SAND2019-5824C

# Environmental Sensitivity and Aging of Composite Solid Lubricant Coatings

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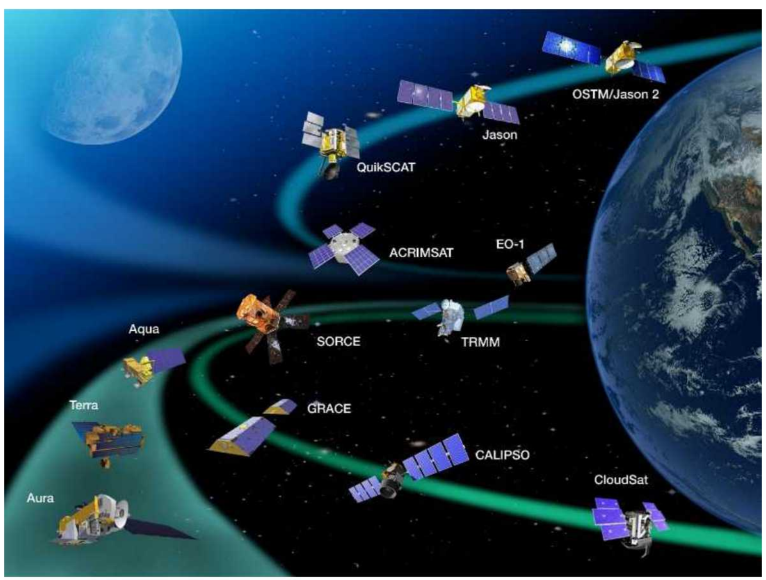
# Outline

- Lubrication Mechanism and Aging
  - shear accommodation in lamellar solids
  - effects of aging on performance
  - evidence of lattice orientation effects in pure $MoS_2$
- Mitigation of Environmental Effects
- Accelerated Aging of Select Lubricant Films
  - experimental approach
  - performance and surface chemistry
  - implications
- Conclusions

# Extreme Environments

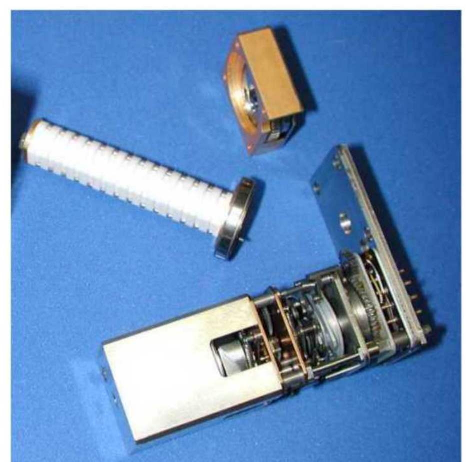
**Space:**

- operate in vacuum (+atomic oxygen in low earth orbit)
- store months – years before use; generally non-serviceable
- operating temperatures from 50 – 300K, depending on location
- large investments of time and money



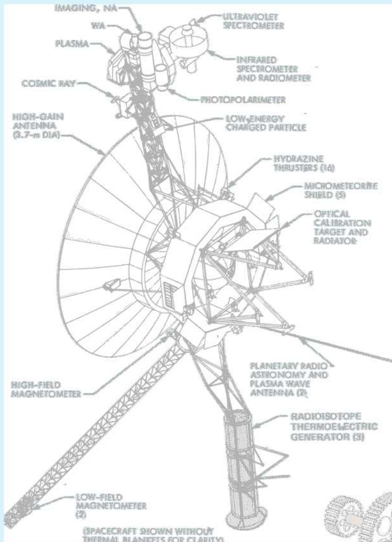

**Precision Mechanisms:**

- inert gas near $P_{atm}$, trace $O_2$, $H_2O$, outgassing species
- store for decades; non-serviceable
- operating temperatures 200 – 350K
- large investments of time and money
- consequences (political, societal) of failure are unacceptable



# Costly Lubrication Failures

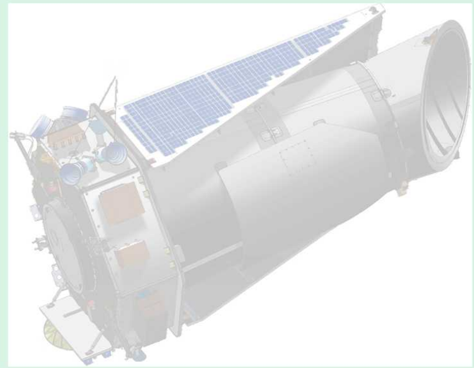
## Voyager 2 ($600M)




**Failure - August 1981** – Science platform seized due to migration of lubricant out of motor gear shaft.

**Cost** - Delayed use for 16 months. All future experiments ran at 0.083°/sec scan speed instead of 1°/sec. [1]

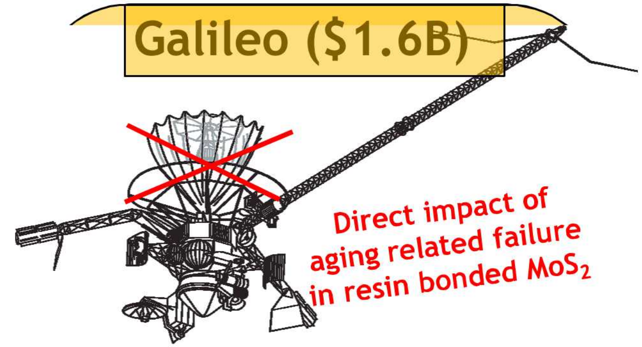
## Kepler ($550M)



**Failure - 2013-2014** - 2/4 reaction wheel seized due to uneven lubrication of mechanical-bearings leading to galling.

**Cost** - Prolonged mission delays. Similar to Voyager 2, combination of heat and radiation pressure from the sun was used to redeposit lubricant [2]

## Galileo ($1.6B)




**Failure – April 1991** – Sticking of 3/18 antenna ribs in stowed position due to high friction between standoff pins and sockets.

**Cost** - Over 100 personnel involved in testing, simulation, analysis, consultation and review. [3]

**Report -** "The use of dry lubricant, specifically molybdenum disulfide, on a mechanism that is going to be operated in an atmosphere should be carefully evaluated."

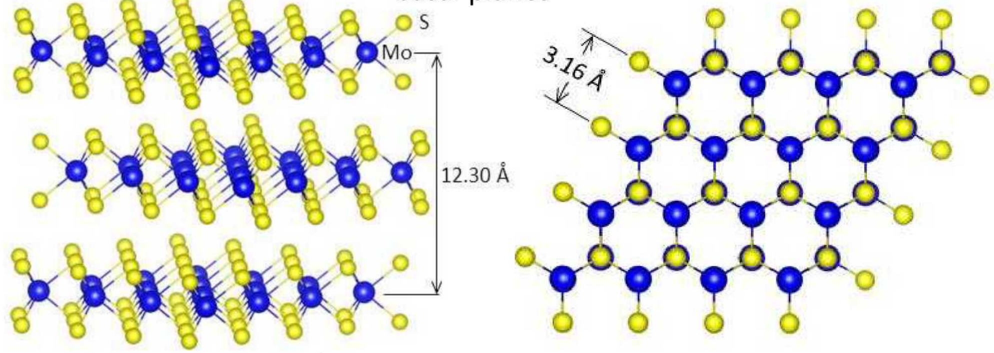
[1] Physics Today 43, 7, 40 (1990); doi: 10.1063/1.881251
[2] Kepler Mission Manager Update: Kepler Returns to Science Mode. (2015, April 15). Retrieved June 10, 2018, from https://www.nasa.gov/mission_pages/kepler/news/keplerm-20132901.html
[3] Miyoshi, K. (1999). *Aerospace Mechanisms and Tribology Technology: Case Studies*.

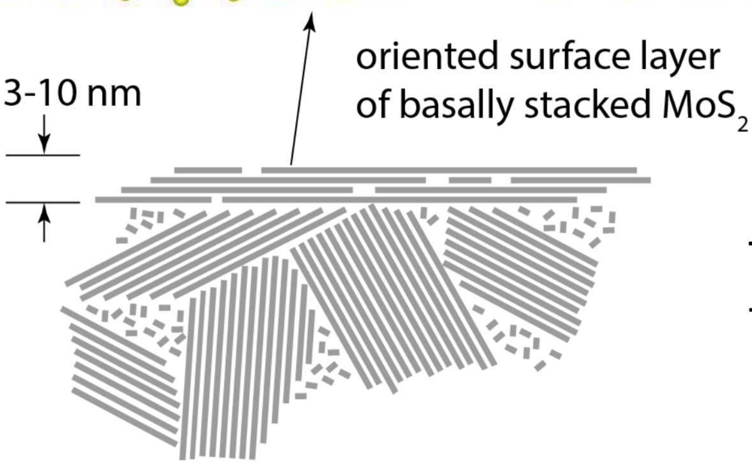
# $MoS_2$ Lubrication Mechanism

***molybdenum disulfide***

**$\mu$ = 0.02 – 0.06 (inert gas/vacuum)**

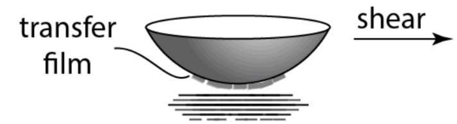
**$\mu$ = 0.15 – 0.25 (humid air)**



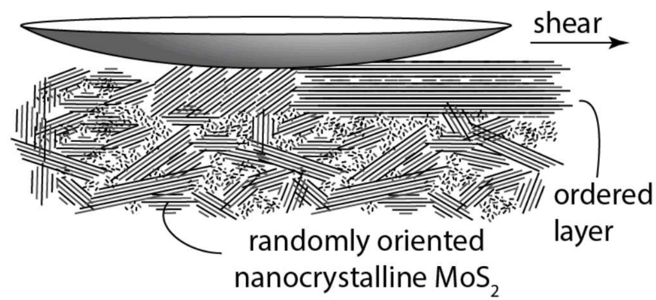




## *Run-In Processes:*

***1) Transfer Film Formation***



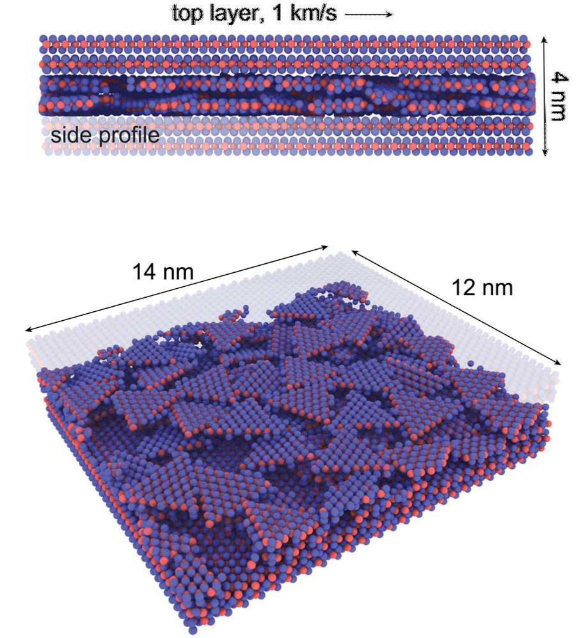

***2) Shear-induced re-orientation and coalescence***

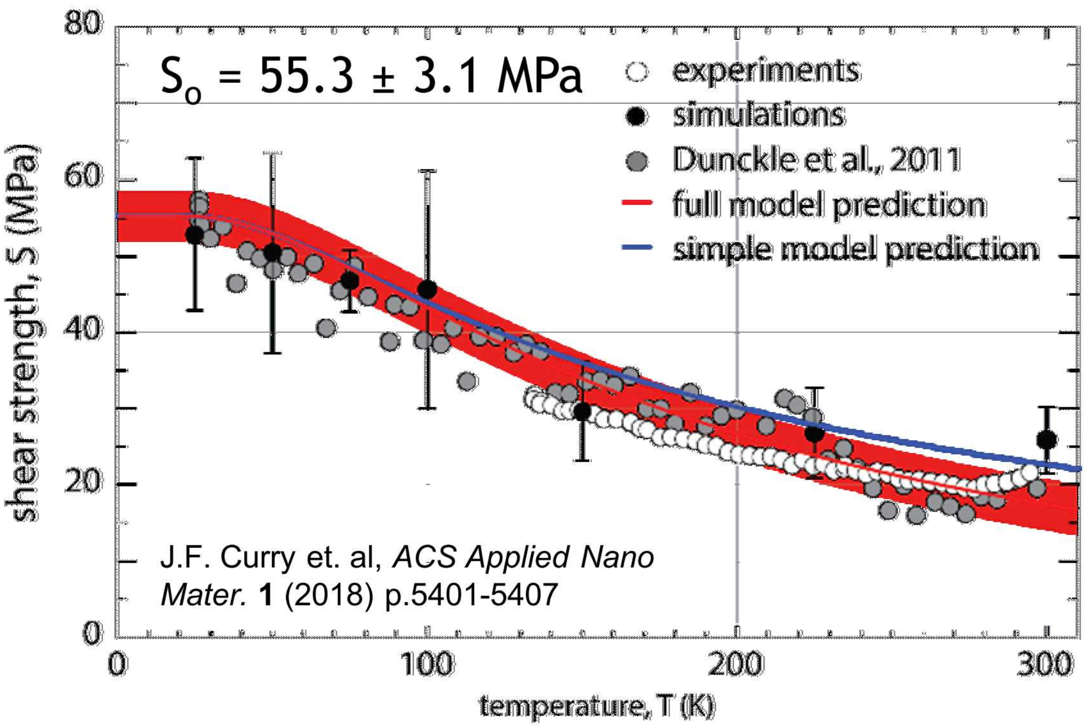



The shear accommodation mechanism of these materials is inter-lamellar sliding

***Sliding occurs between weakly bonded basal planes***

# Model of $MoS_2$ Shear Strength




**simple model prediction** $$S(T) = S_0\left(1-\exp\left(-\frac{\Delta E_i + \Delta E_r}{k_B T}\right)\qquad\qquad\qquad\right)$$

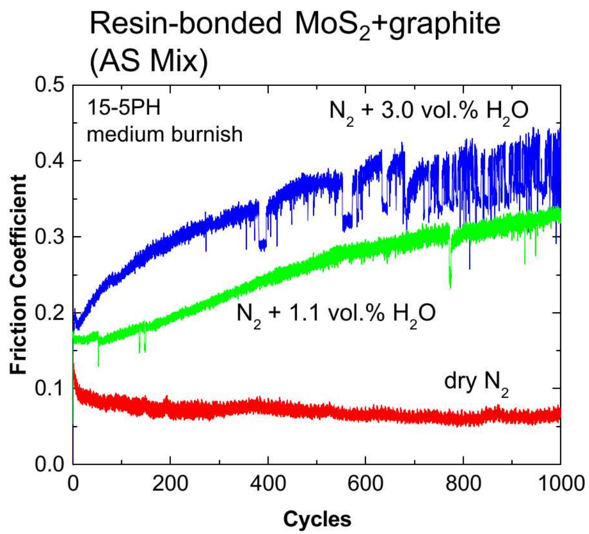
zero kelvin
shear strength, $S_0$(T=0K)

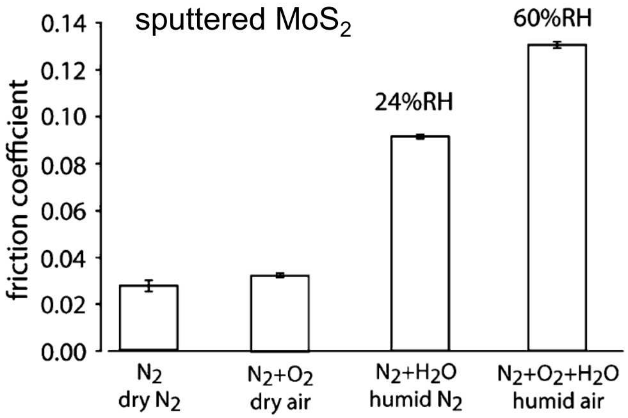
successfully rotate;
slide incommensurately

failure to rotate;
slide commensurately

# $MoS_2$ Environmental Effects

- Water vapor in the operating atmosphere increases friction coefficient
  - water absorption into structure
  - friction increase due to alteration of transfer film adhesion and dynamics



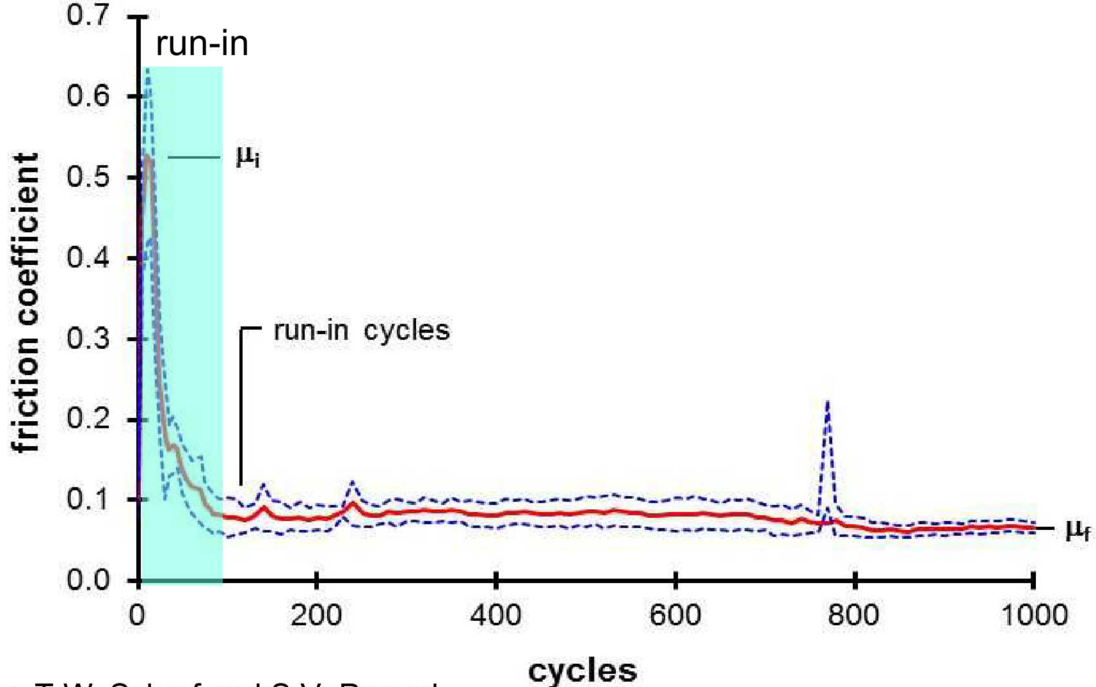

- Steady-state friction coefficient at 30°C of sputtered $MoS_2$
  - friction increases with water vapor content
  - friction is far less sensitive to oxygen

H. Khare and D. Burris, Tribology Letters **53** (2014) p.329-336

$O_2$ has little influence on dynamic friction, while $H_2O$ in the atmosphere significantly increases friction

# $MoS_2$ Aging Effects

- Surface oxidation can dramatically increase the initial friction coefficient
- in this example, atomic oxygen reacted with top 100 nm of film



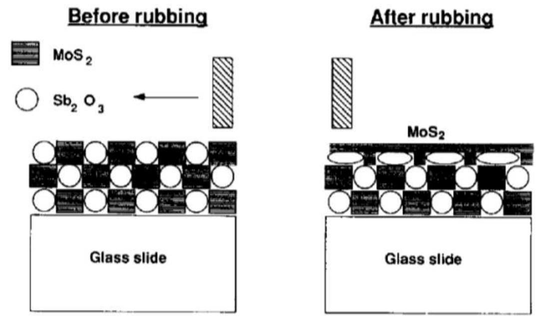

M.T. Dugger, T.W. Scharf and S.V. Prasad, *Adv. Mat. and Processes* **172** (2014) p.35-38

Some aerospace mechanisms "live" in run-in

- dormant for months/decades, then operate once/few cycles

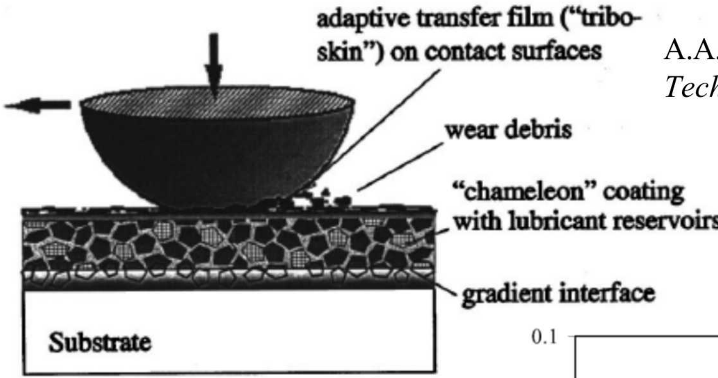
# Mitigation of Environmental Effects

Strategies
- dopants (Ni, Ti, Au, …)
- compositing - multilayers, multiple phases ($Sb_2O_3$, Ni, AuPd, …)
- ion bombardment during growth

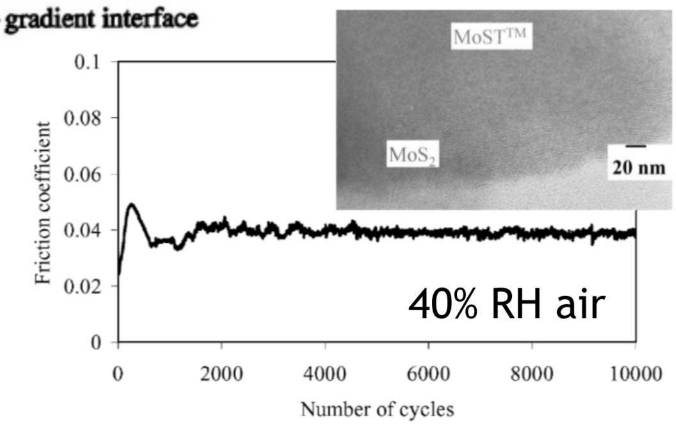



J.S. Zabinski et al, *Wear* **165** (1993) p. 103

Proposed Mechanisms
- densification
- increased hardness
- preferential orientation
- sacrificial oxidation of dopants
- passivation of $MoS_2$ edge sites
- crack arresting




A.A. Voevodin et al, *J. Vac. Sci. Tech.* **A20** (2002) p. 1434

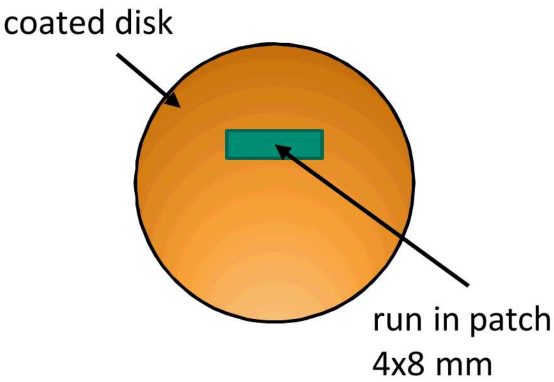



D.G. Teer, *Wear* **251** (2001) p. 1068

How do dopants/composite phases influence interaction with the environment?

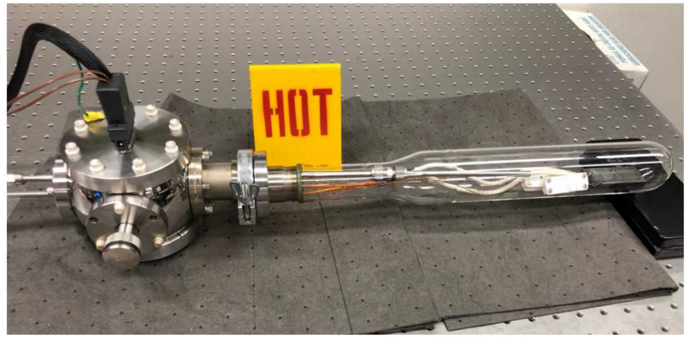
# Experimental Setup

## Run In



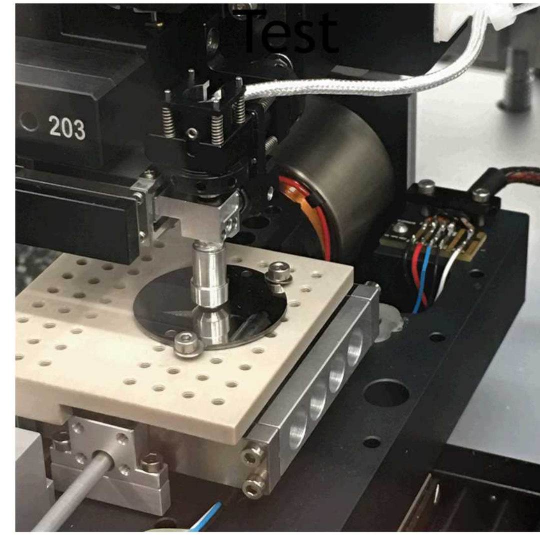

- 13-8PH or 440C stainless steel disks
- run in at 530 MPa, 50 passes, overlapping areas

## Accelerated Age




- 200$^{o}$C, dry (DP < -60$^{o}$C) air, 5 SCFH
- 12 hours

## Friction (Stripe) Test




- 440C ball, 3.2 mm dia.
- 1 mm/s sliding speed
- Hertz contact pressures of 275, 530 and 785 MPa

**Materials Investigated:**

- $N_2$ (pure $MoS_2$ sprayed with $N_2$)
- DC (pure DC sputtered $MoS_2$)

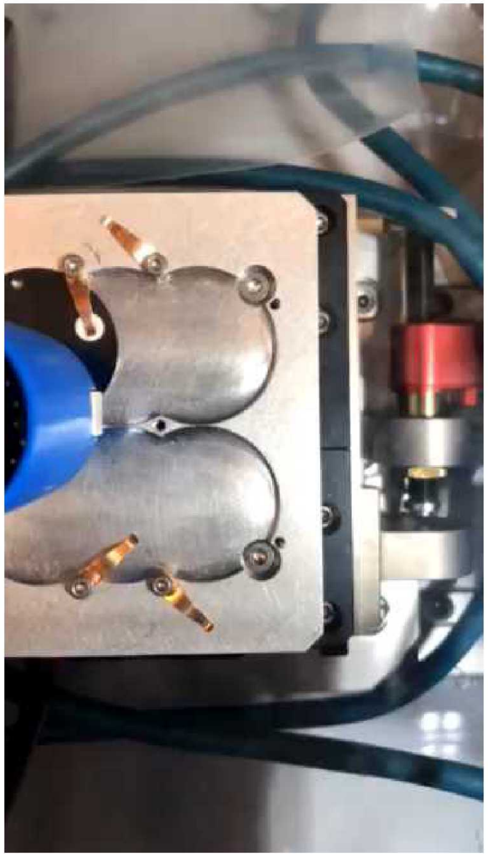
} **Pure $MoS_2$**

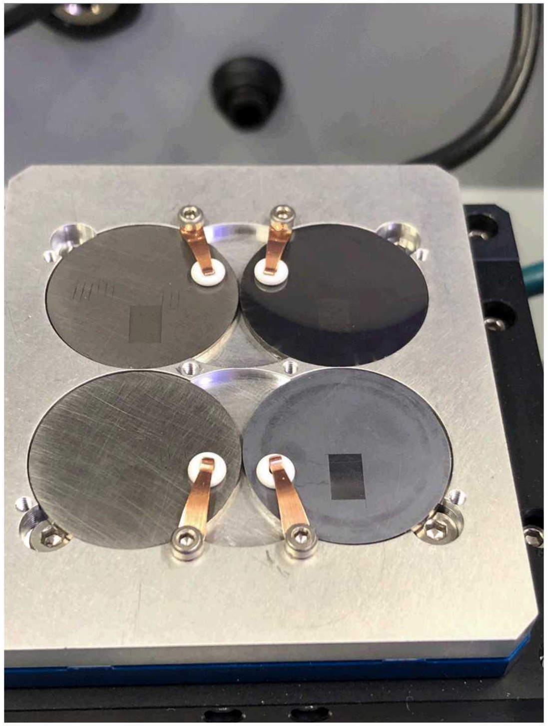
- Ti (RF sputtered $MoS_2$, Ti-doped)
- $Sb_2O_3$/Au (RF sputtered $Sb_2O_3$+Au-doped $MoS_2$)

} **Doped $MoS_2$**

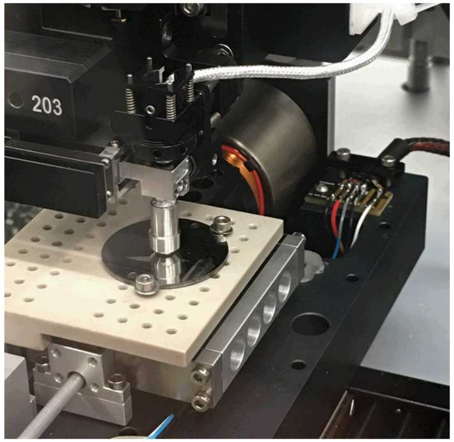
# Run-In Area

- Perform XPS inside versus outside rubbed area
- Return to run-in area after aging for additional friction testing



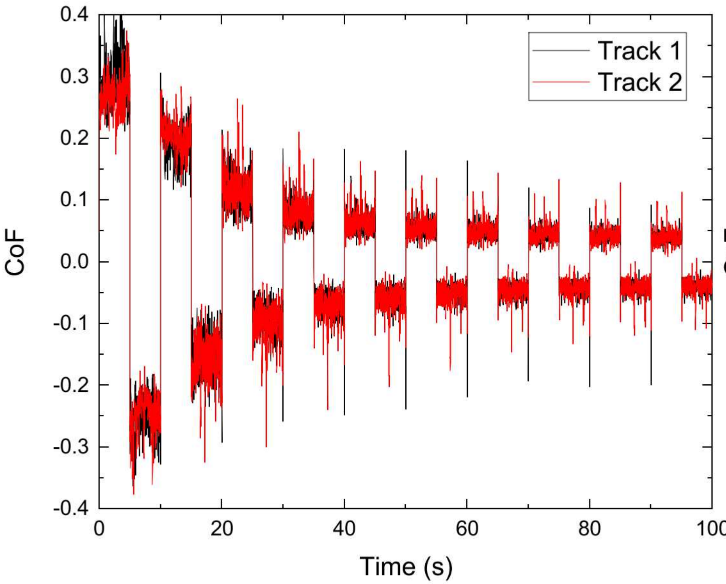


# Friction Measurements: “Stripe” Tests

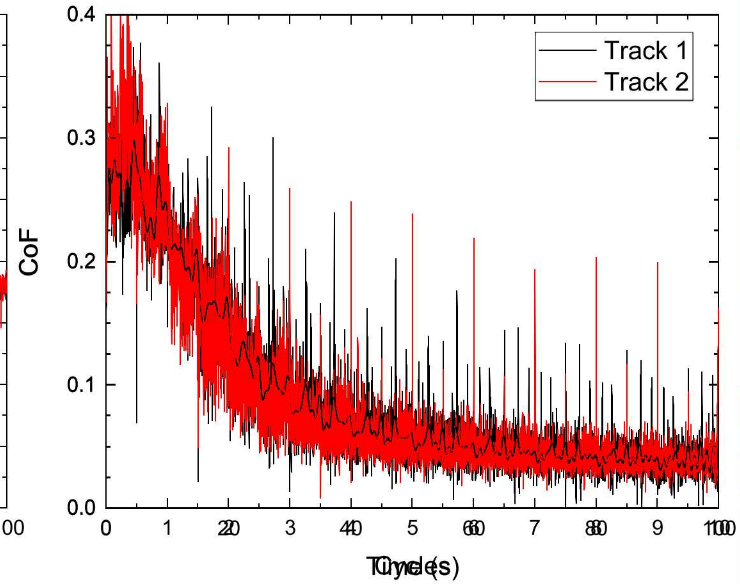



| Load, mN | Max Pressure, MPa | Track Length, mm | Test Sequence | Cycles | Total Distance, mm |
|---|---|---|---|---|---|
| 21 | 275 | 5 | L1 | 300 | 1500 |
| 149 | 530 | 3 | L2 | 500 | 3000 |
| 484 | 785 | 1 | L3 | 1500 | 4500 |

**Raw Data**

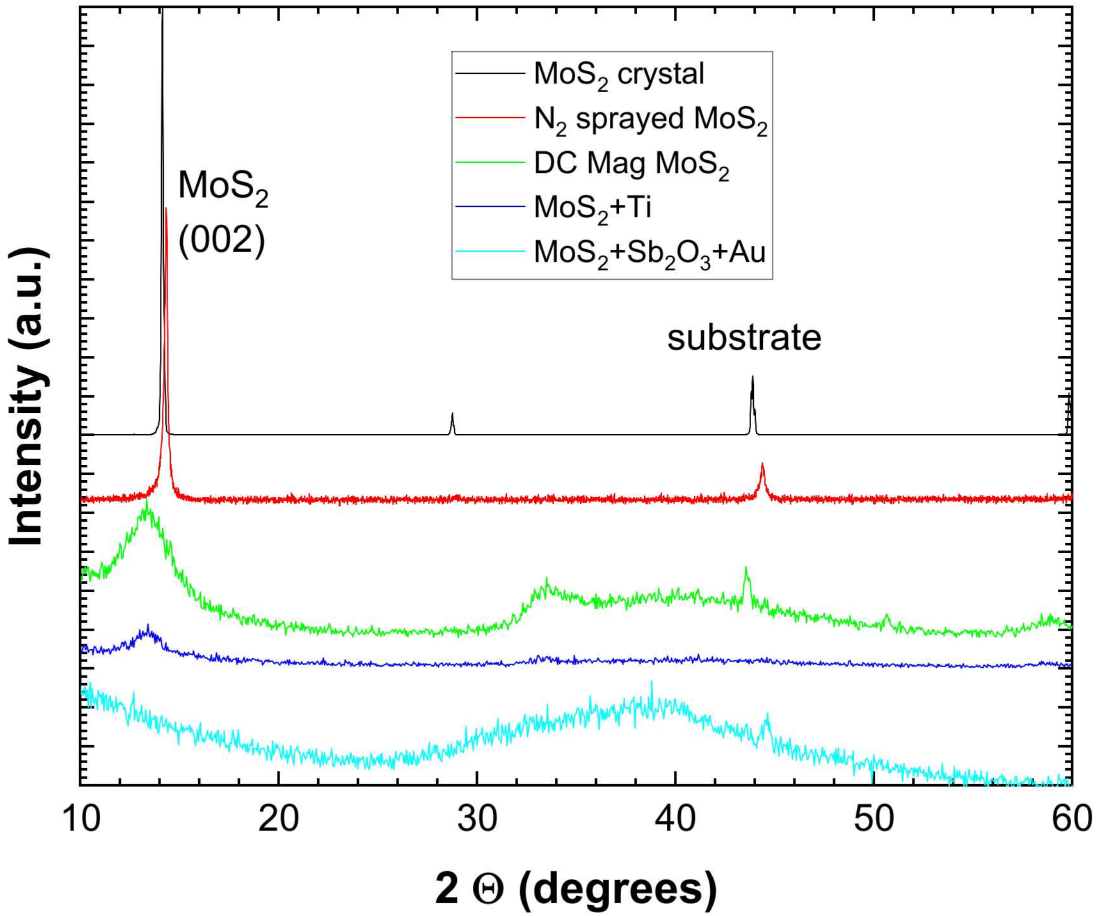



**ABS(CoF) Low Pass (ABS(CoF))**




Permits performance assessment over a range of contact pressures

# X-Ray Diffraction

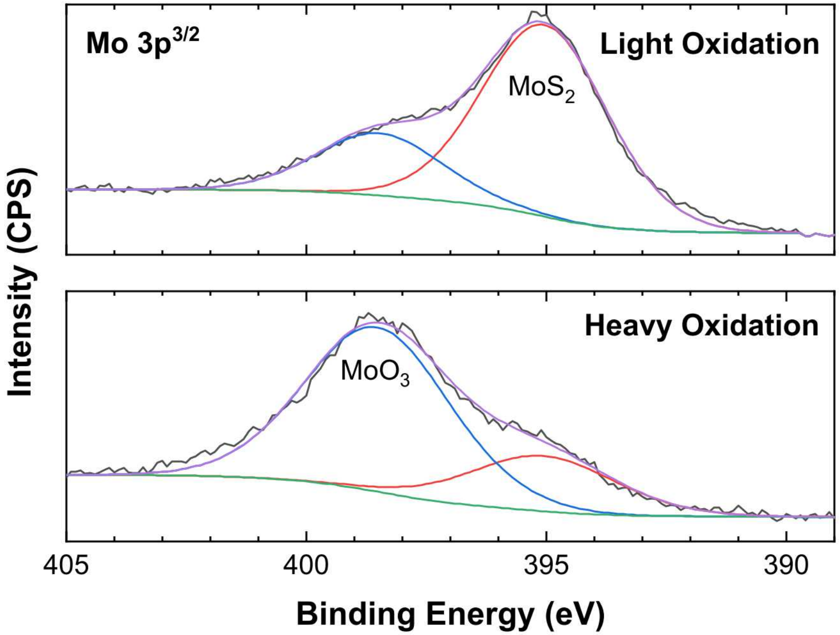


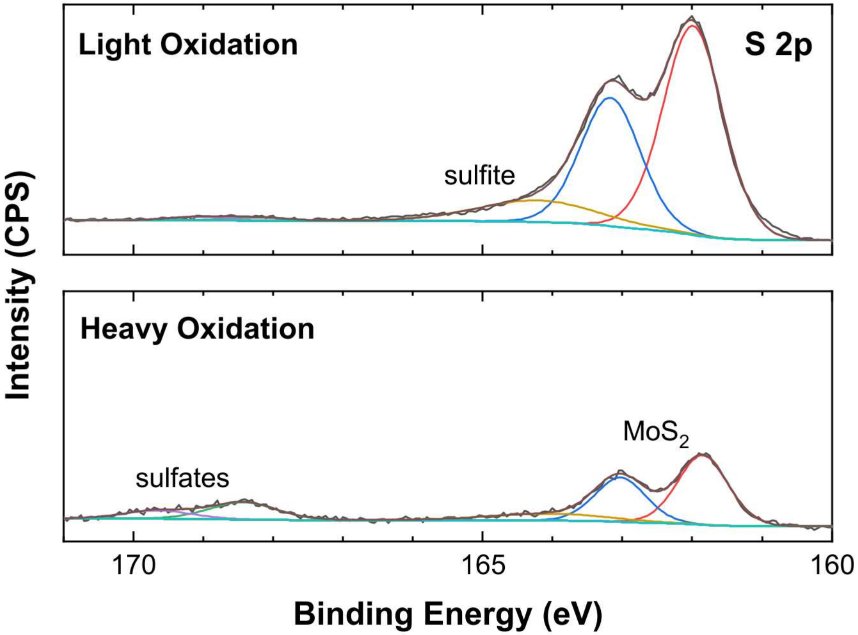

- $N_2$ sprayed $MoS_2$ exhibits large crystals and basal orientation
- Pure sputtered $MoS_2$ and $MoS_2$+Ti exhibit small crystals, some basal orientation
- $MoS_2+Sb_2O_3$+Au is amorphous

# Quantifying $MoS_2$ Oxidation

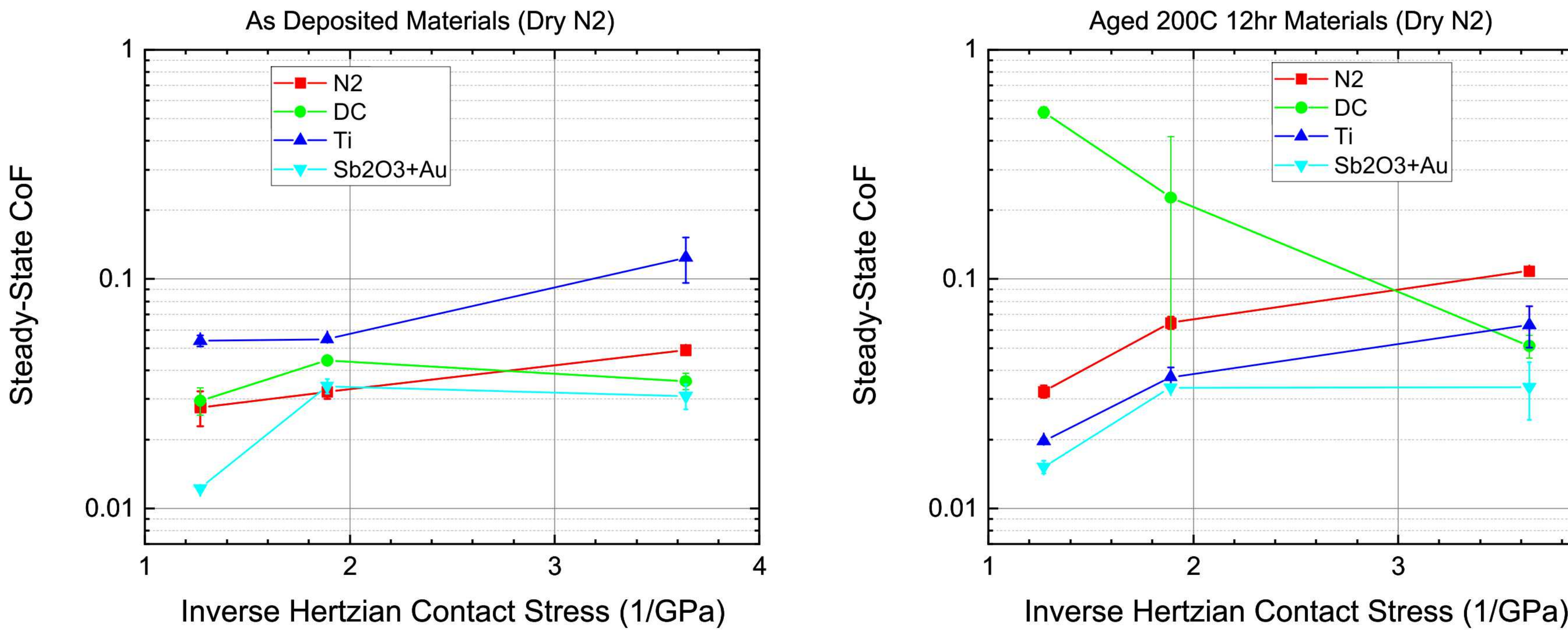
X-ray Photoelectron Spectroscopy (XPS) for surface chemical analysis

- survey scan for concentration of major elements present
- detailed scans of Mo3p, S2p spectral regions
- deconvolution of detailed scans to determine amount of Mo, S bonded to one another compared to oxidized species ($MoO_3$, sulfates, sulfites, etc.)
- surface sensitive – analyzing the top few nanometers



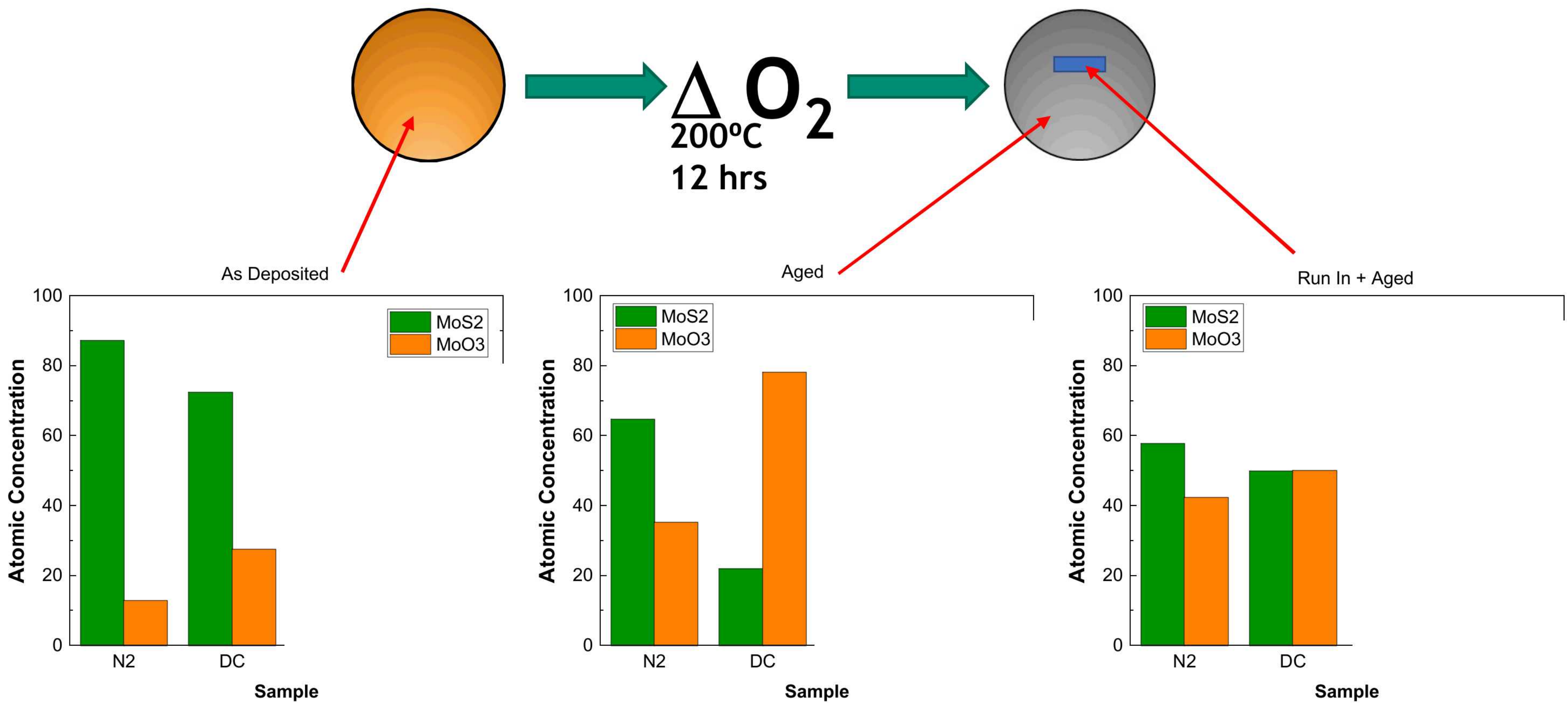



# Steady-State Friction Response to Accelerated Aging

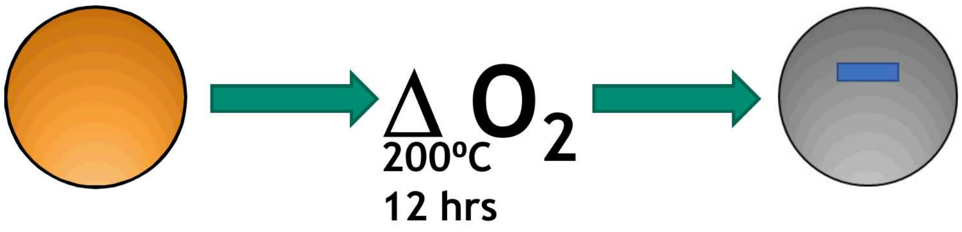



- the DC sputtered pure $MoS_2$ film failed at all but the lowest contact stress after aging
- $N_2$ sprayed and composite films fare well after aging

# XPS of Aged Samples

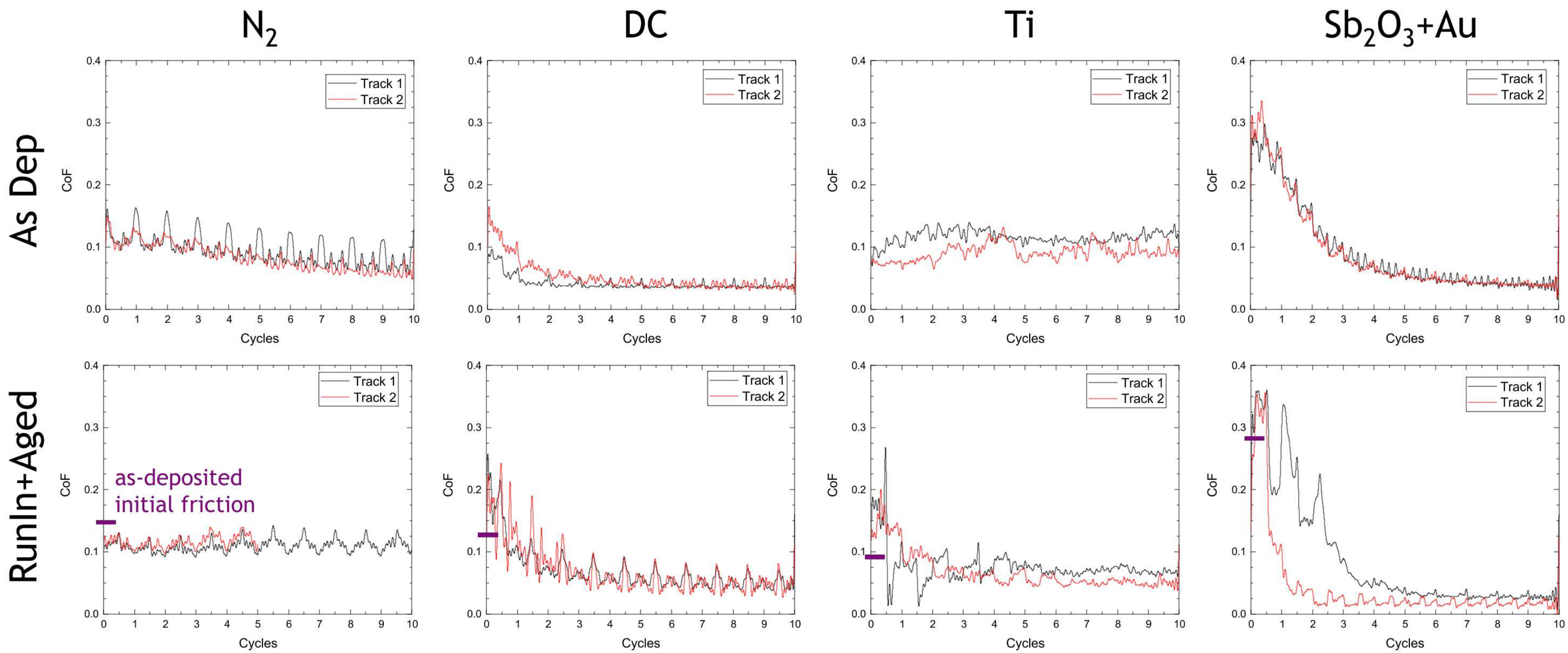


# XPS Summary



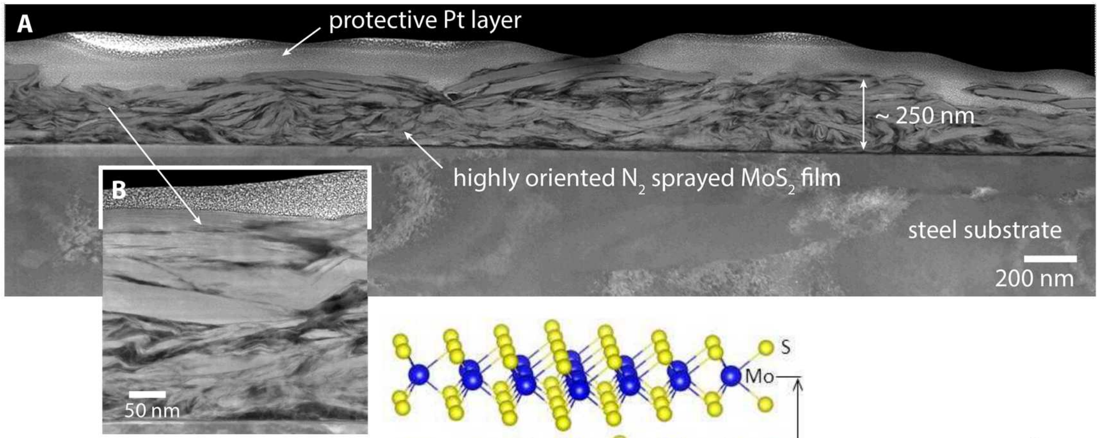

- Pure $MoS_2$ films initially exhibit a majority of Mo present as sulfide
- DC $MoS_2$ exhibits significant oxidation as-deposited, but responds to aging similar to $N_2$ $MoS_2$ after run-in
- Doped films exhibit Mo primarily as sulfide before aging
  - Aging produces a majority of Mo-oxide
  - Previously run-in surfaces respond to aging similar to the as-deposited surfaces

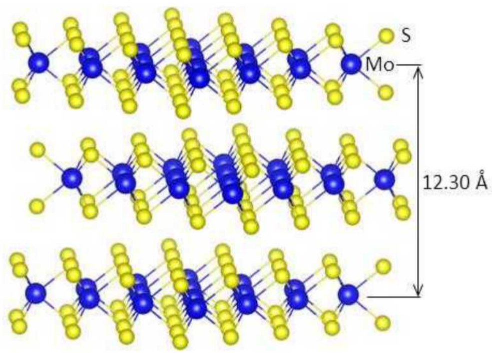
# Run-In Behavior (First 10 Cycles)

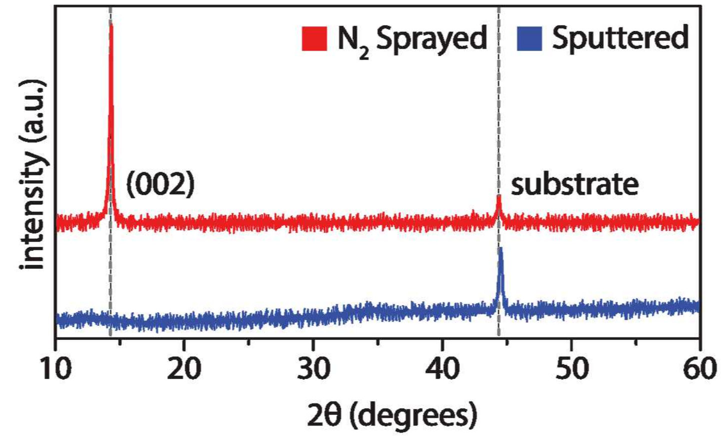



- All as-deposited films except Ti-doped exhibit some degree of run-in
  - relative to steady state, the $Sb_2O_3$+Au-doped film exhibits the largest change
- All run-in and aged films except $N_2$ sprayed $MoS_2$ exhibit 15-100% increased initial friction compared to as-deposited behavior, with more variability

# Effect of Structure on Run-In

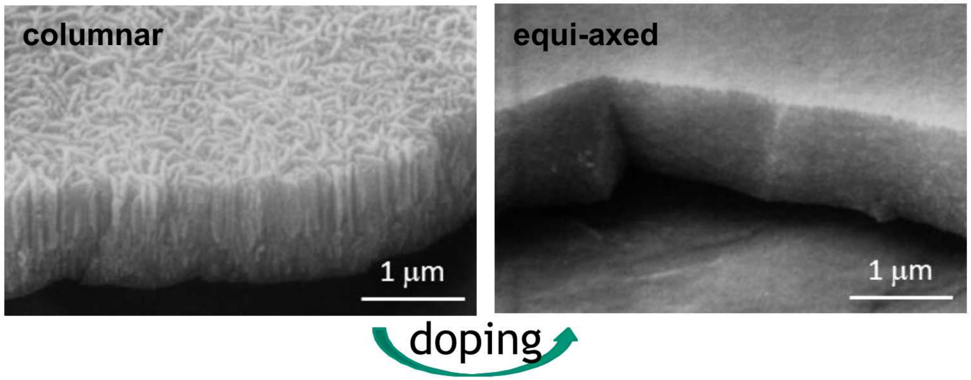



- run-in exposes S-terminated, oriented basal planes
- minimizes defects where oxidation initiates

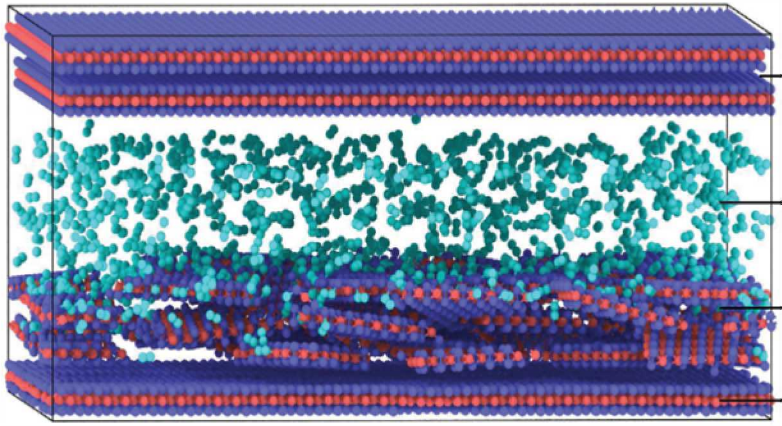
- sputtering produces highly defective, small crystals
- doping densifies the films

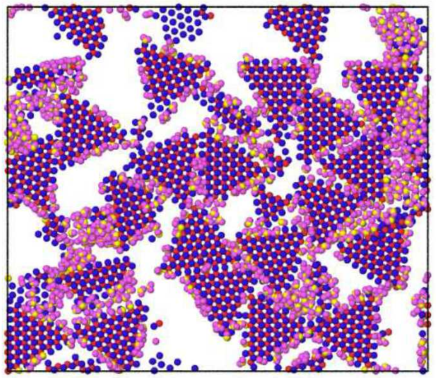



M.R. Hilton, et al., *Surf. Coatings Tech.* **53** (1992) p.13-23

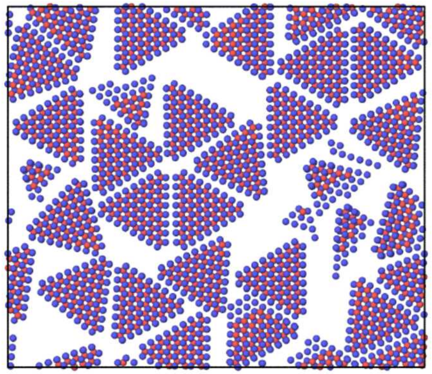
# Effects of Environment on Inter-Platelet Bonding

- Use reactive MD simulations to study chemical reactions of $MoS_2$ with environment
- Prepare system by allowing $H_2O$, $O_2$ or atomic O to diffuse into layers

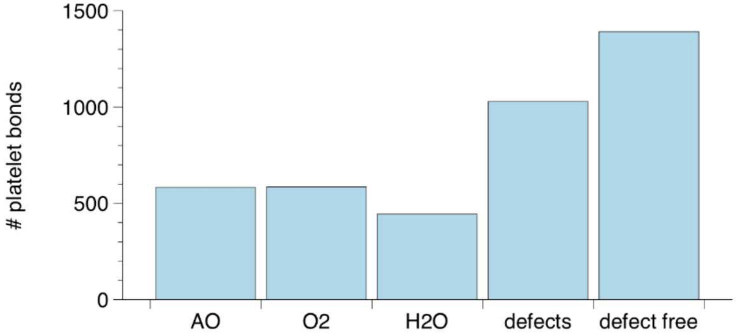


water passivated



defect free




- Environmental species interrupt formation of larger flakes
- Hypothesize that dopants can similarly interrupt flake aggregation

# Conclusions

- **Impingement $MoS_2$ coatings resist oxidation and changes in initial friction with aging**
  - deposition process results in basal planes oriented with the sliding direction
  - S-terminated basal planes present few reactive sites for interaction with environmental species
- **Pure sputtered $MoS_2$ becomes more resistant to oxidation after reorientation by sliding**
  - initially small crystals are formed during deposition
  - contact and shear reorients basal planes parallel to the sliding direction
  - the absence of dopants allows $MoS_2$ flakes to grow larger, behaving more like impingement coatings
- **Doped films resist aging effects on steady-state friction by sequestration of unreacted $MoS_2$**
  - disruption of crystal growth by dopants during deposition creates dense films
  - dopants also prevent aggregation of flakes during contact and shear
  - smaller crystallites on the run-in surface create many reactive sites for oxidation, but this is confined to the top few layers

# Acknowledgments

- Mike Brumbach for XPS measurement of $MoS_2$ oxidation states
- Mark Rodriguez for XRD of coatings
- Morgan Jones and John Wellington-Johnson for tribology testing and coating aging

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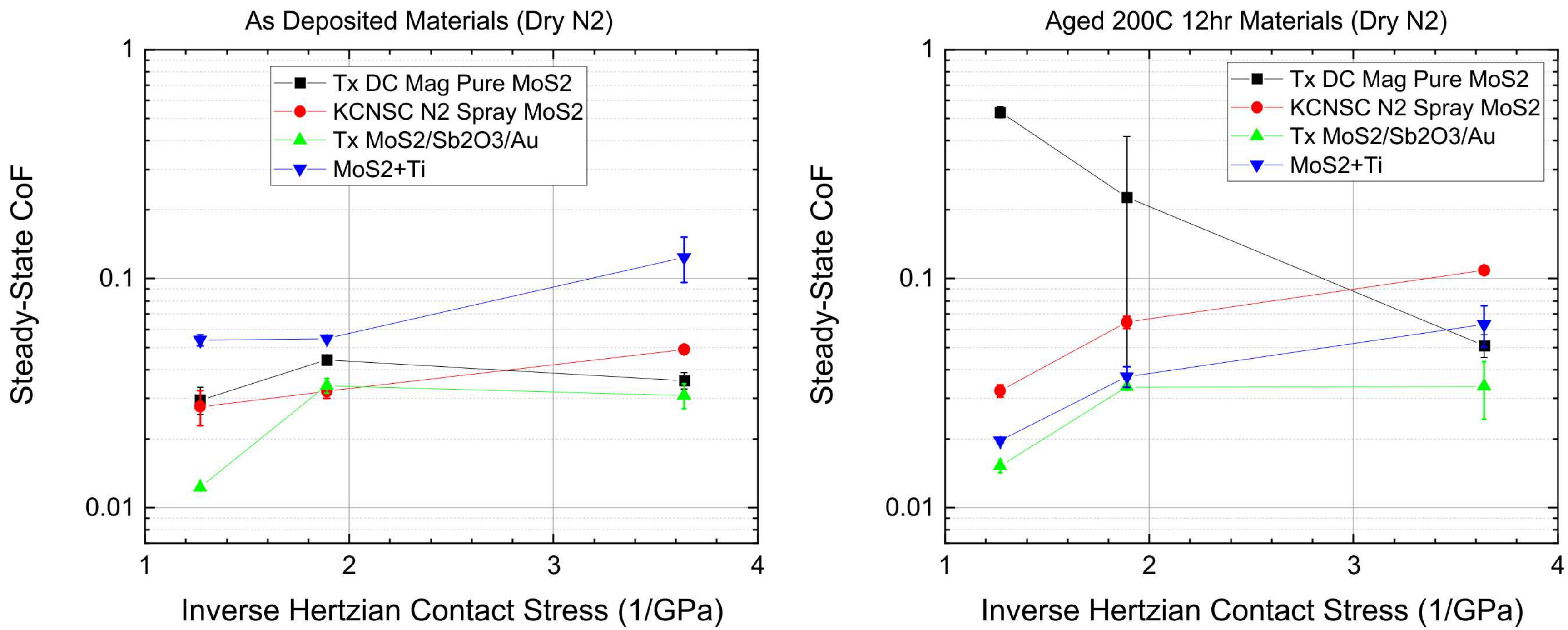
Backup

# Steady-State Friction Response to Accelerated Aging

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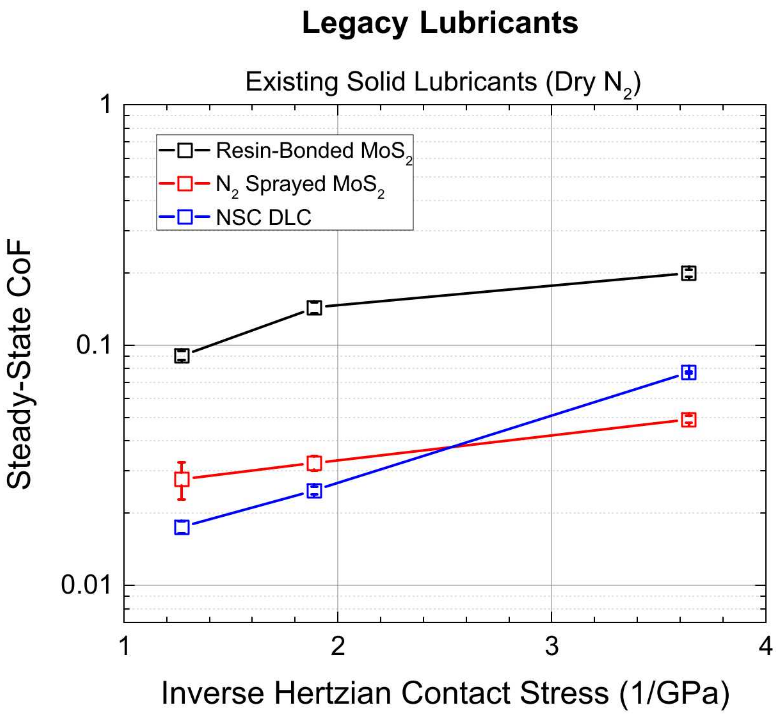
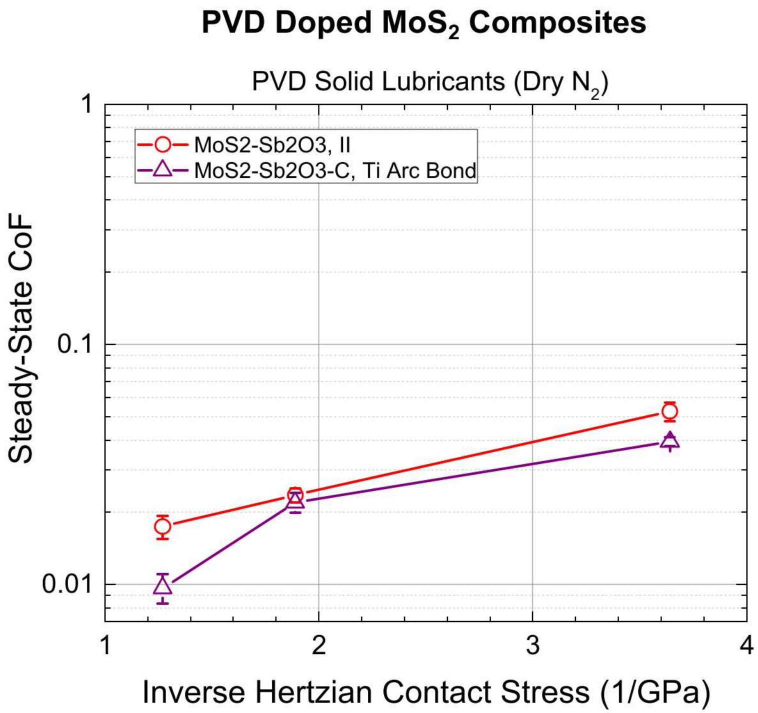
# Future Work

- Include adsorption and oxidation effects in shear model for pure $MoS_2$
- Incorporate defects, dopants and composite phases in MD model for $MoS_2$ composites
- Use $MoS_2$ shear model to design environment- and aging-resistant PVD solid lubricant for electromechanical mechanisms

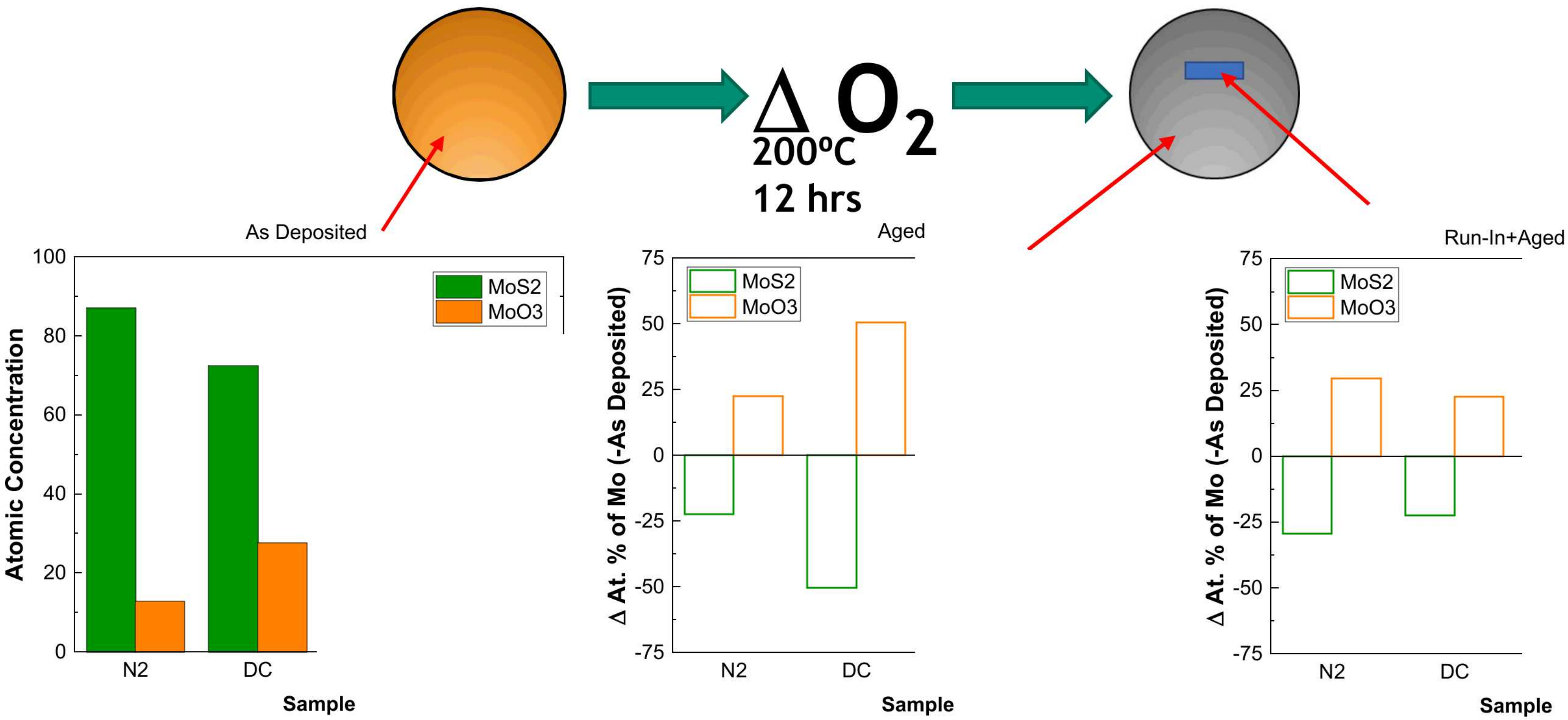
# Friction vs Stress in Dry $N_2$




- Impingement pure $MoS_2$ exhibits steady-state friction ≤ 0.05 at all stresses
- All doped $MoS_2$ composites exhibit lower friction coefficient than resin-bonded legacy coatings
    - several also exhibit lower friction than $N_2$ sprayed $MoS_2$ and DLC

# XPS of Aged Samples

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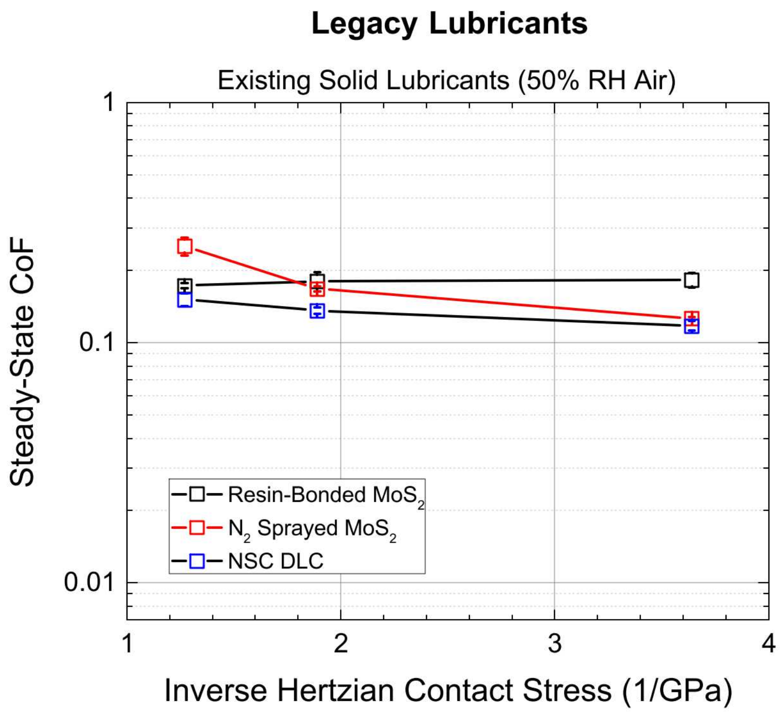
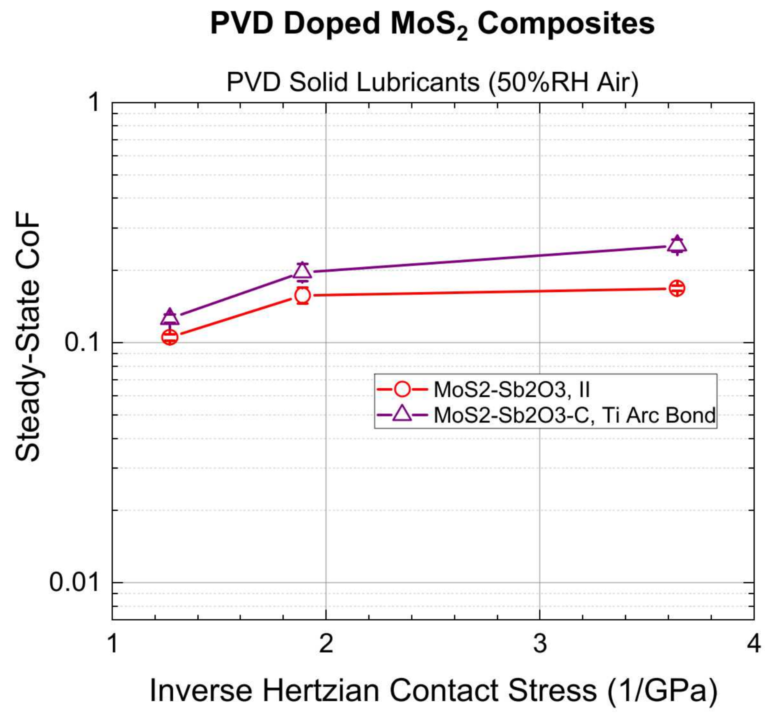
- Doped films exhibit Mo primarily as sulfide before aging
  - Aging produces a majority of Mo-oxide; previously run-in surfaces respond similar to the as-deposited surfaces

# Friction vs Stress in 50% RH Air




- All films exhibit increased friction compared to that in inert gas
  - the resin-bonded legacy film is the least impacted
- Several PVD coatings ($MoS_2$+$Sb_2O_3$+C) exhibit friction coefficient comparable to that of the legacy coatings

# Legacy Solid Lubricants and Processes

Resin-bonded films
- blast surface with $Al_2O_3$
- clean, mask, spray, cure, burnish, clean
- few parts at a time
- high volatile organic solvent use; carcinogens
- 2.5 μm minimum thickness

Spraying $MoS_2$ mixed with polymer binder

$N_2$ Sprayed $MoS_2$
- clean, mask, spray, clean
- one to few parts at a time
- 150 nm maximum thickness

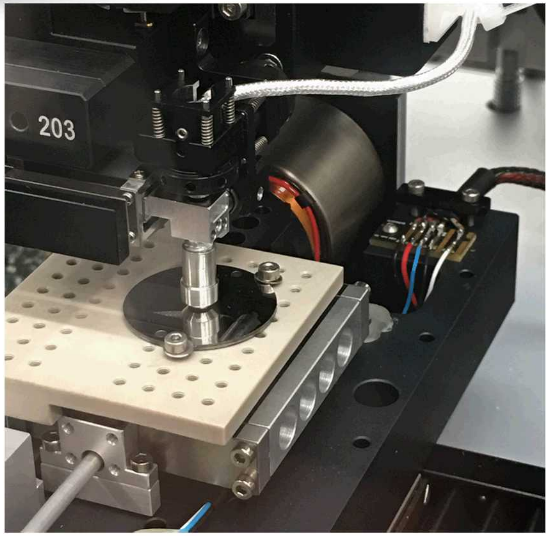
$MoS_2$ powder sprayed with $N_2$

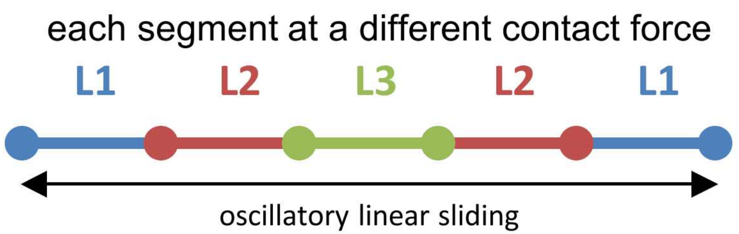
Harperized $MoS_2$
- clean, mask, tumble, clean
- batch process
- 150 nm maximum thickness

Parts tumbled in drum with $MoS_2$

# Friction Measurements: “Stripe” Tests

| Load, mN | Max Pressure, MPa | Track Length, mm | Test Sequence | Cycles | Total Distance, mm |
|---|---|---|---|---|---|
| 21 | 275 | 5 | L1 | 300 | 1500 |
| 149 | 530 | 3 | L2 | 500 | 3000 |
| 484 | 785 | 1 | L3 | 1500 | 4500 |



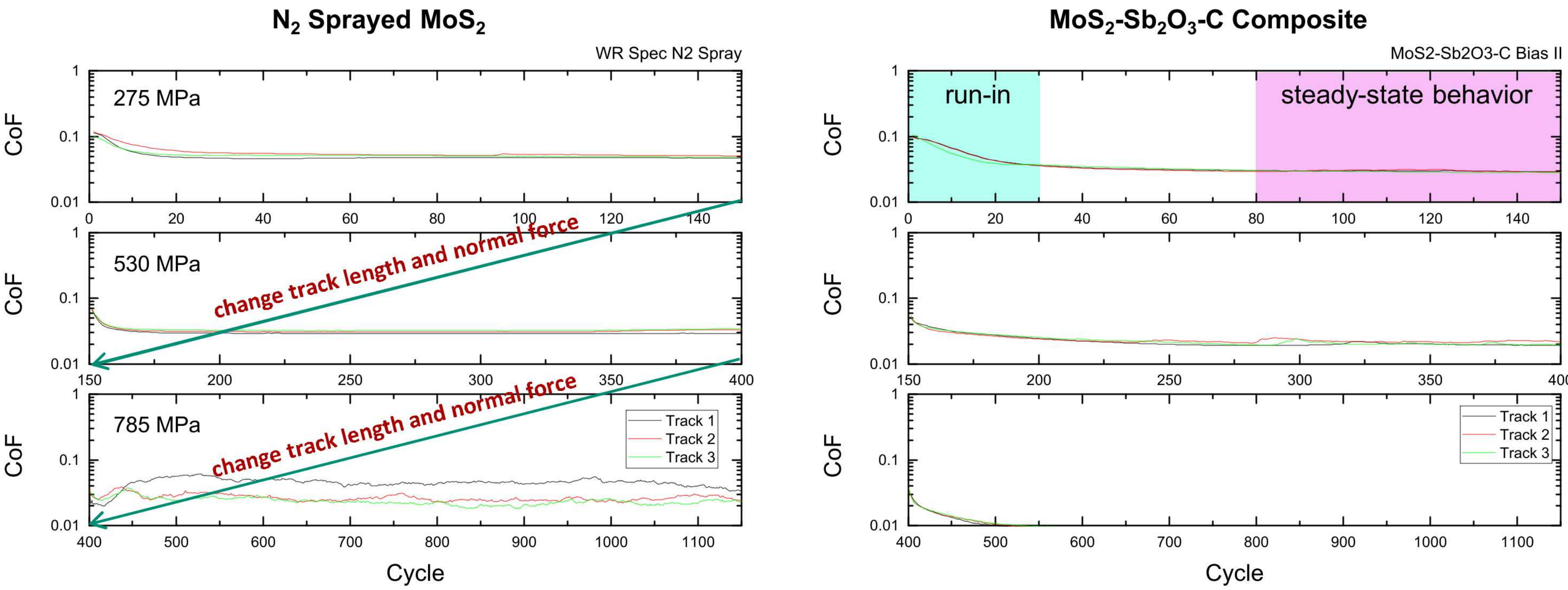




Test parameters:

- 440C ball, 3.2 mm diameter
- 1 mm/s sliding speed
- Controlled atmospheres:
    - dry $N_2$ (<10 ppm $O_2$, <50 ppm $H_2O$)
    - 50% RH air

Permits performance assessment over a range of contact pressures

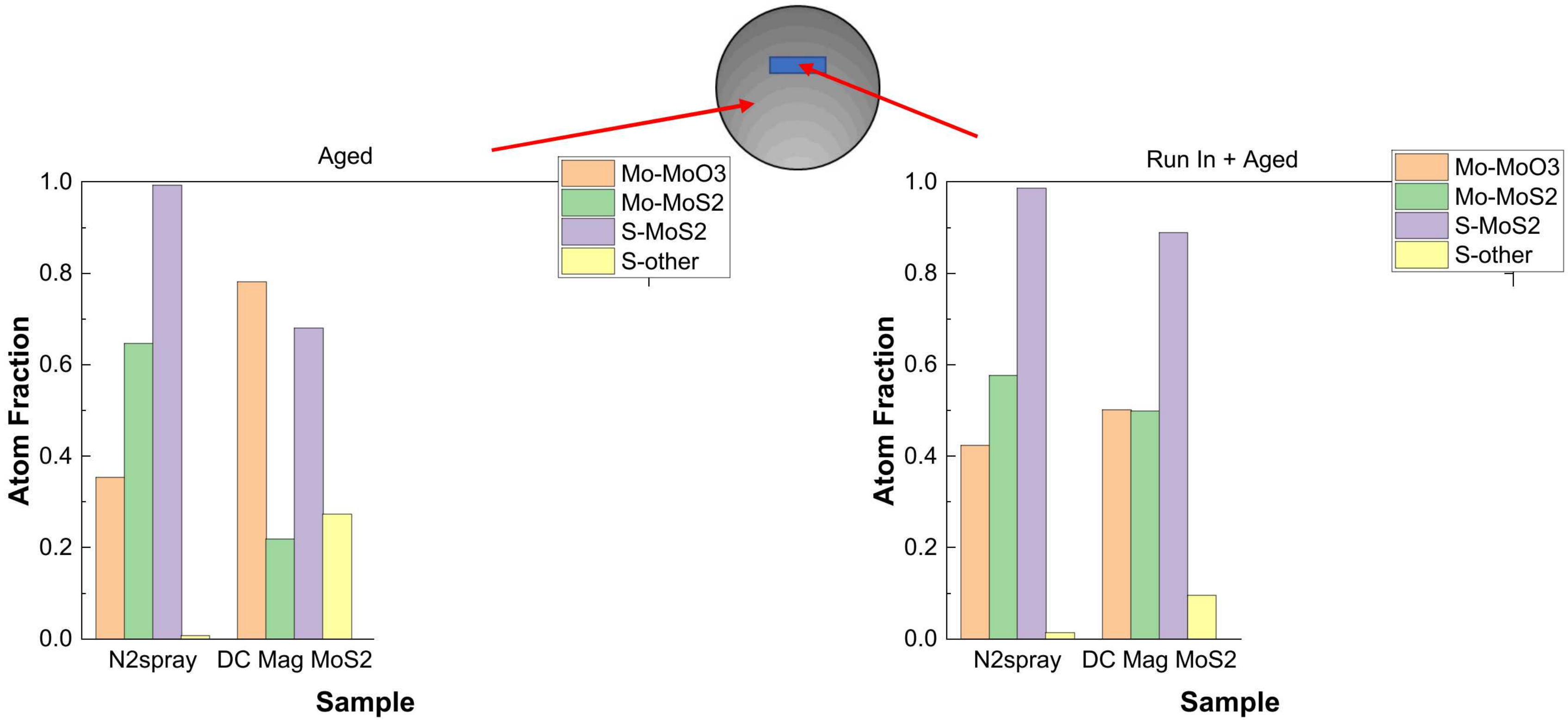
# Friction Coefficient Traces from "Stripe" Tests




Friction coefficient decreases as stress increases, typical of solid lubricant behavior

Consider steady-state performance at each stress

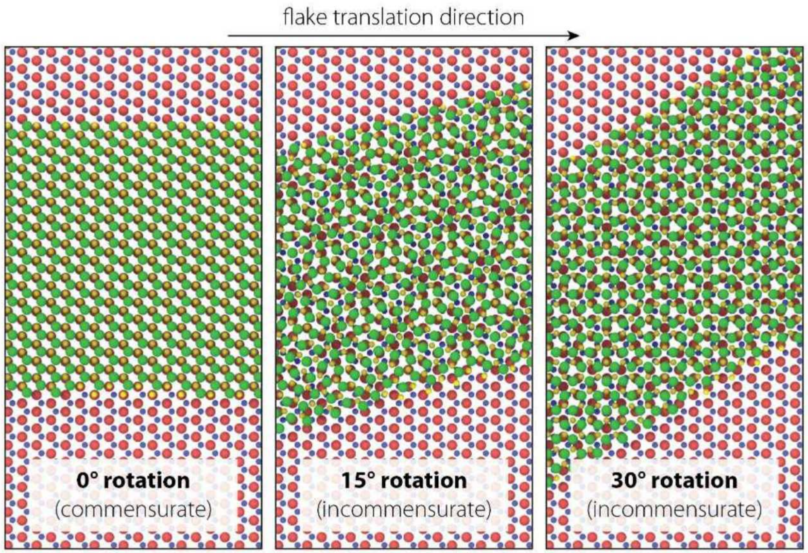
# XPS of Aged Samples

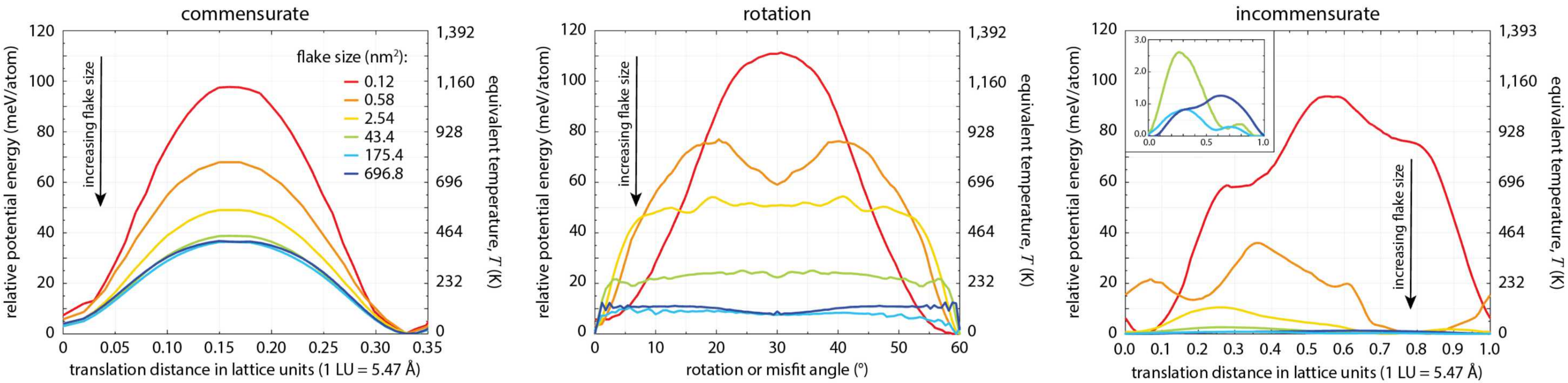



- The DC magnetron sputtered pure $MoS_2$ responds to aging similar to $N_2$ sprayed films after run-in
- Oxidation of the $N_2$ sprayed and doped-$MoS_2$ surfaces are minimally impacted by run-in prior to aging

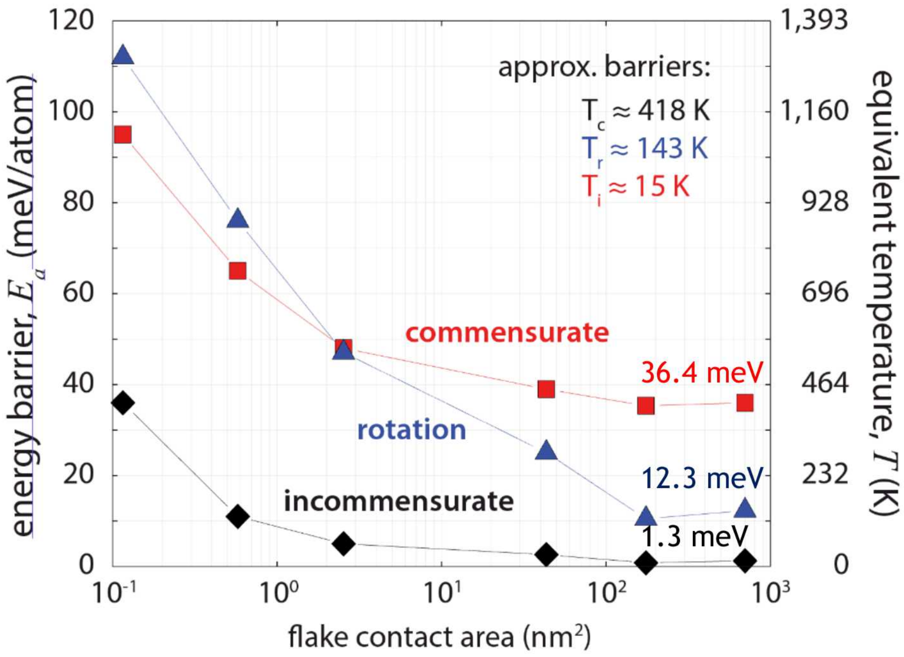
# NEB Calculation of Energy Barriers

- Flakes of increasing size forced to translate/rotate and calculated required energies
- Energy barriers converge at larger flake sizes
- Commensurate sliding most energetically expensive route; incommensurate sliding **28X** less expensive



# Converged Barriers & Analytical Model




The probability ($p_n$) and failure ($f_n$) to overcome a barrier:

$$p_n = A\exp\left(\frac{-\Delta E_n}{k_B T}\right)$$

$$f_n = 1 - p_n$$

The probability to slide and fail to slide (friction):

$$p_{slide} = p_r p_i + f_r p_c$$

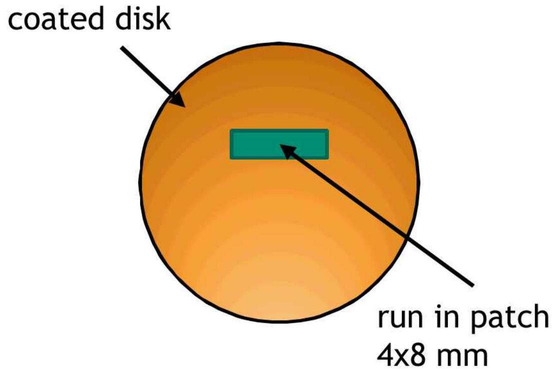
$$f_{slide} = 1 - p_{slide}$$

$$= 1 - \left(p_r p_i + f_r p_c\right)$$

- Model based on probability to overcome energy barriers to translation & rotation (Arrhenius)
- Expressed as inverse (1-exp) due to failure to thermally diffuse and slide under shear

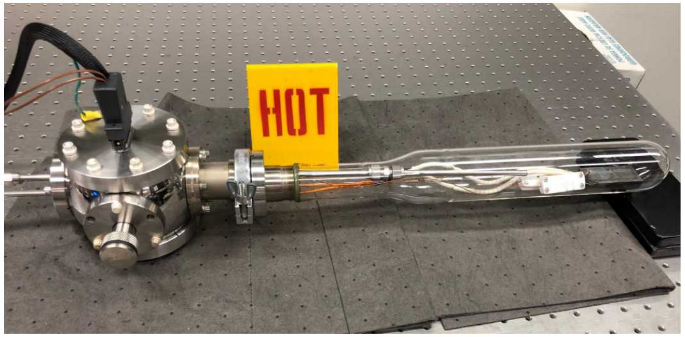
# Experimental Setup

## Run In



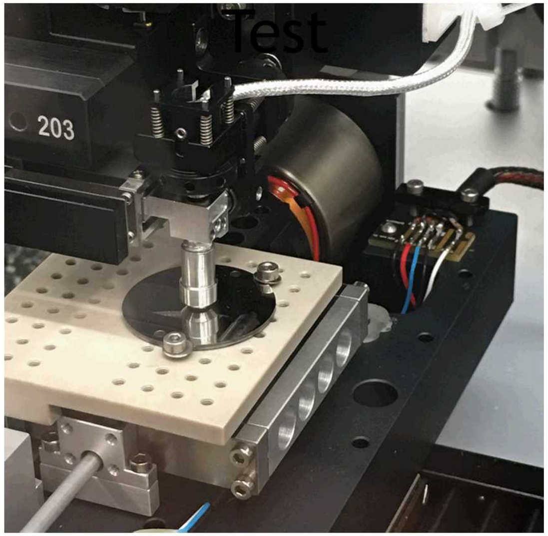

- 13-8PH or 440C stainless steel disks
- run in at 530 MPa, 50 passes, overlapping areas

## Accelerated Age




- 200ºC, dry (DP < -60ºC) air, 5 SCFH
- 12 hours

## Friction (Stripe) Test




- 440C ball, 3.2 mm dia.
- 1 mm/s sliding speed
- Hertz contact pressures of 275, 530 and 785 MPa

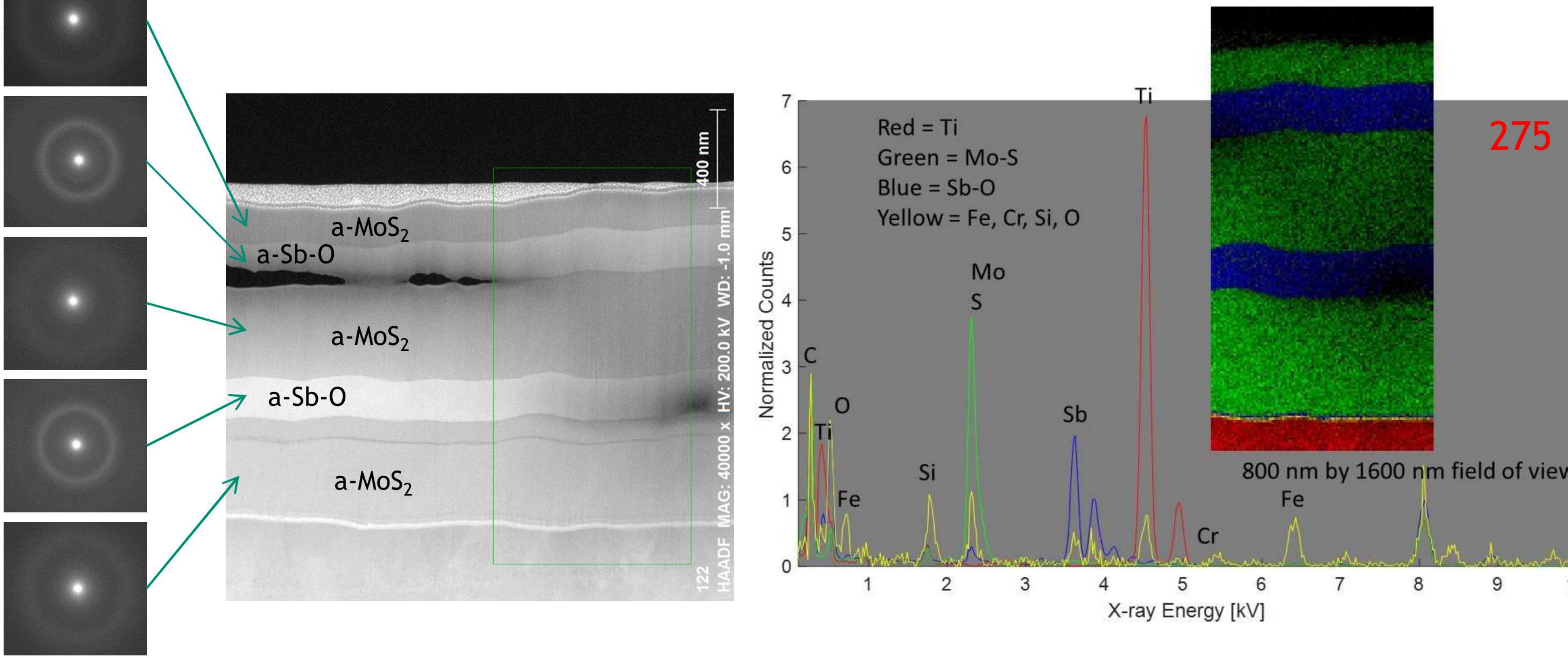
Samples were run-in prior to aging to examine the effects of accelerated aging on the structurally modified lubricant surfaces

# Film Compositions Investigated

- $N_2$ Sprayed $MoS_2$
- DC Magnetron Sputtered $MoS_2$ (Tribologix)
- RF Magnetron Sputtered $MoS_2$+$Sb_2O_3$+Au (Tribologix)
- RF Magnetron Sputtered $MoS_2$+Ti by (Teer)

**Pure $MoS_2$** (first two items)

**Doped $MoS_2$** (last two items)



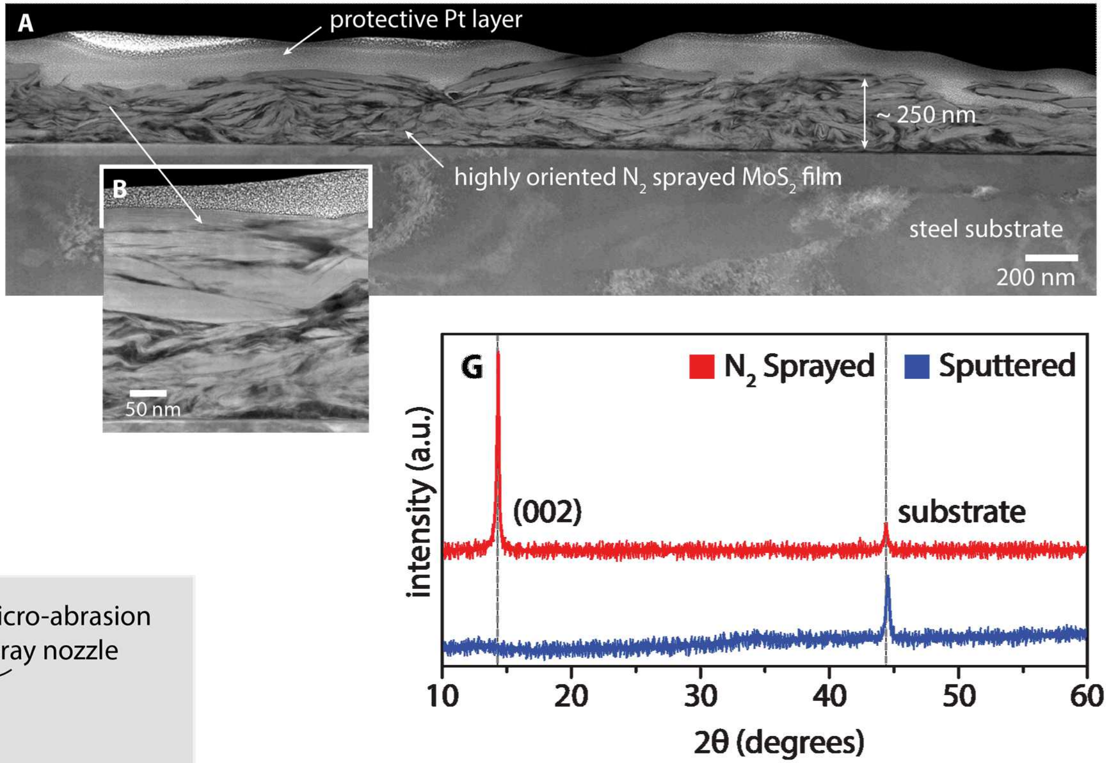
# Highly Ordered $MoS_2$ Coatings

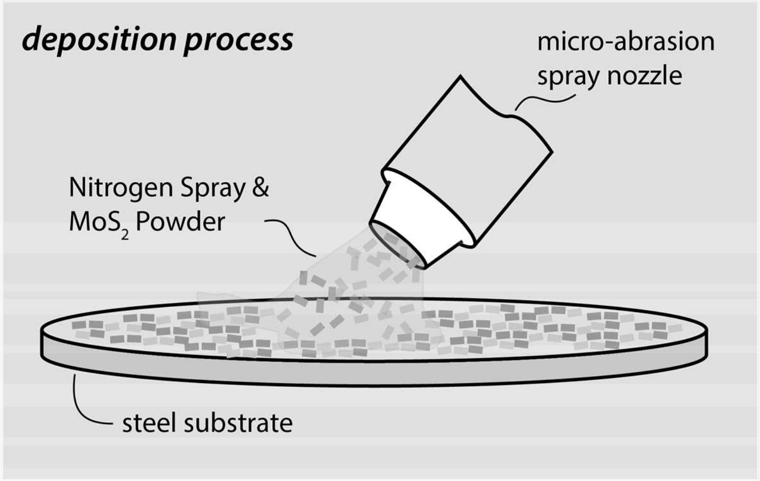
**Nitrogen Spray Deposited $MoS_2$**

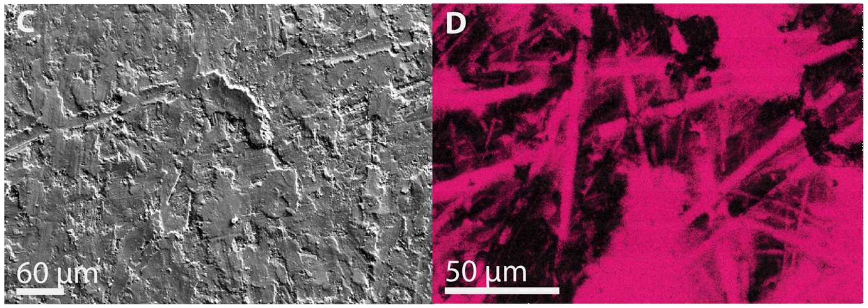
- Deliver $MoS_2$ powder to surface in dry $N_2$ gas

- High kinetic energy imparted shears $MoS_2$ onto surface to produce a higher orientation of basal planes.

- Similar to burnishing, large continuous crystallites will form, reducing presence of surface defects



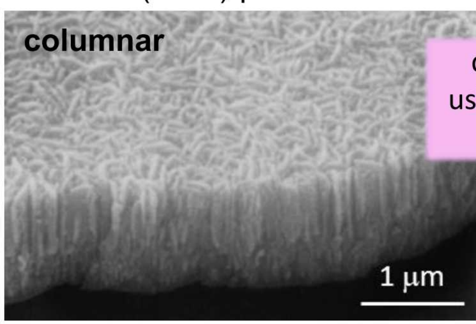



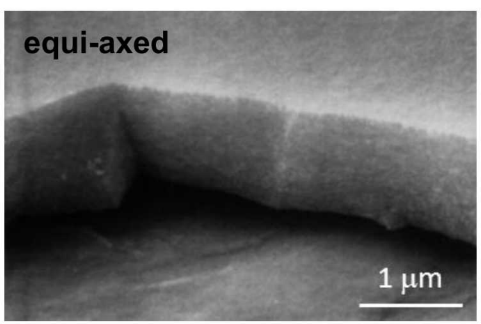
# Doping in $MoS_2$ Films Increases Density

- Tailored film structures improve performance in a range of atmospheres
- Wear rates are improved by densification and inclusion of hard, load-supporting phases

M.R. Hilton, et al., *Surf. Coatings Tech.* **53** (1992) p.13-23

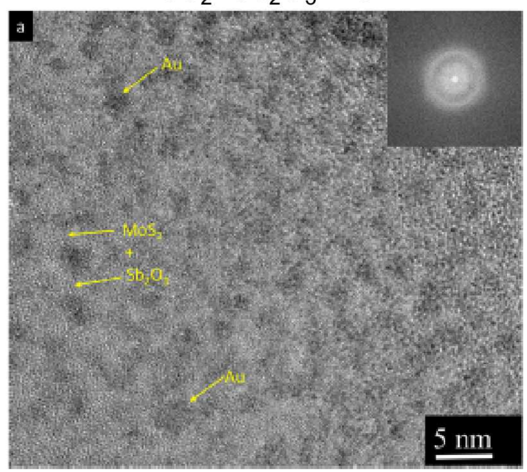



densification using deposition parameters



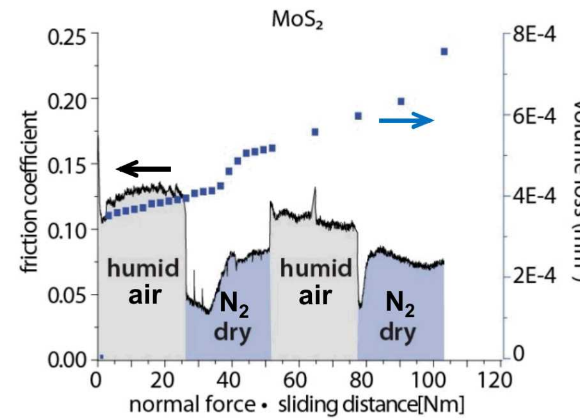

*densification through composition control*

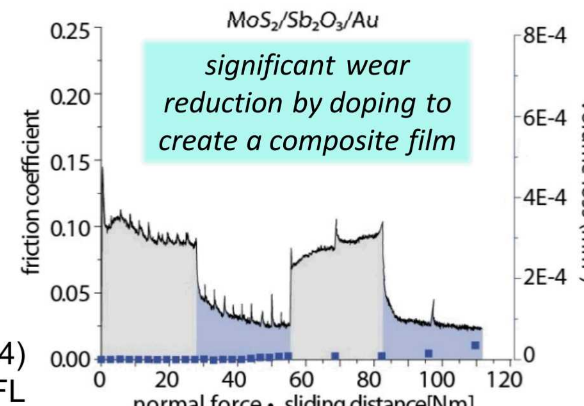
$MoS_2$+$Sb_2O_3$+Au




H. Singh et al., *Surf. Coating Tech.* **284** (2015) p. 281-289

R.S. Colbert, *Ph.D. Dissertation* (2014) U. of Florida, Gainesville, FL

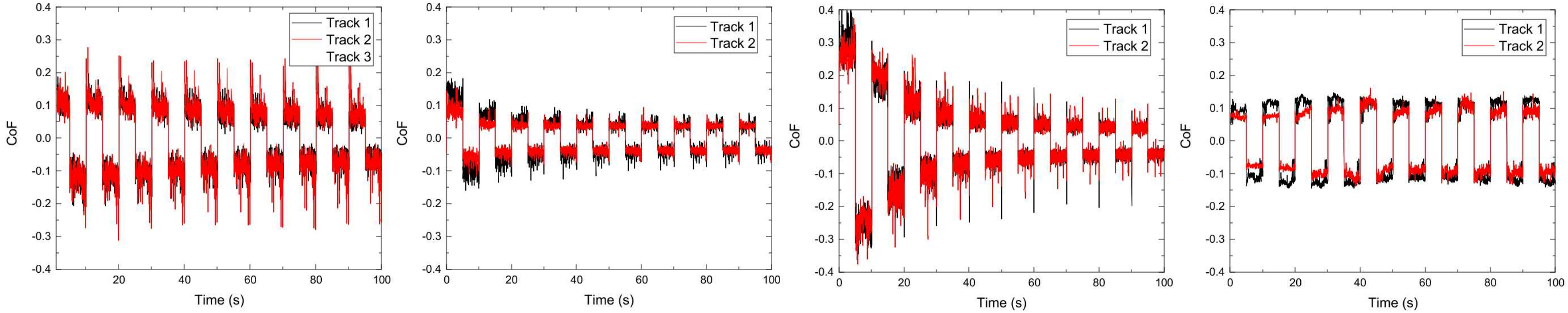


# Run-In Behavior

$N_2$ Spray | DC Mag $MoS_2$ | $MoS_2$+$Sb_2O_3$+Au | $MoS_2$+Ti

As Dep




- $N_2$ sprayed $MoS_2$ and $MoS_2$+Ti exhibit no run-in during as-deposited tests
- Aging increases initial friction coefficient in all except $N_2$ sprayed and $MoS_2$+$Sb_2O_3$+Au