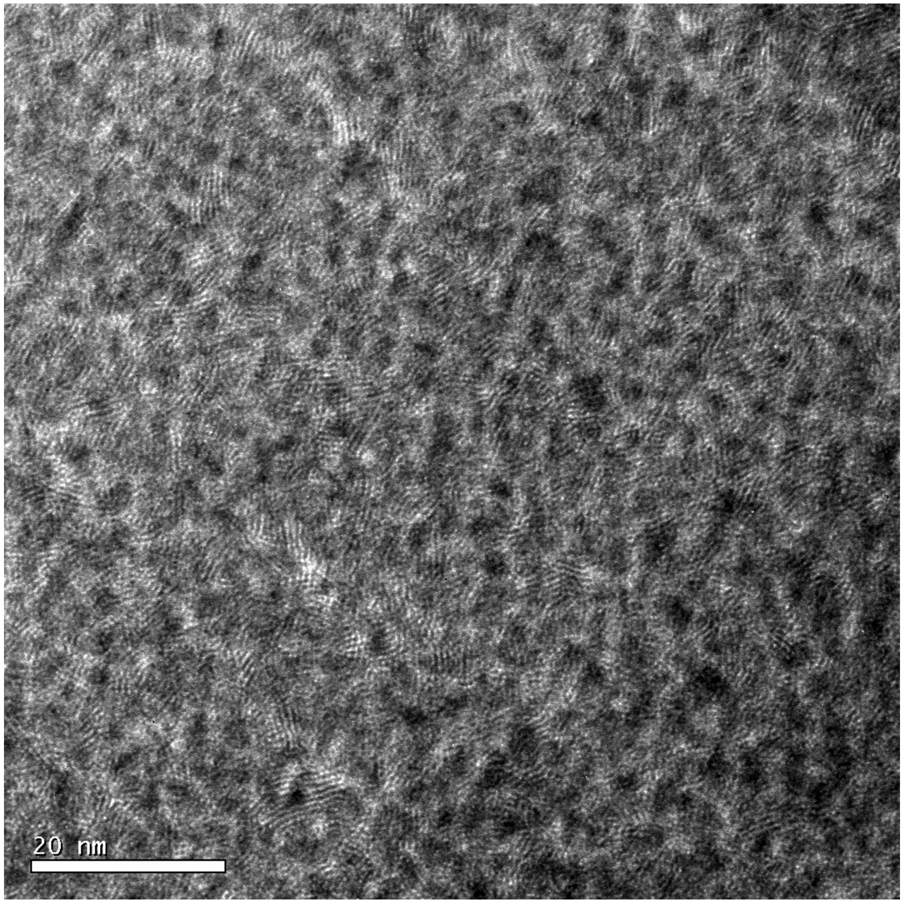
HAADF-STEM…nanocrystalline Au (~2nm) and MoS_2
Selected-area diffraction

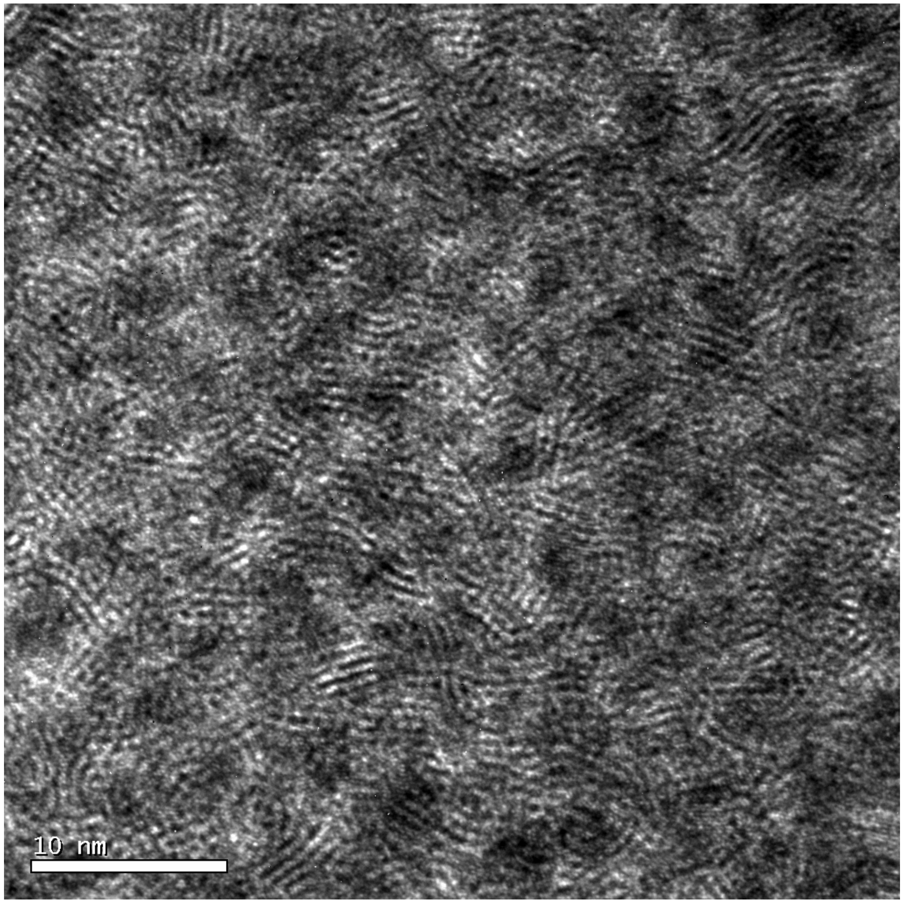
Plan view SEM of MoS_2 - Au RT film, nanoparticles of Au visible in porous MoS_2 film



MoS_2 – Au nanocomposite

Xsect HRTEM reveals nanocrystalline Au and MoS_2

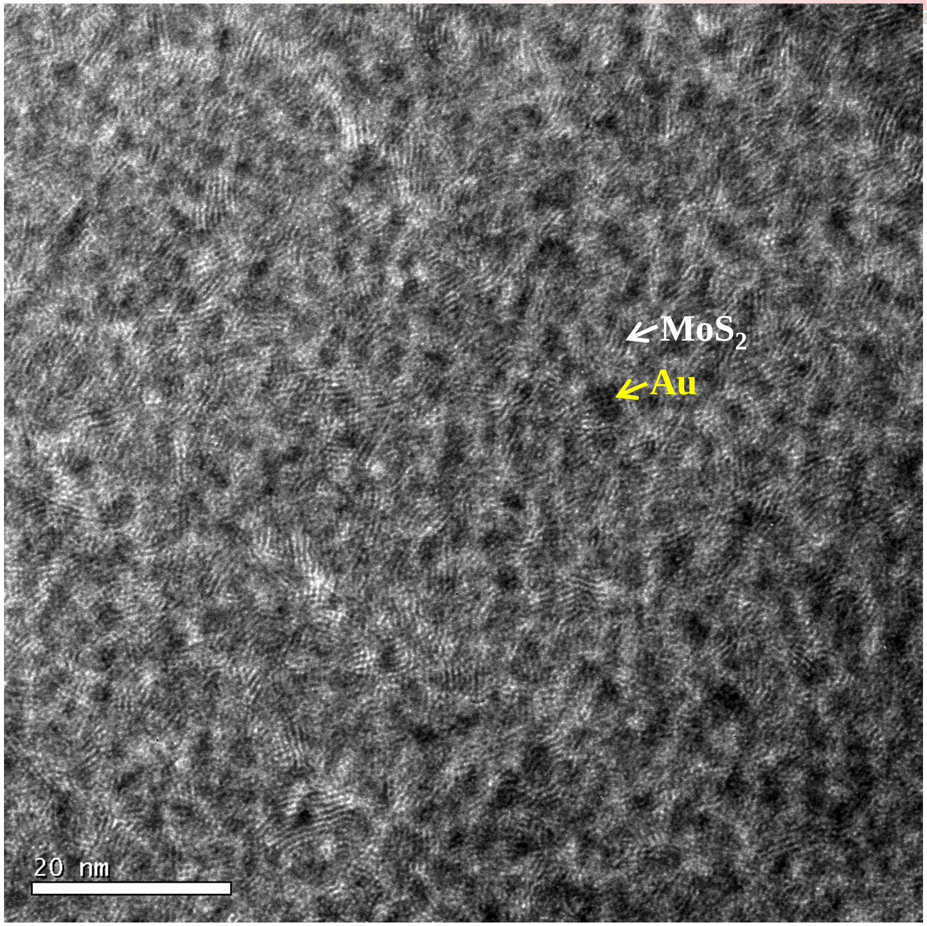




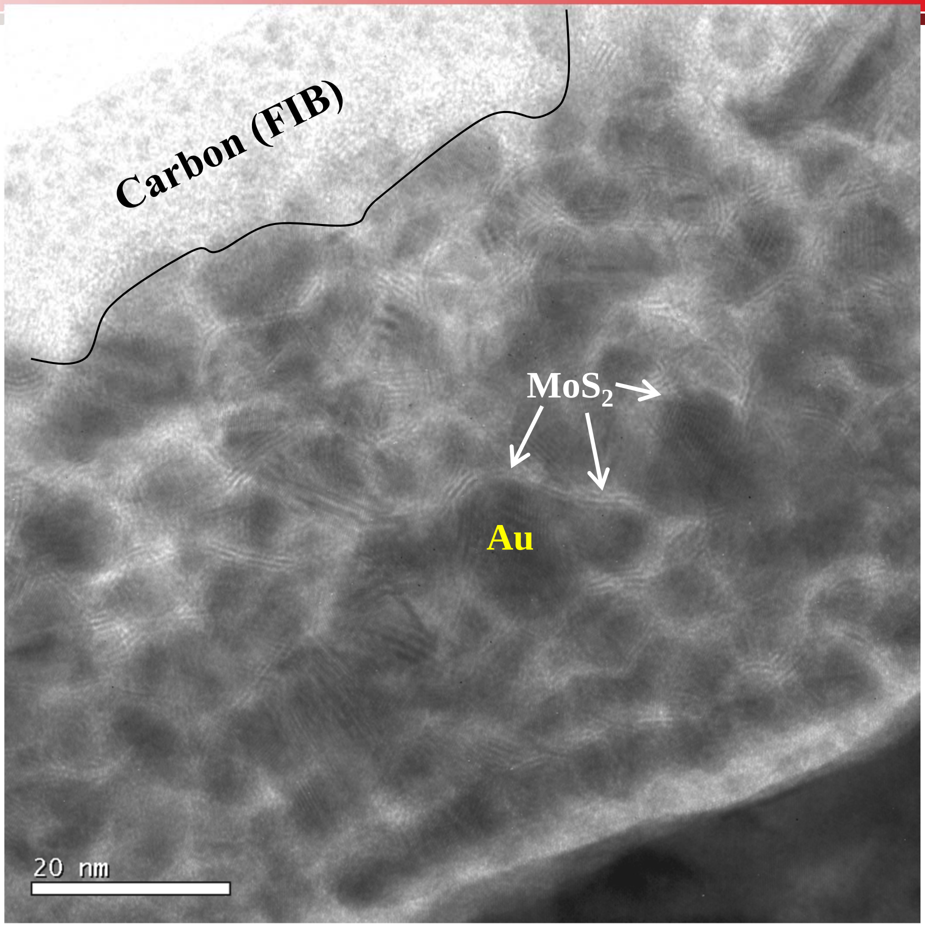
Au-MoS_2 nanocomposite deposited at room temperature.
Nano-crystalline Au (~2nm) and MoS_2 (~2nm) with prominent basal lattice planes (~6A).

MoS_2 – Au nanocomposite

Coarsening of Au nanoparticles with temperature



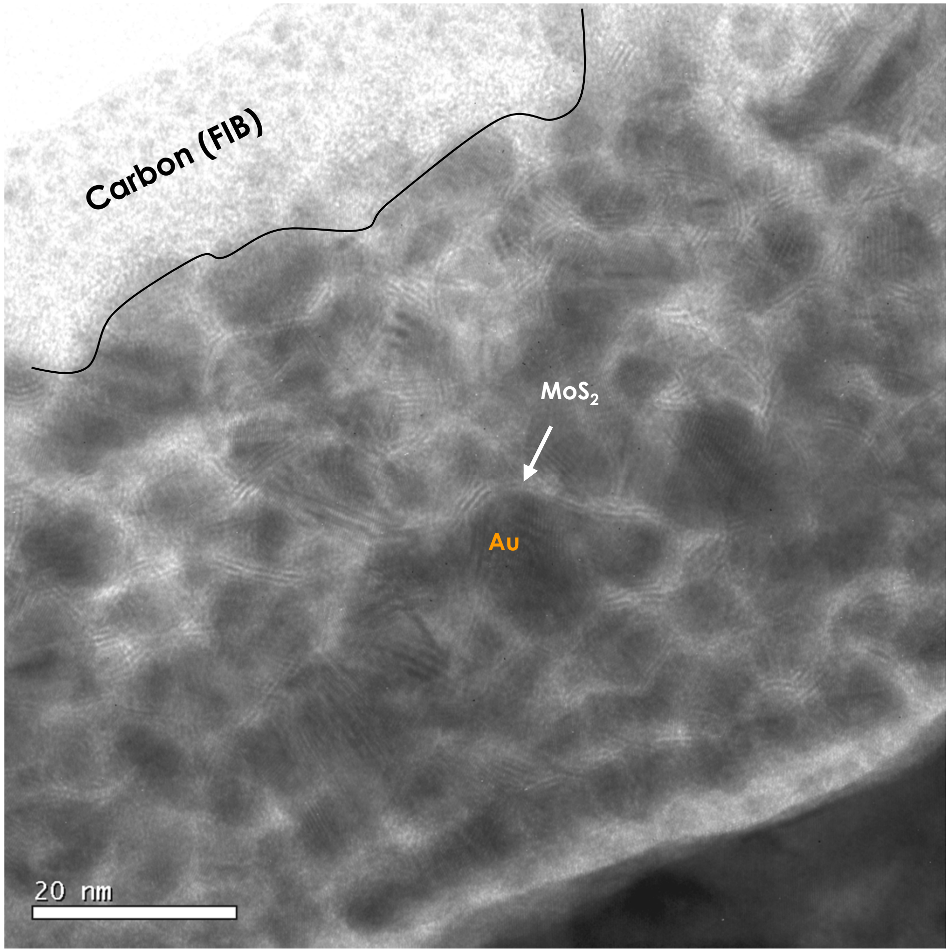
Room temperature deposition
2 nm Au & MoS_2

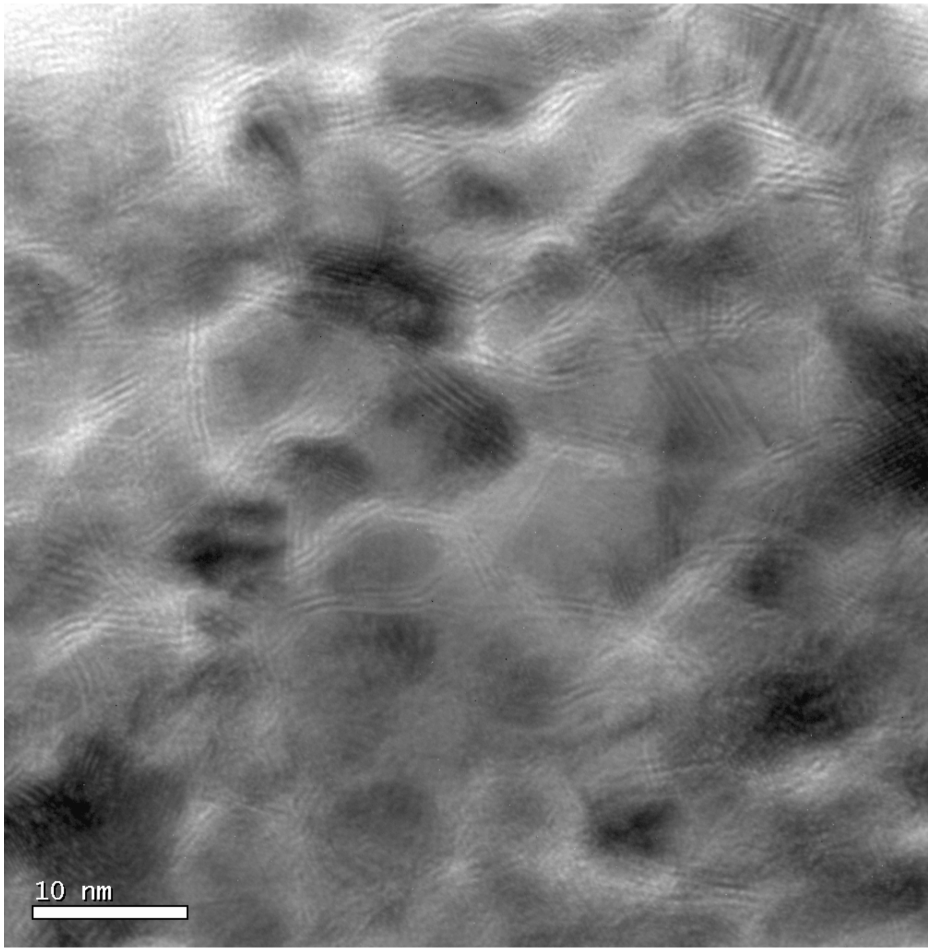


200°C deposition: Au coarsened to 10 nm and MoS_2 basal lattice planes thermally evolved to encapsulate the Au forming a closed MoS_2 shell (Au seed MoS_2 nano-onions.)

MoS_2-Au nano-onions

MoS_2 basal planes wrap around Au nanoparticles



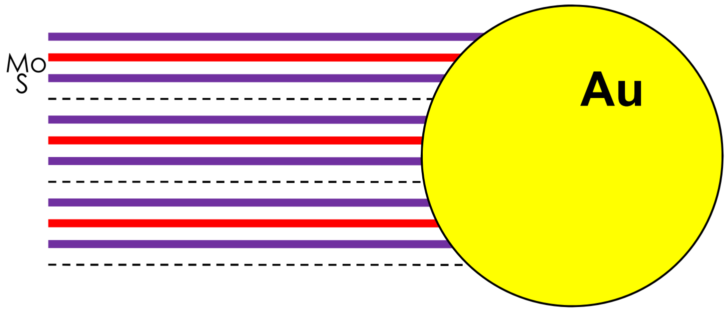


Cross-sectional BFTEM images of the Au-MoS_2 nanocomposite grown at 200°C. Nanocrystalline Au (~10 nm) core with MoS_2 basal plane closed shell. The top layer corresponds to protective carbon layer.

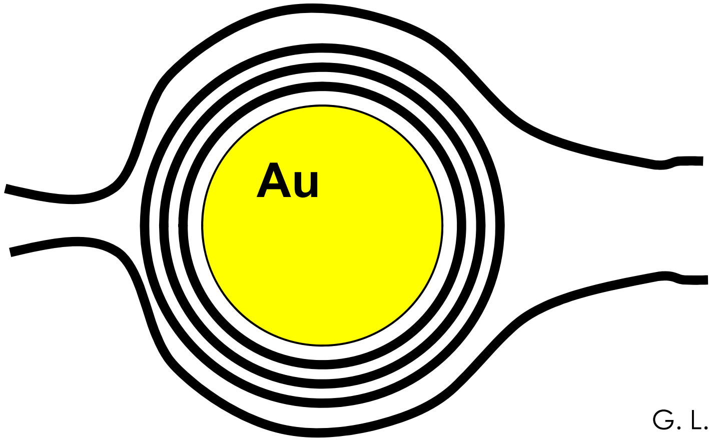
Reduced Edge Planes

Similar to IF-MoS_2

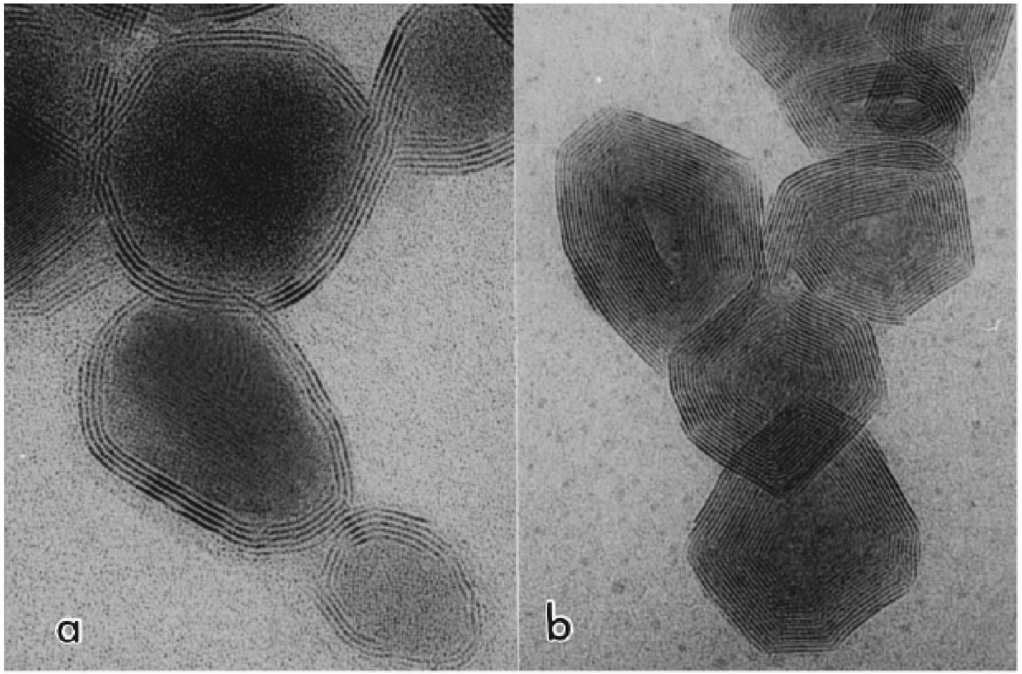
Initial objective



Experimental Result



Inorganic Fullerenelike MoS_2 or IF-MoS_2

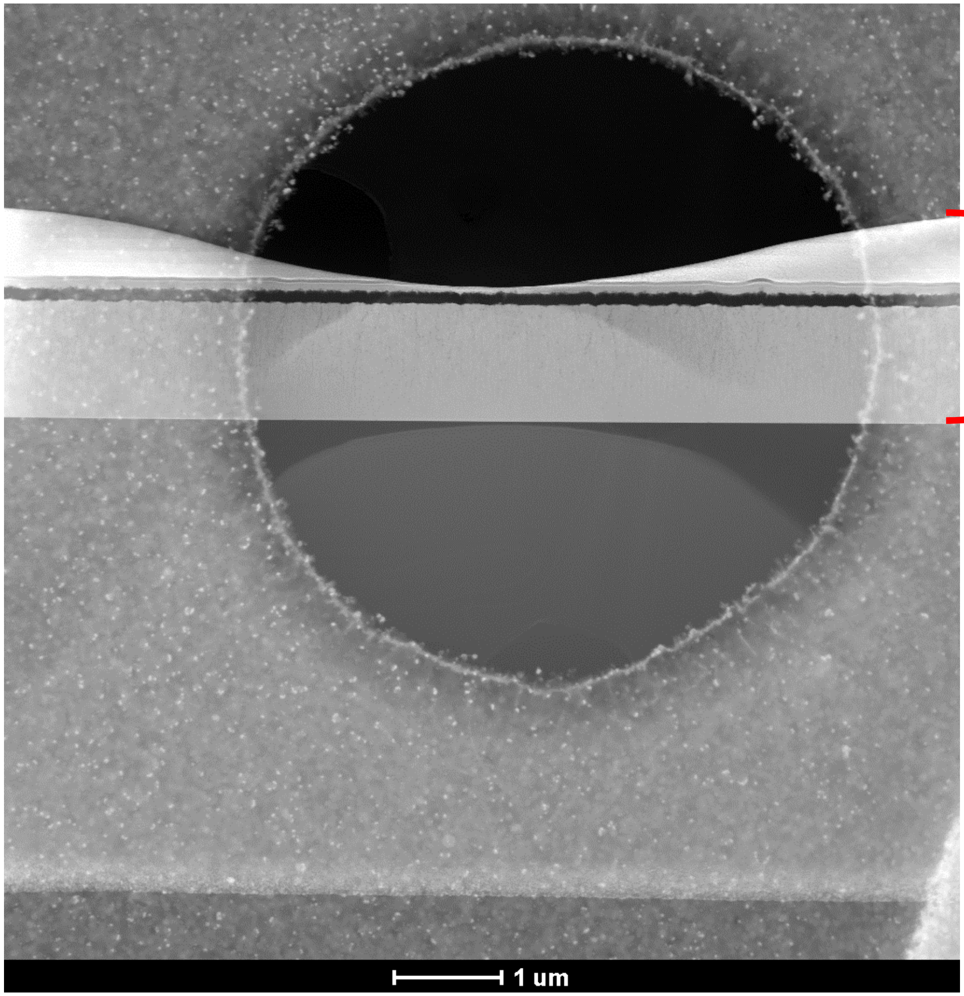


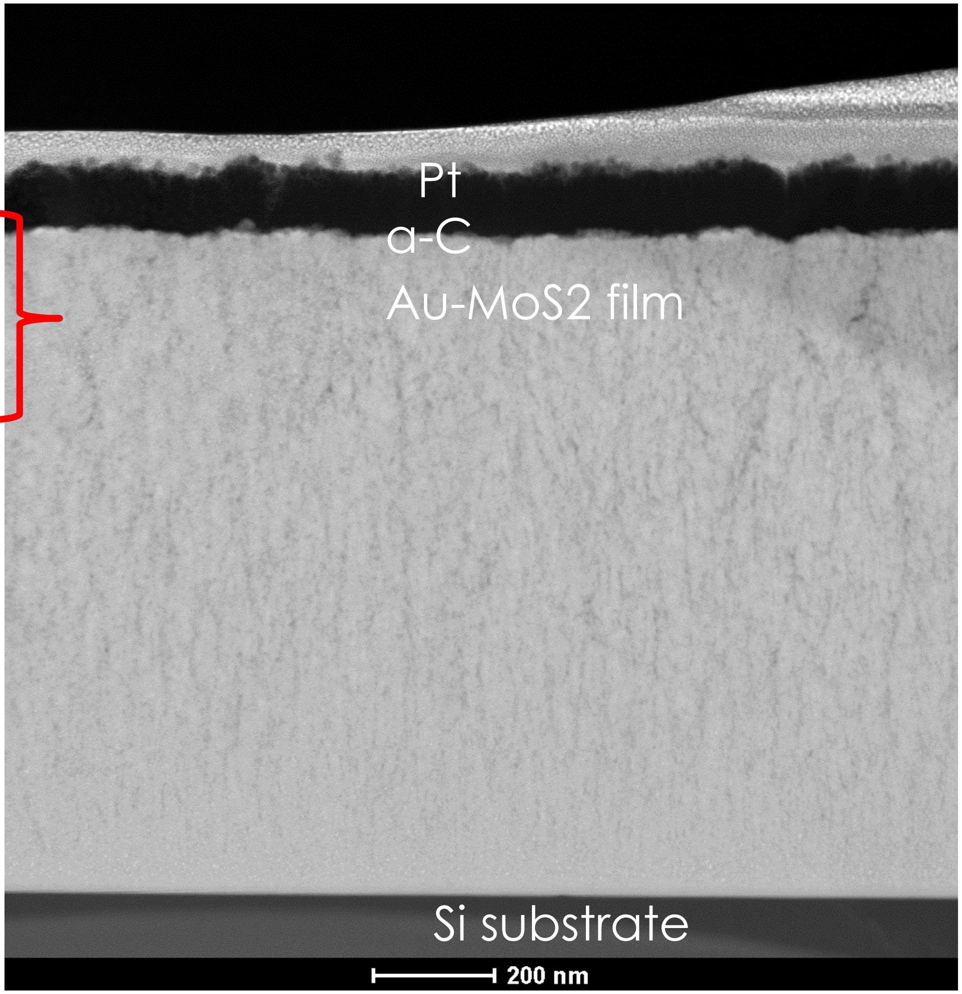
From annealing MoO_2 in H_2S atmosphere

G. L. Frey, S. Elani, M. Homyonfer, Y. Feldman and R. Tenne, *Physical Review B*, ***57, 6666 (1998)***

In-situ TEM heating

X-section sample heated post deposition in TEM



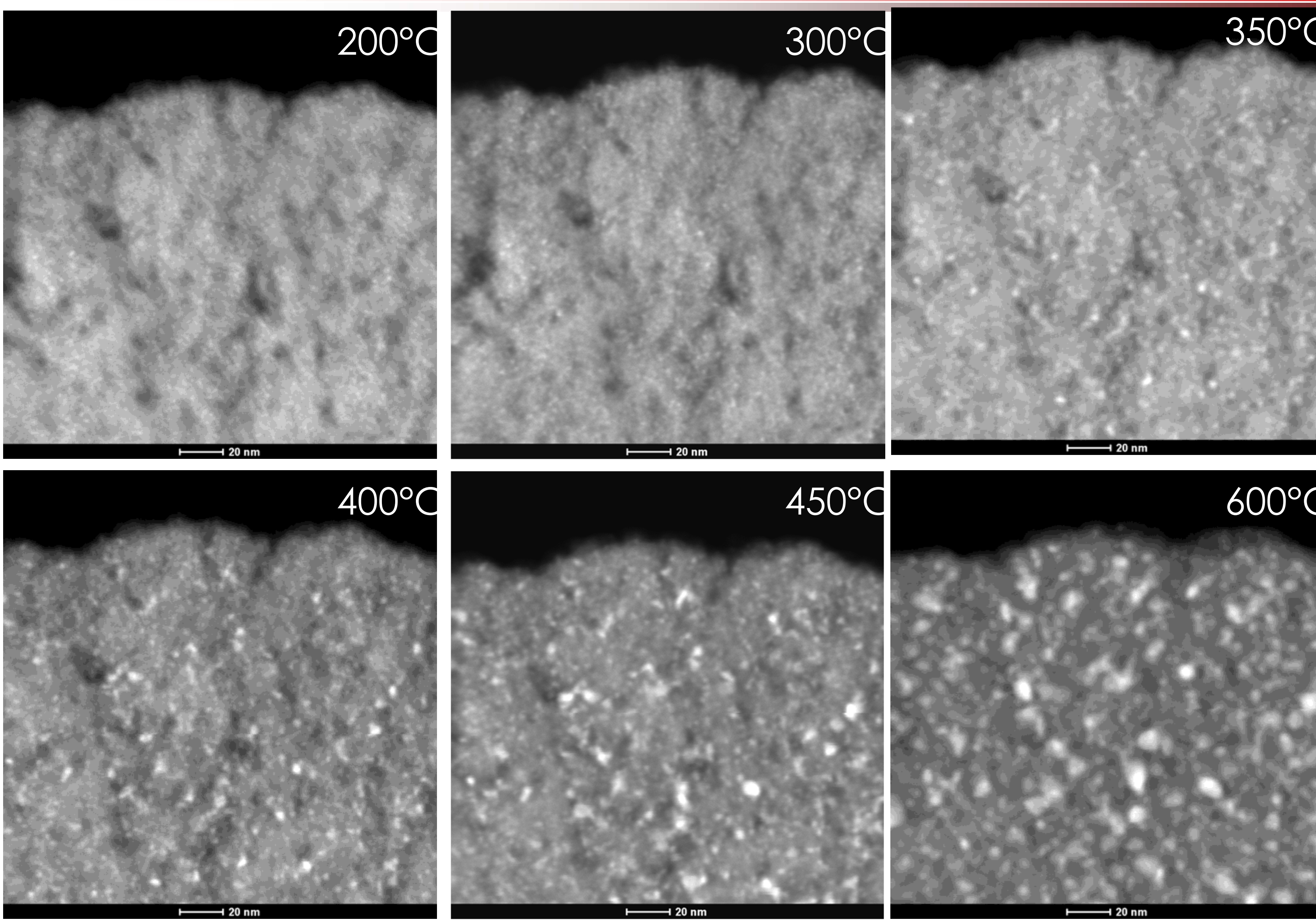


Protochips Aduro in situ TEM heating stage showing sample cross-section over electron transparent hole.

Protochips
interactive real-time microscopy™

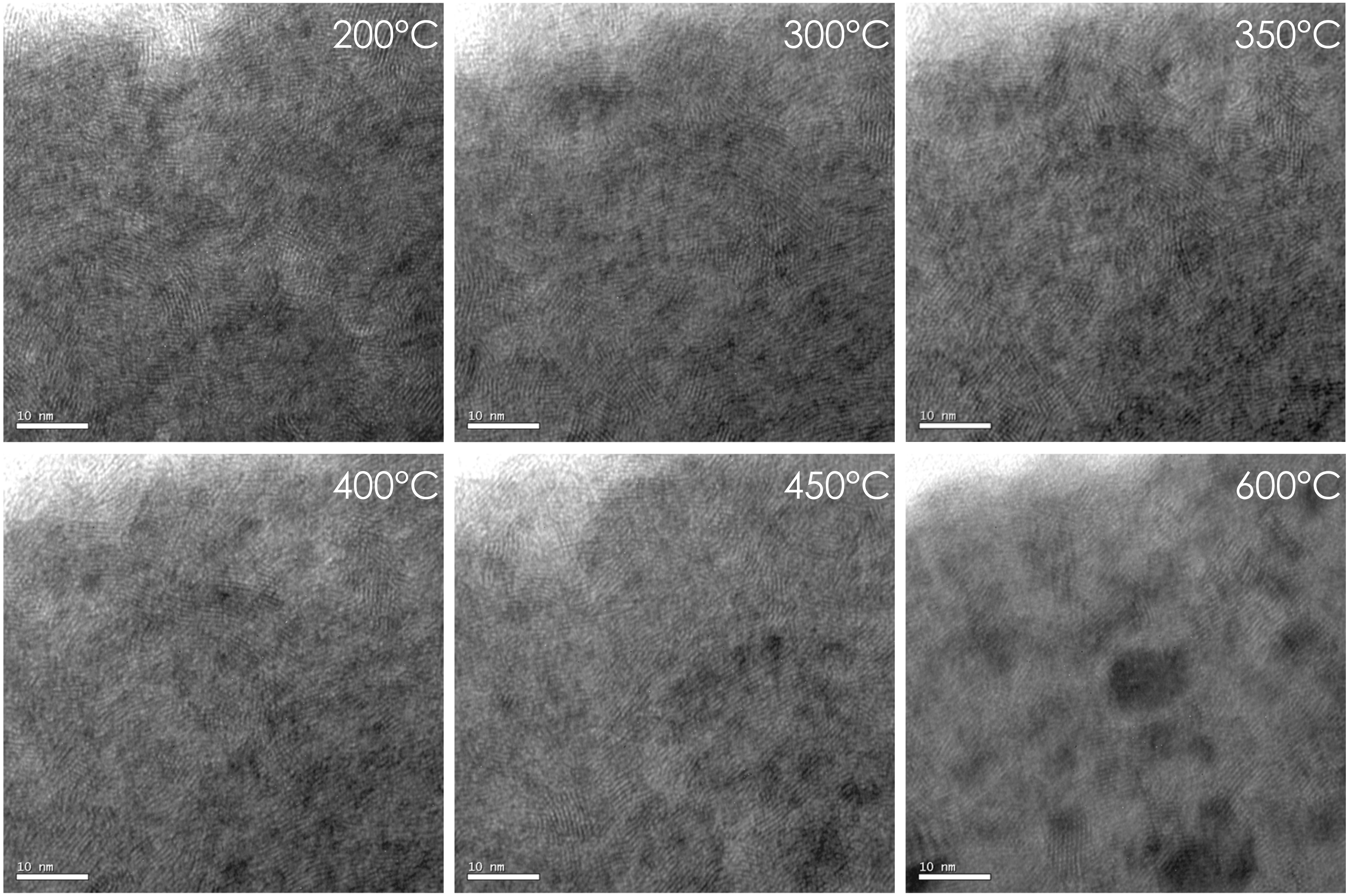
STEM/HAADF in situ heating

Film densification and Au coarsening visible



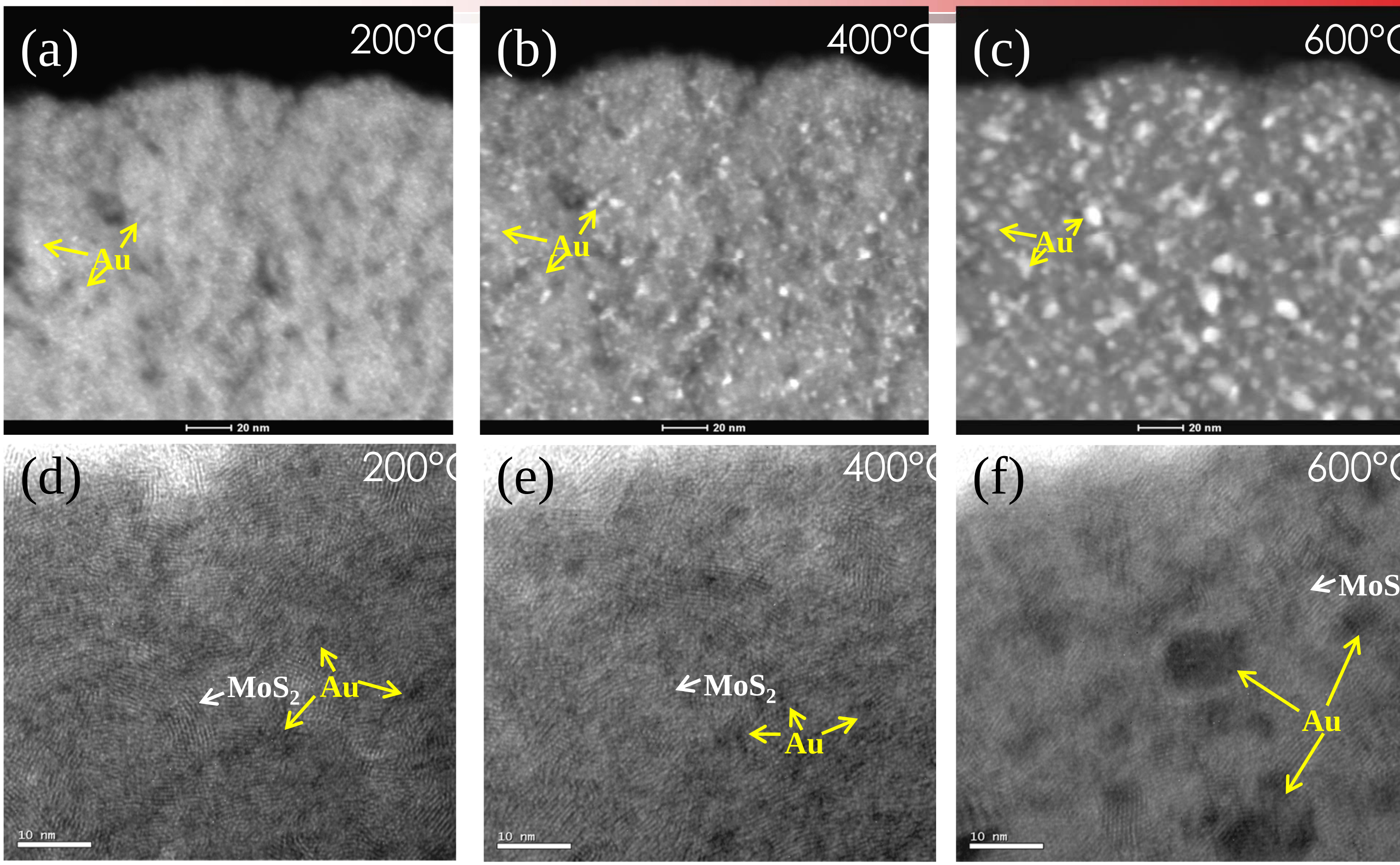
HRTEM in situ heating

No closed MoS_2 basal plane shell formation



TEM In situ heating

Comparing HRTEM – STEM/HAADF

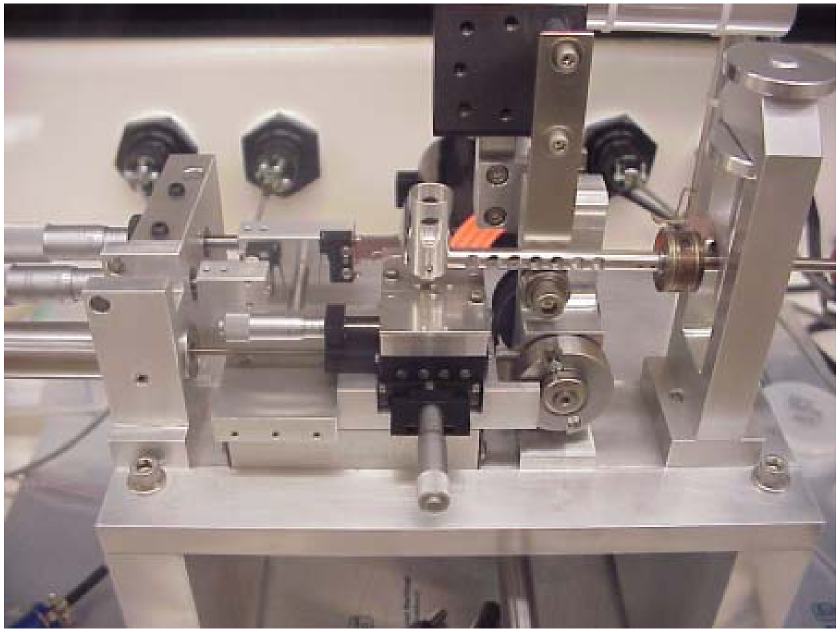


(a)-(c) STEM/HAADF images of Au coarsening and nanocomposite film densification with increasing temperature

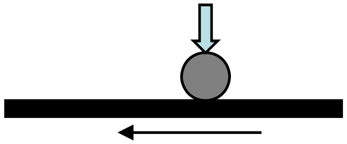
(d)-(f) HRTEM images. Arrows indicate examples of coarsening, no shell formation

Tribological measurements

Controlled Environment Tribometer at SNL



Linear Wear Tester
(Ball-on-Flat configuration)



Counterfaces: Si_3N_4 Ball (3.175 mm dia)

Normal Loads: 0.95 GPa (100 grams)

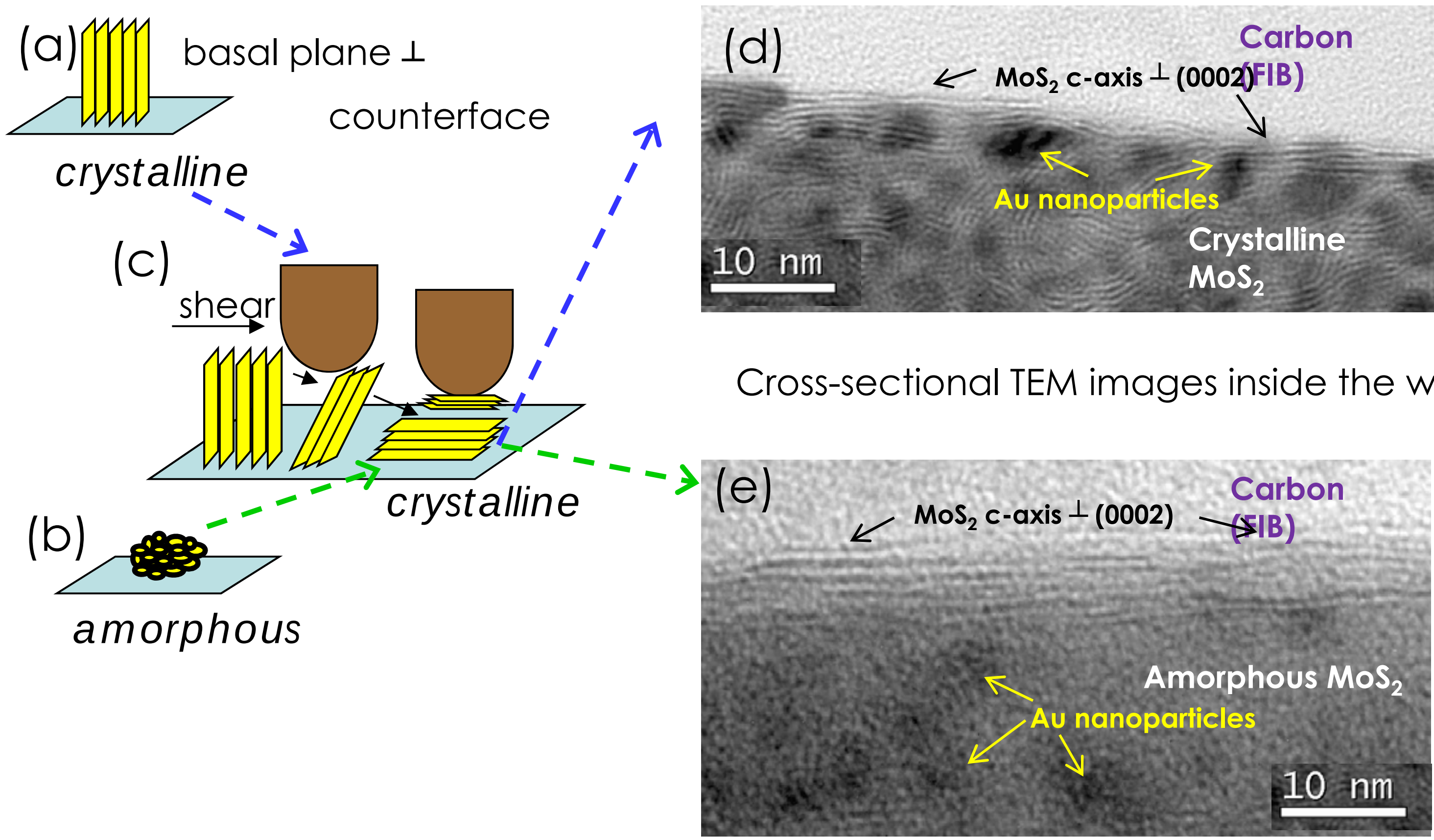
Environments: Dry Nitrogen, and Air with 50 %RH

Environmental Control

Crystallinity in Wear Scar

Shear testing creates surface parallel basal planes

(a→c→d) reorientation of perpendicular (randomly orientated) basal planes parallel to the sliding direction to achieve low friction

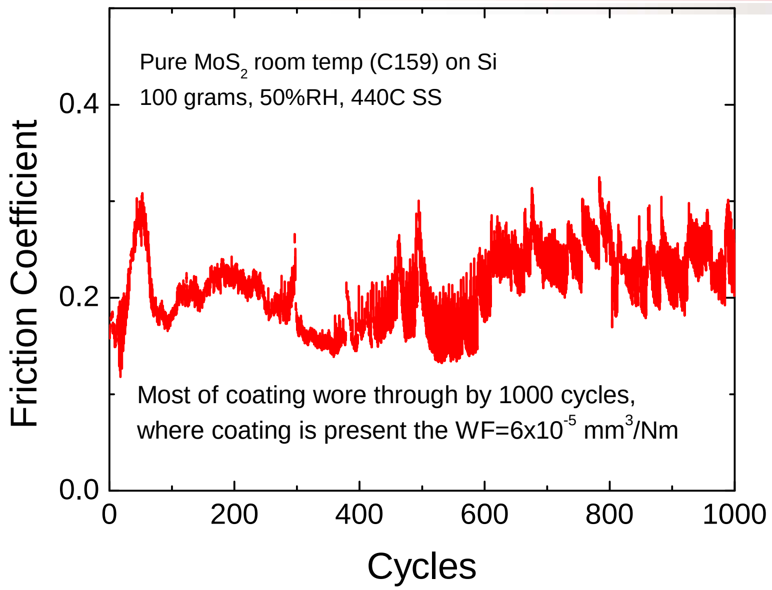


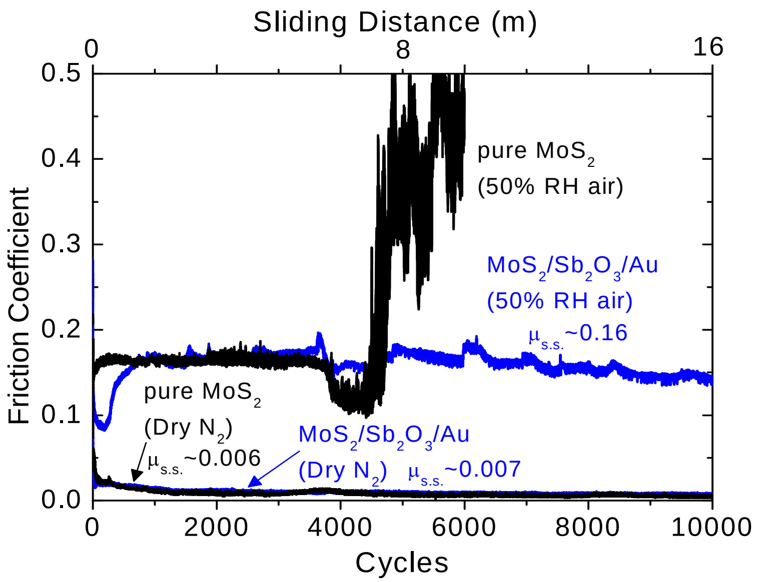
Cross-sectional TEM images inside the wear track.

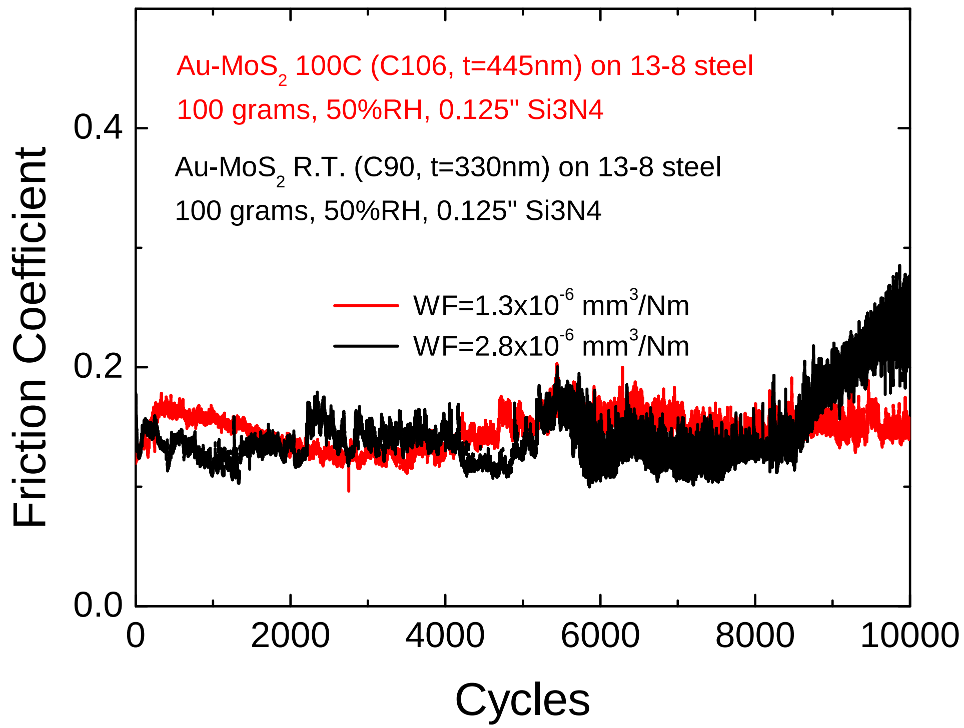
(b→c→e) amorphous to crystalline transformation to achieve low friction

Friction Coefficients

MoS_2/Au films @ 50% RH







Conclusions

- Sputter co-deposition system for doped transition metal chalcoginides developed
  - Independent control of film composition
  - Substrate heating (film density, crystallinity, nano particle size)
  - Substrate biasing (film density, crystallinity)

- Novel Nano-onion like structures fabricated at 10 wt% gold enabled by deposition on heated substrate (T_s = 200 – 300°C)

- These MoS_2/Au films exhibited enhanced performance in humid environments

Acknowledgements:
The authors appreciate the efforts by R. Grant for EPMA, C. Sobsczak for thin film deposition and funding from Sandia National Laboratories.