



Exceptional service in the national interest

STRUCTURAL, ENVIRONMENTAL AND MECHANOCHEMICAL INTERACTIONS AT THE INTERFACES OF LUBRICATED PRECISION MECHANISMS

UC Merced Seminar

September 27th, 2024

Dr. John F. Curry

Sandia National Laboratories

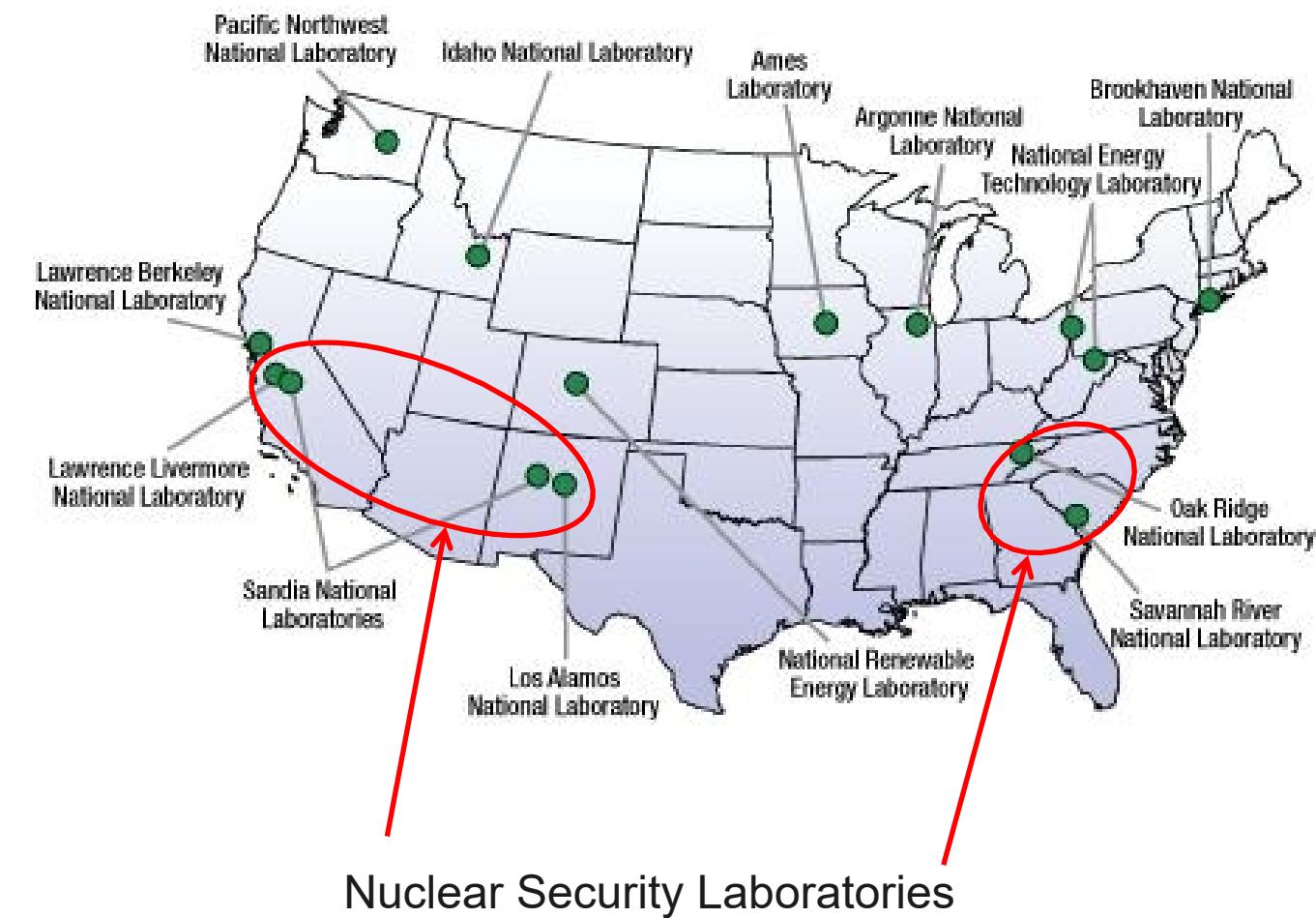


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SANDIA NATIONAL LABORATORIES – WHERE WE ARE



A U.S. Department of Energy multi-program laboratory, with responsibility for the safety, security and reliability of the nation's nuclear deterrent.



SANDIA NATIONAL LABORATORIES – WHO WE ARE



Division

Science & Engineering Foundations



Directorate

High Perf. Computing

Engineering Sciences

Materials, Physical & Chemical Sciences

Microfabrication S&T

Nuclear Weapons S&T

Pulsed Power

Radiation Science



Department

Advanced Ceramics

Computational Mat. Sci.

Optical & Electronic Matls

Materials Characterization

Metallurgy & Joining

Coatings & Additive Mfr.

Mechanics & Tribology

Organic Materials Science

Materials Aging & Reliability

What's that?





TRIBOLOGY: /TRĪ' BÄLƏJĒ/ NOUN (FROM GR “TRIBOS” TO RUB)

THE SCIENCE OF INTERACTING SURFACES IN RELATIVE MOTION; THE STUDY OF FRICTION, WEAR, AND LUBRICATION

Cookware

- Anti-stick coatings
- Knife edges
- General wear & tear

Consumer Electronics

- Connectors & chargers
- Handheld electronics

Transportation

- Tire tread wear
- Engine wear & additives
- Frictional losses to heat



IT'S ALL AROUND US IN
EVERYDAY LIFE

Furnishings

- Textiles & Fabrics
- Caster wheels & joints
- Protective finishes on handles/knobs

Fitness & Apparel

- Shoe treads
- Clothing feel & wear
- Anti-friction gels

Personal Hygiene

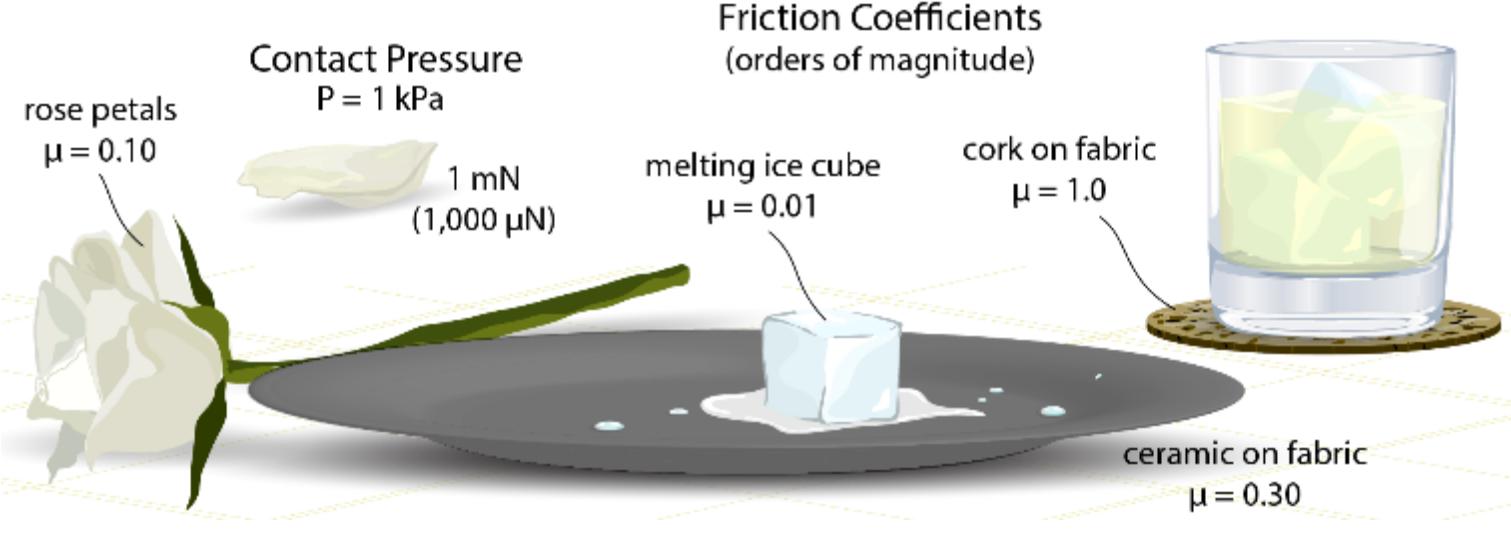
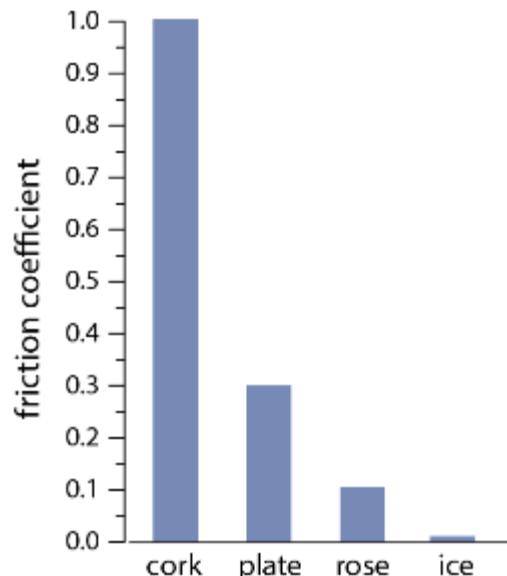
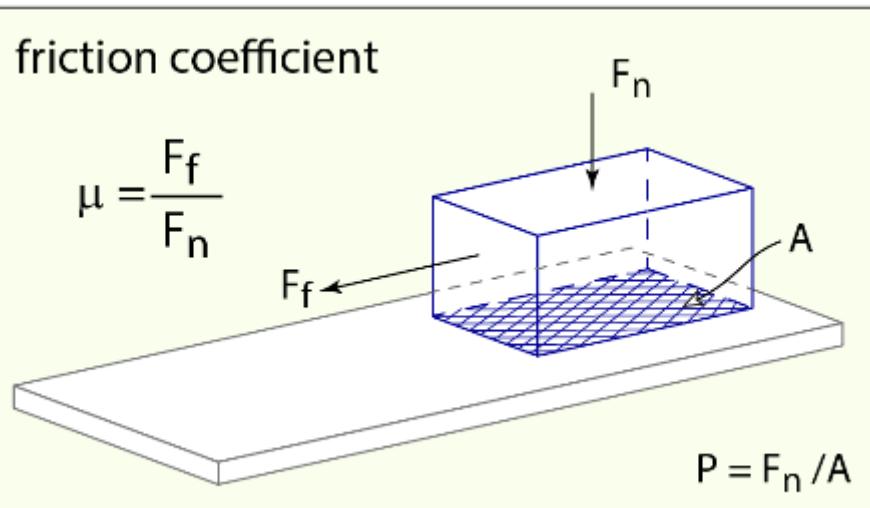
- Contact Lens Friction
- Plaque & Enamel Wear
- Lotion/Cream Physico-Tribology

TRIBOLOGY FUNDAMENTALS – FRICTION & WEAR



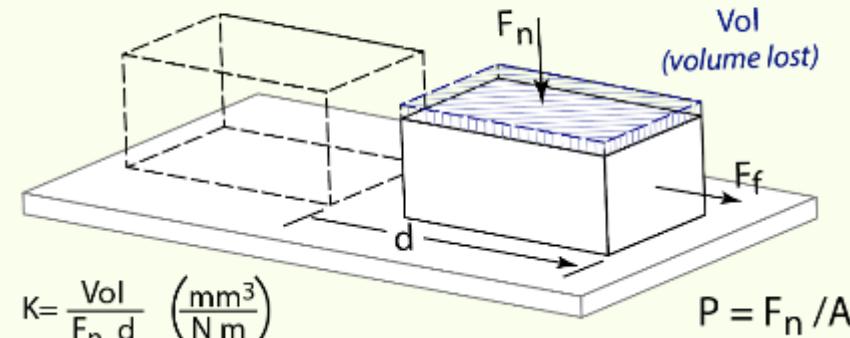
friction coefficient

$$\mu = \frac{F_f}{F_n}$$

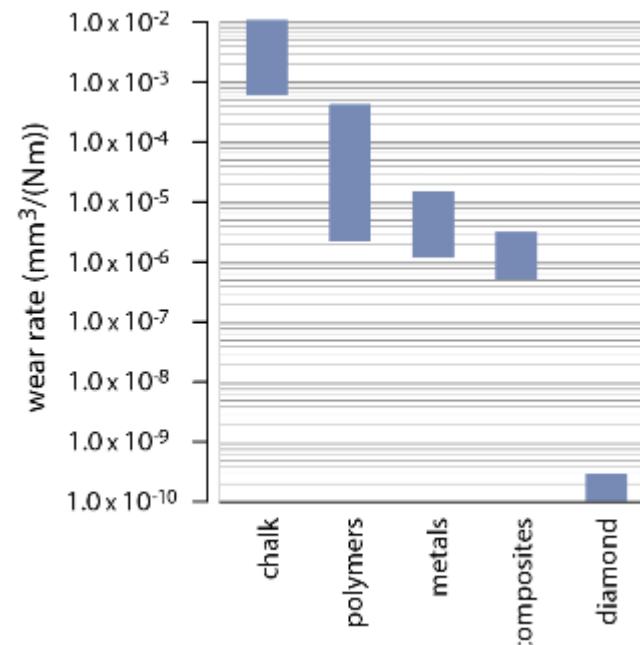


wear rate

(volume lost per unit normal load per distance of sliding)



$$K = \frac{Vol}{F_n \cdot d} \left(\frac{\text{mm}^3}{\text{N m}} \right)$$



high performance carbon materials
 $K \sim 1 \times 10^{-10} \text{ mm}^3/\text{Nm}$

SUBSTANTIAL IMPACTS ACROSS MAJOR SECTORS

Power Generation

Advances in tribological materials increase efficiencies of power generation systems and enable renewable technologies (i.e., wind energy) to be more competitive. Collectively can save ~4 quads energy/ year.



Transportation & Manufacturing

These sectors account for well over 50% of energy use in US economy. One third of this (~ 8 quads) is spent overcoming friction and wear.



Aerospace

Wear, limitations in performance, reliability product life, and maintenance cost the US DoD billions of dollars annually.



With peak US energy consumption over 100 quads (quadrillion BTUs) in 2019, advances in technologies enabled by targeted research support in tribology alone could save 20% (20 quads) of energy annually.¹



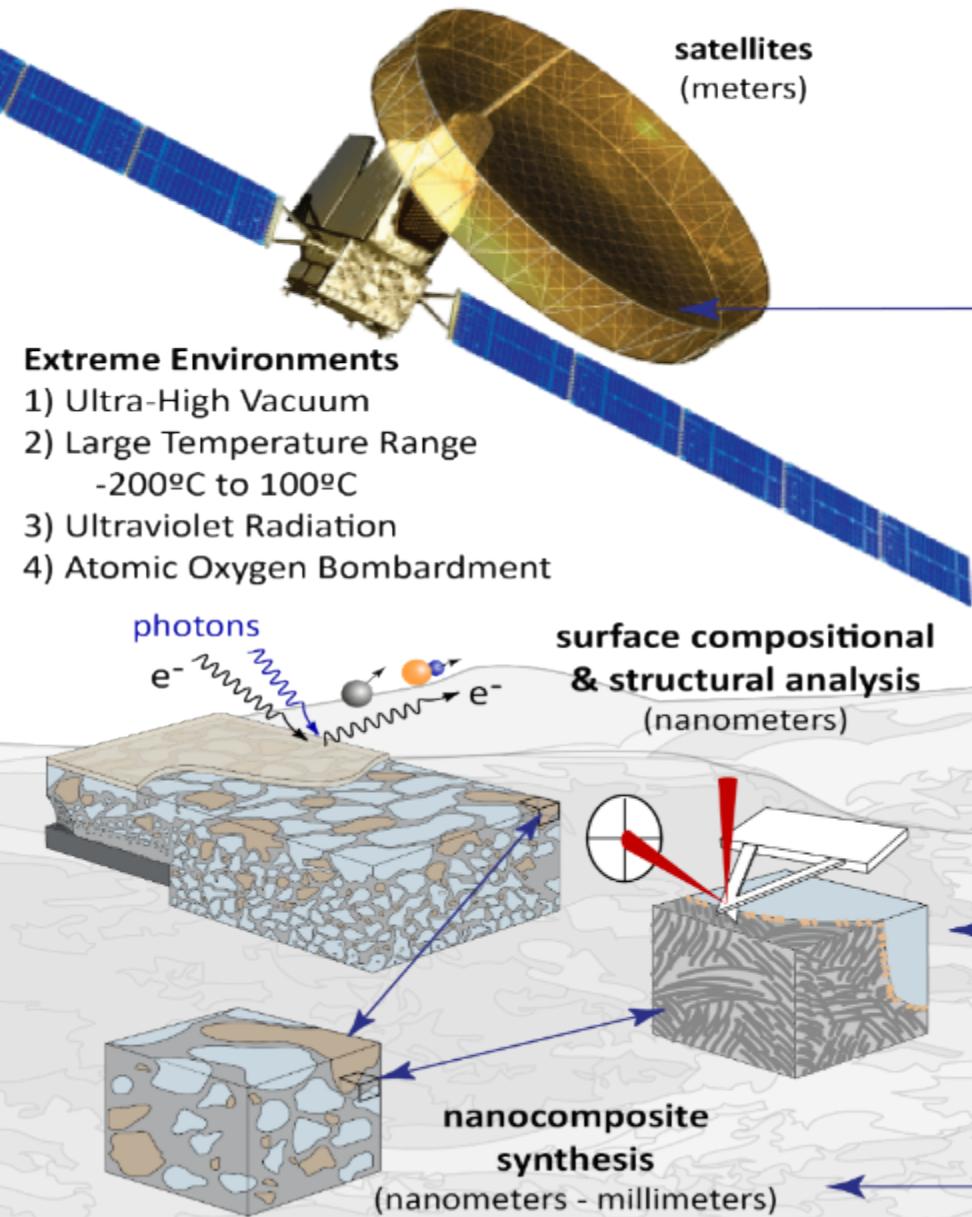
[1] Carpick, R. W. et al. *Tribology & Lubrication Technology* 72, 44 (2016).

BioTech

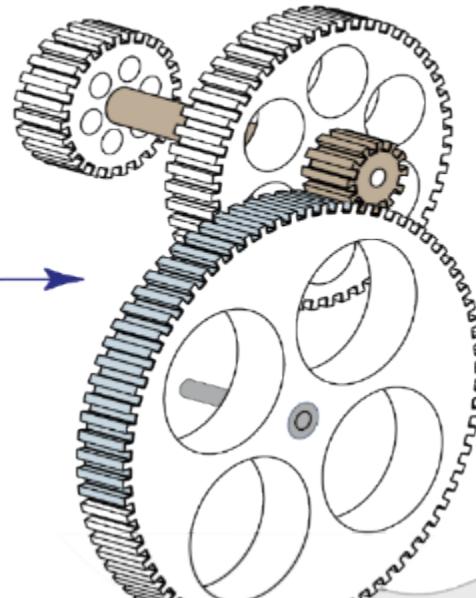
Over 280,000 Americans receive knee replacements annually for the treatment of arthritis — 10% of implanted knee replacements are revisions.



FUNDAMENTAL & APPLIED CHALLENGES FOR AEROSPACE (SNL)

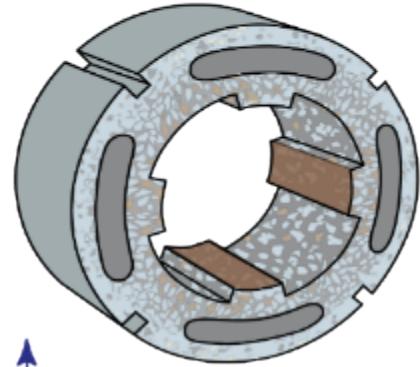


moving mechanical assemblies (millimeters - centimeters)



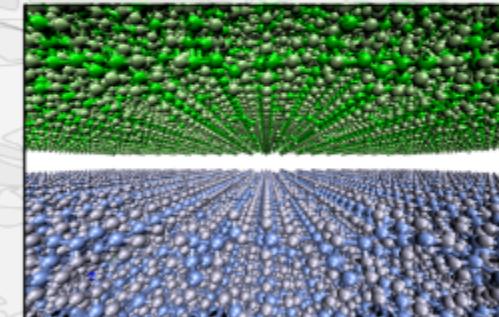
moving mechanical assemblies often have 1,000:1 reductions and friction management is essential for successful operation (almost every surface has a coating)

(1) Solid lubricant coatings & (2) electrical contacts (millimeter - micrometers)

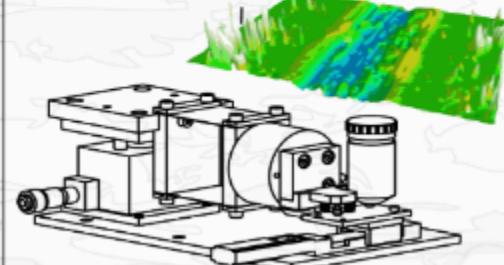


Other Examples:
vacuum products, biomedical, semiconductors, x-ray equipment, spectrometers, furnaces, etc...

molecular dynamics design of adaptive tribofilms



multiscale & multivariate tribometry (nanometers - millimeters)

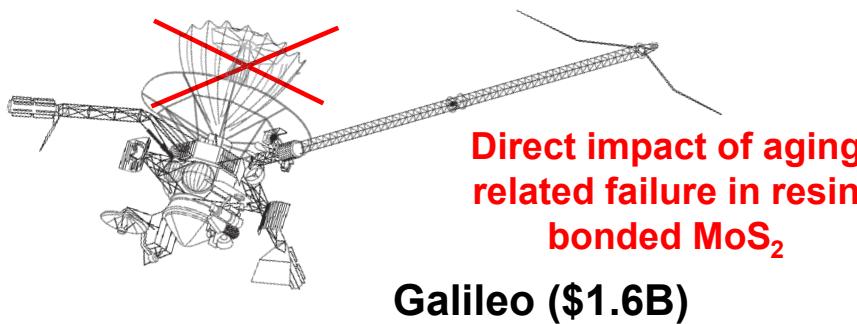


NO FAILURE OPTION FOR PRECISION MECHANISMS



Aerospace

- 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



Failure: Antenna failure due to high friction between standoff pins and sockets.

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.”

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





ADVANCED DEVELOPMENT MOS_2 SOLID LUBRICANTS

MOLYBDENUM DISULFIDE (MoS_2) SOLID LUBRICANTS

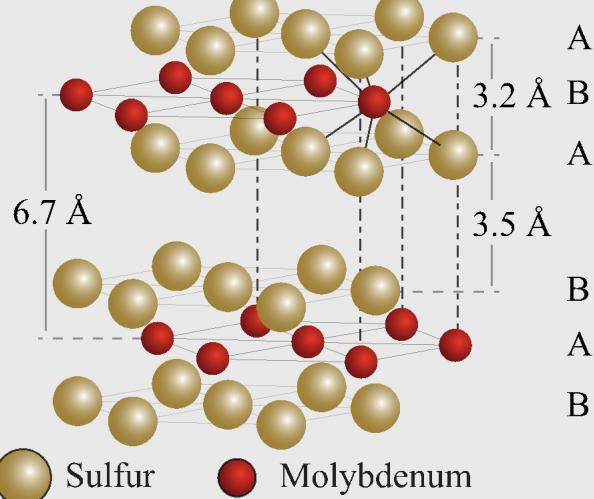
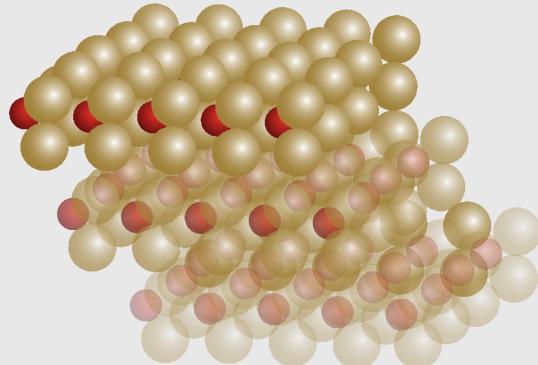


What is it?

molybdenum disulphide

$\mu = 0.02 - 0.06$ (inert @ 1N)

$\mu = 0.15 - 0.25$ (humid air @ 1N)

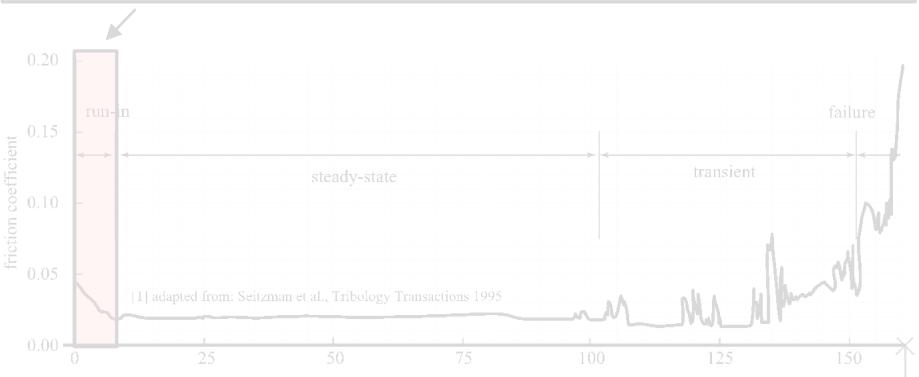
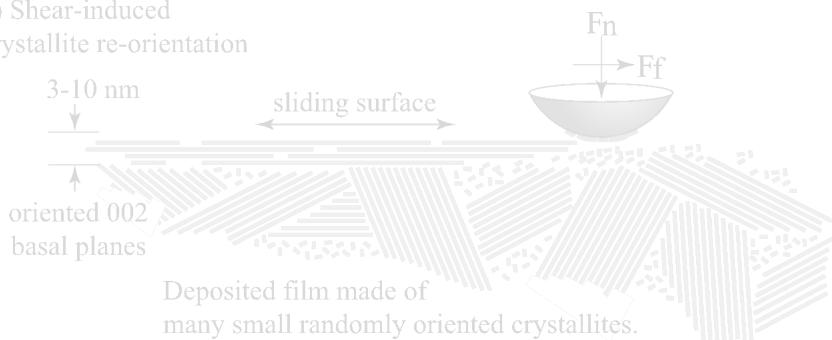


How does it work?

generalized run-in processes



2) Shear-induced
crystallite re-orientation



How is it made?

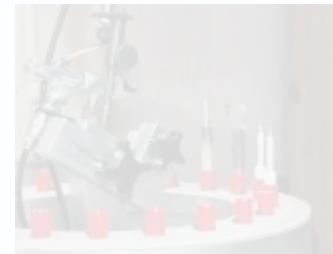
Unbonded (1860s+)

- Burnished or sprayed powder
- Typically basally oriented
- Easy/cheap to apply on parts
- Poor adhesion/thickness control



Resin-bonded (1939+)

- Bead-blasted surfaces
- Resin/MoS2 powder mix
- Sprayed and cured
- 1-10 μm thick



Sputtering (1967+)

- Physical vapor deposition
- Precise thickness, adhesion, densification, dopants
- Composites that operate in different environments
- Expensive – reticence in adoption



ENVIRONMENTAL SENSITIVITIES – STEADY STATE



UV Ozone / Atomic Oxygen



Wu & Hawthorne et al, unpublished

Water

room temp oxidation pathway for H_2O & O_2



Am. C 123, 7486-7494 (2019)

Reaction and diffusion
at the surface layer
interrupts
oxidation.



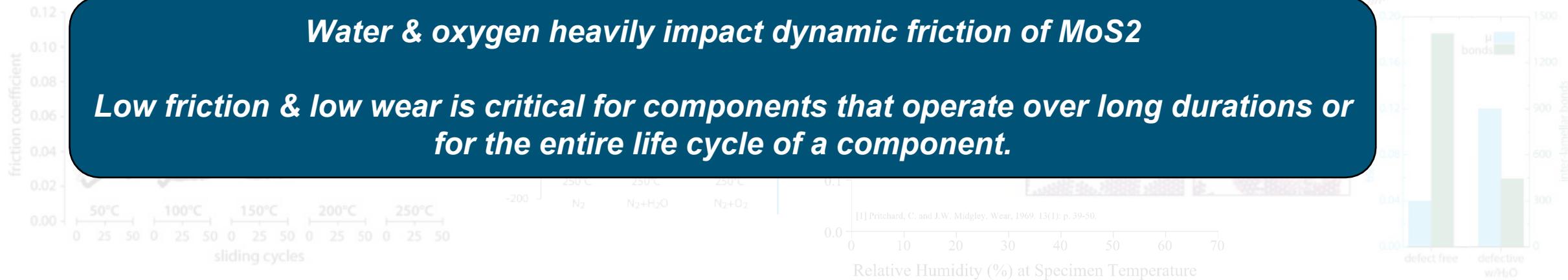
Air (O_2 & H_2O)

Water & oxygen heavily impact dynamic friction of MoS₂

Low friction & low wear is critical for components that operate over long durations or for the entire life cycle of a component.



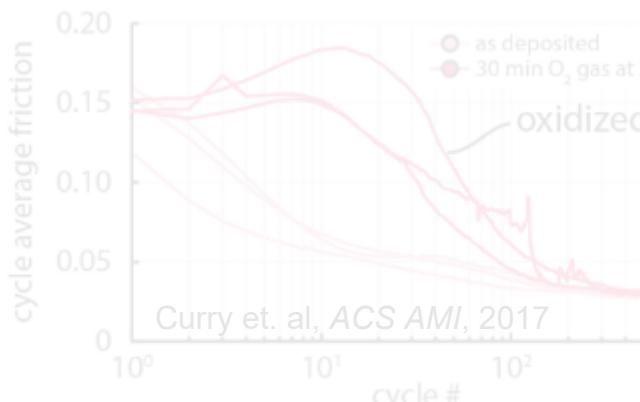
Relative Humidity (%) at Specimen Temperature



ENVIRONMENTAL SENSITIVITIES – INITIAL FRICTION & AGING



Oxidative Aging Effects On Friction & Wear Behavior

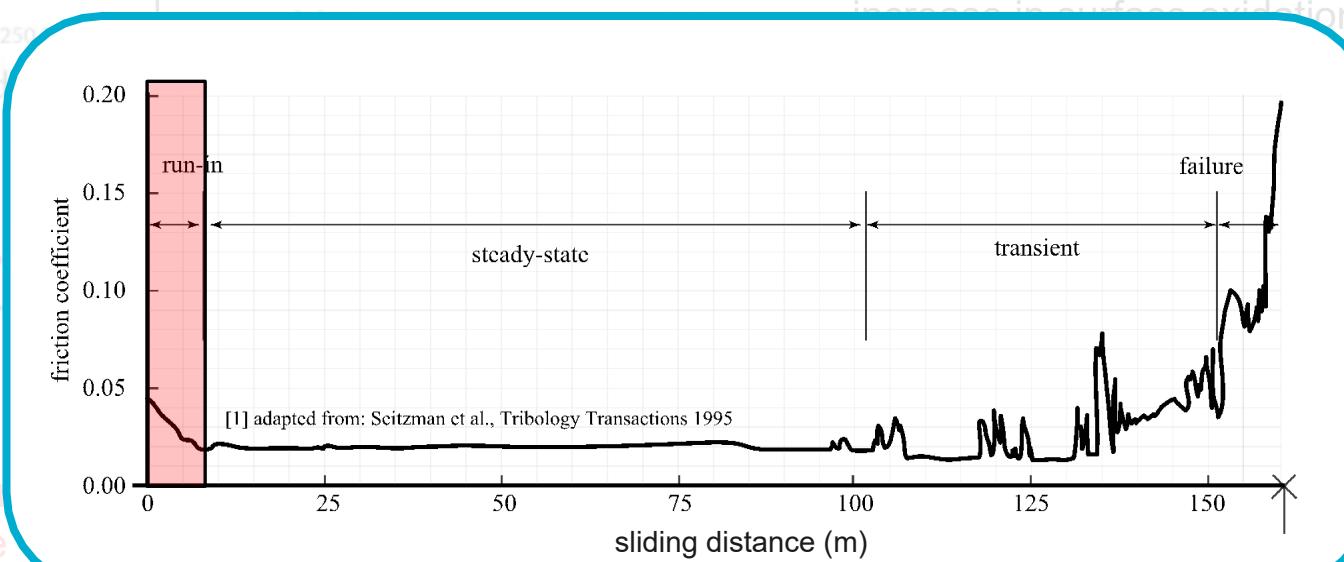


80% reduction in coating lifetime

Impact of Crystallinity/Orientation

Mo 3p signal - Mo₃:MoS₂ ratio

Amorphous films have ~5x longer lifetime for crystallization



Aging & oxidation heavily impact initial friction where many components operate

Influences motor torque/size, fuel/energy budgeting across entire mechanisms

Extremely important to understand how to manipulate/control



Babuska et. al., ACS Nano Letters, 2023

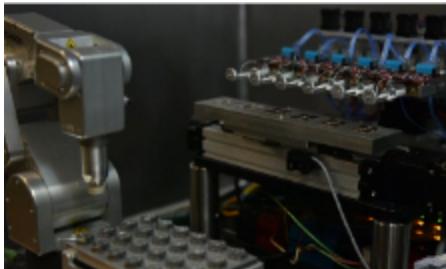


TECHNICAL APPROACH & CAPABILITIES



Mechanical, Topographical & Aging Test Capabilities

High-throughput Friction Testing

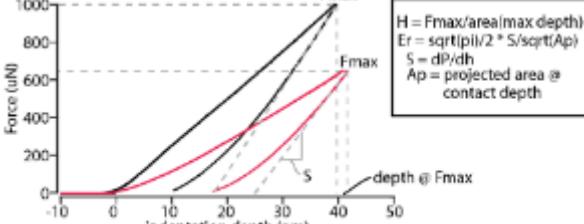
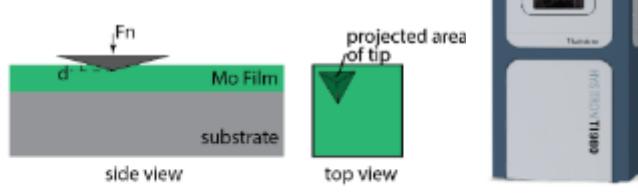


Custom-built; test 6 coatings at once

- Initial friction
- Run-in behavior
- Steady-state friction

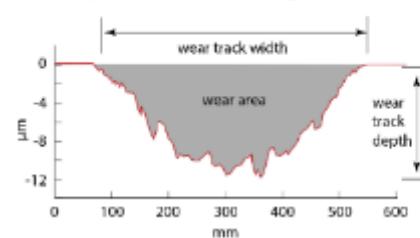
Nanoindentation

- Hardness/modulus



Scanning White Light Interferometry (SWLI) - Wear Rate (mm³/Nm)

A representative 2D slice through the wear track.



Oxidative Aging

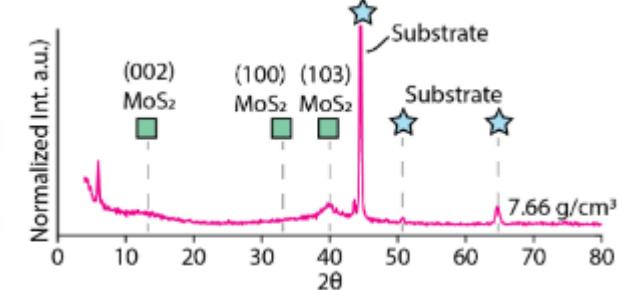
- 48 hours @ 300°C



Many methods above can be done rapidly, capturing insightful information on structural elements for development.

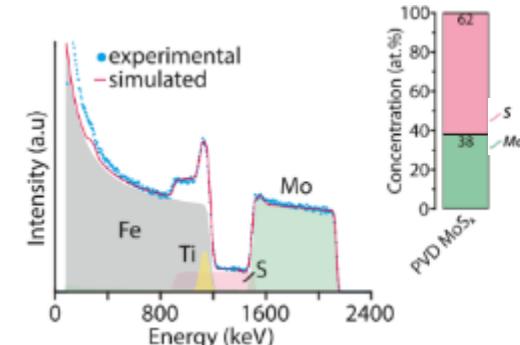
X-Ray & Ion Scattering Spectroscopies

X-Ray Diffraction (XRD)



- Crystallographic information

Rutherford Backscattering Spectrometry (RBS)



Babuska et. al.,
Langmuir, 2024

- Areal density (at/cm³), composition

INFLUENCE OF PVD PROCESS VARIABLES ON HARDNESS

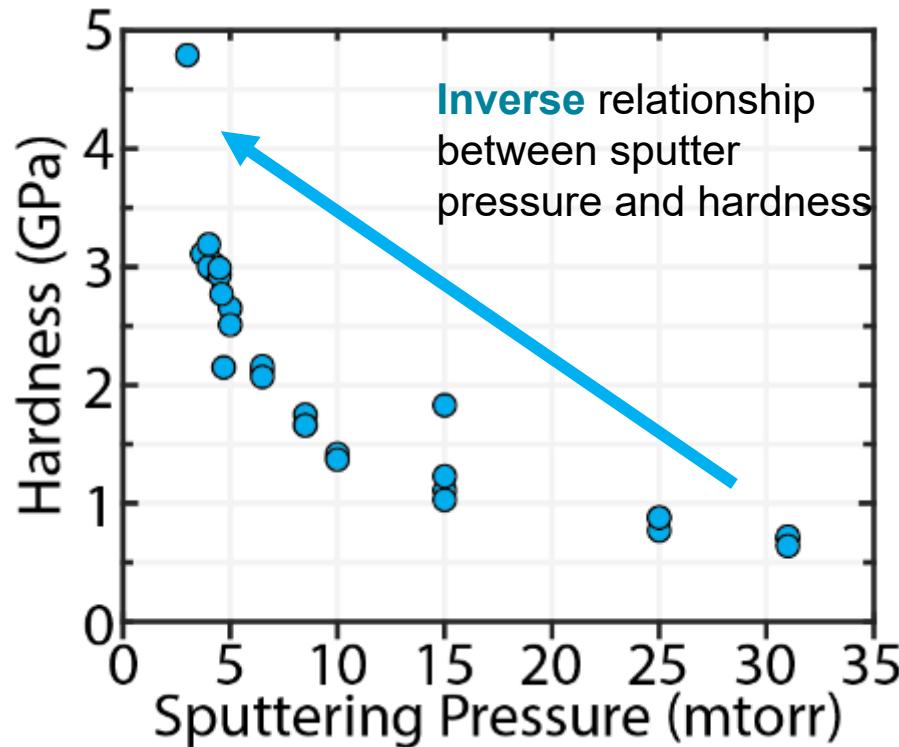


Process Variables

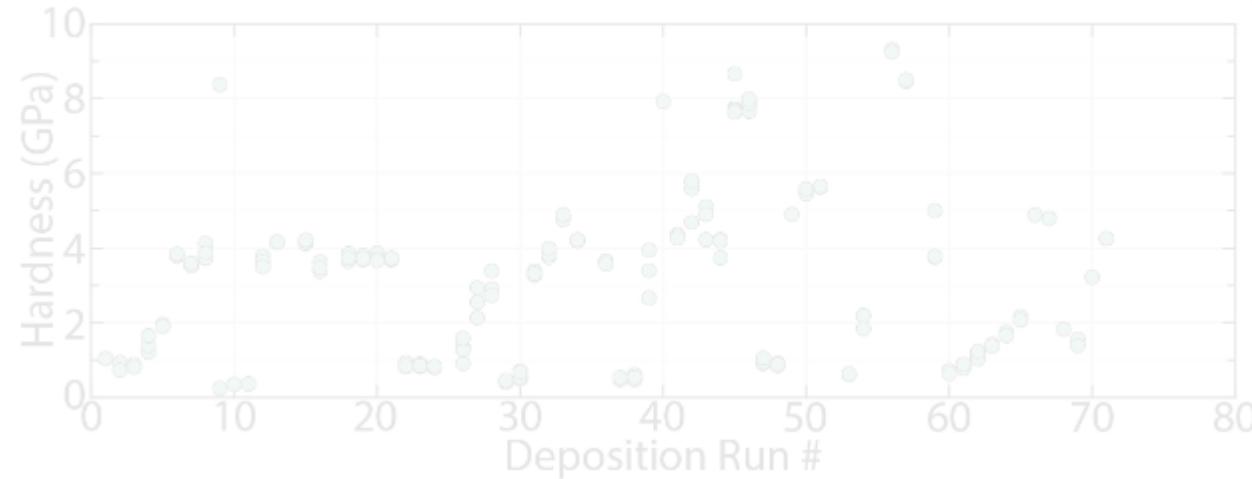
Depending on deposition type: **DC, RF, HIPIMS, PDC**

AND process parameters such as:

↓ Sputtering pressure ↓ Power ↑ Bias Voltage ↑ Dopant concentration (added metal/metal oxides)



Observed changes in Hardness across Dep. Runs



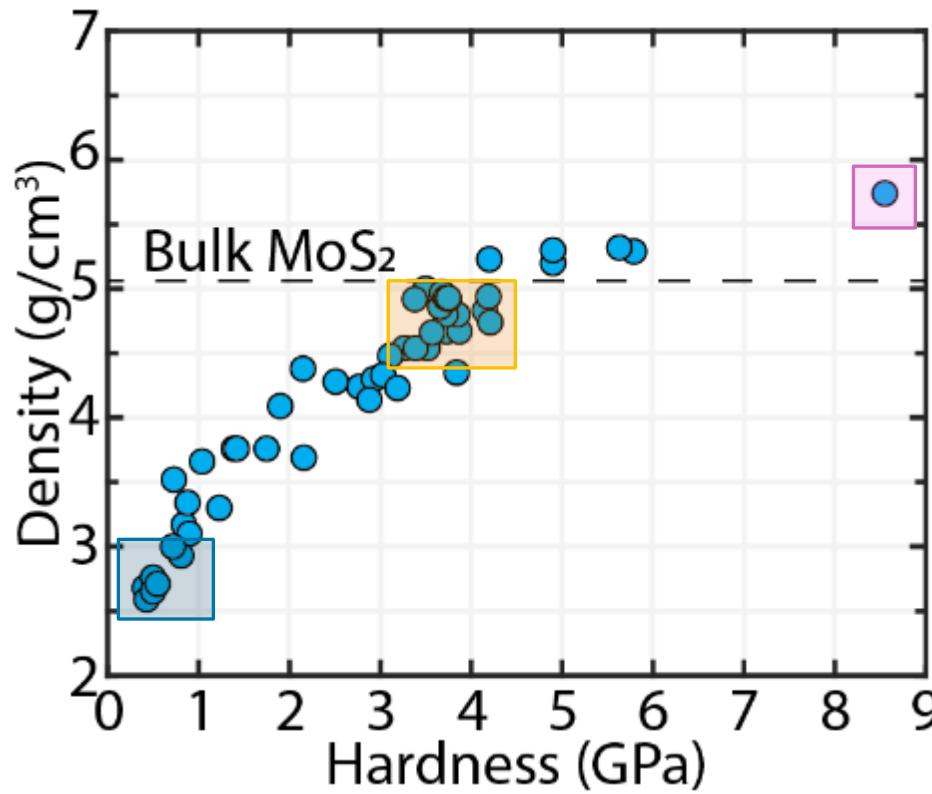
Observations:

1. Nearly 10X difference in hardness among varying deposition conditions!

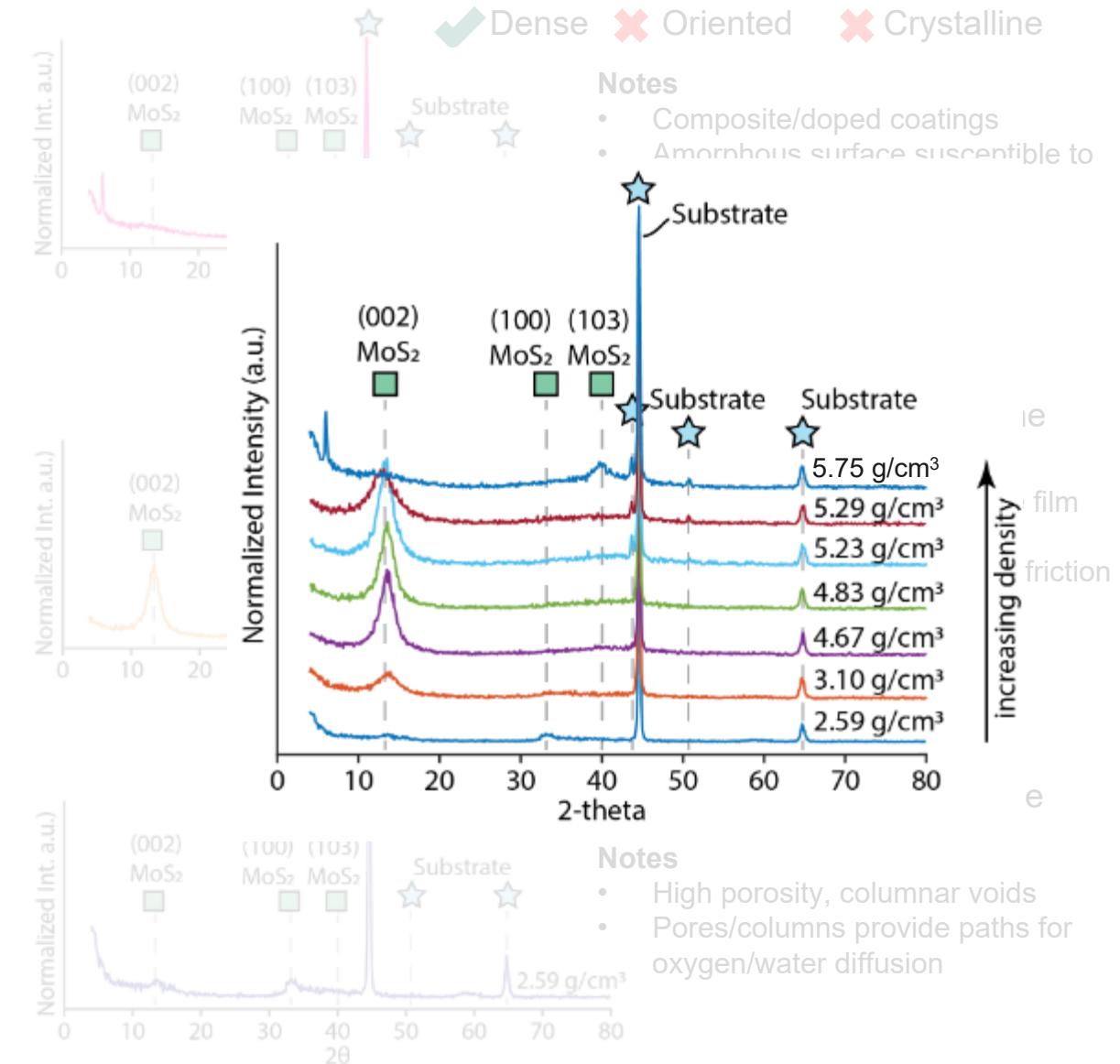
Questions:

1. What structural aspects is hardness capturing?
2. What is the optimal hardness (is it meaningful)?

HARDNESS VS DENSITY – STRUCTURAL ASPECTS



- Distinct increase in hardness with increasing density, up to bulk value
- Hardness regimes are a great way to classify coatings by their structure, orientation and density

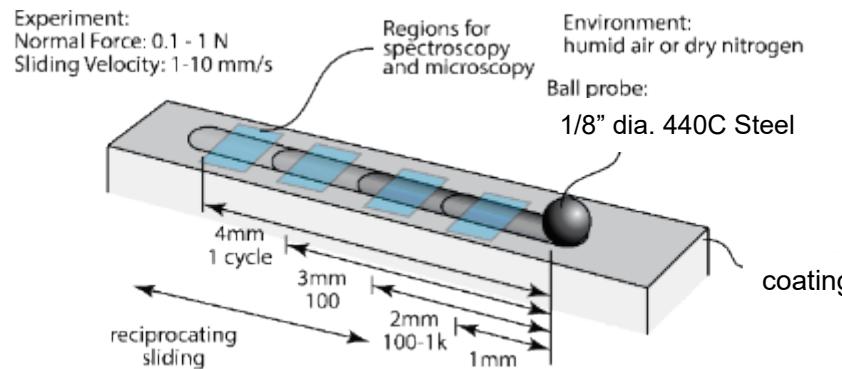


Coating Density: Rutherford backscattering spectroscopy
 Orientation & Crystallinity: X-ray diffraction

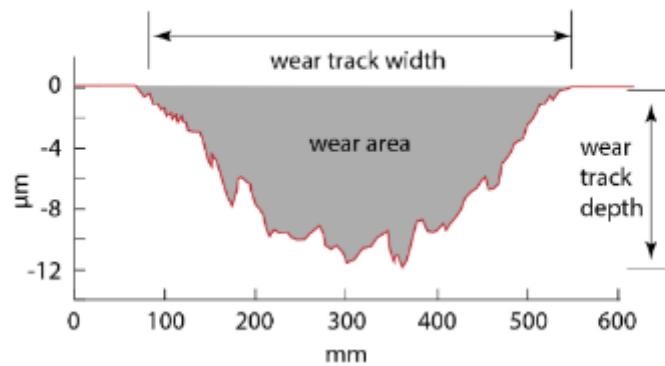
WHAT ABOUT FRICTION & WEAR?



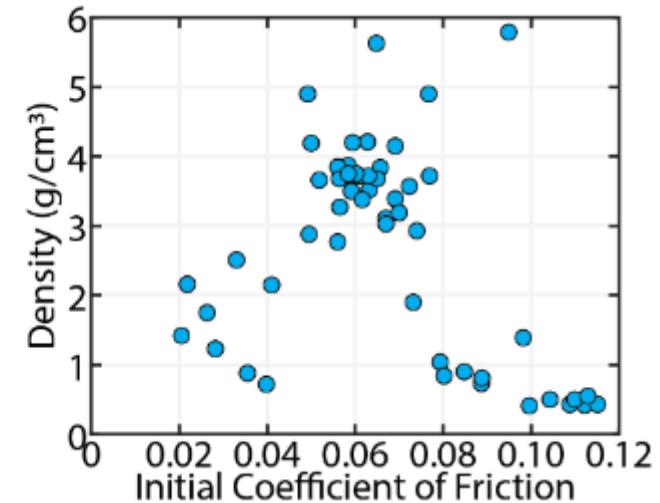
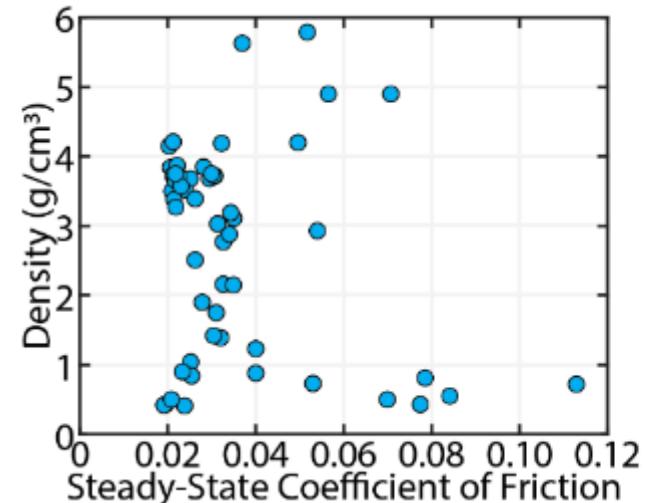
Friction Testing & Wear Measurements



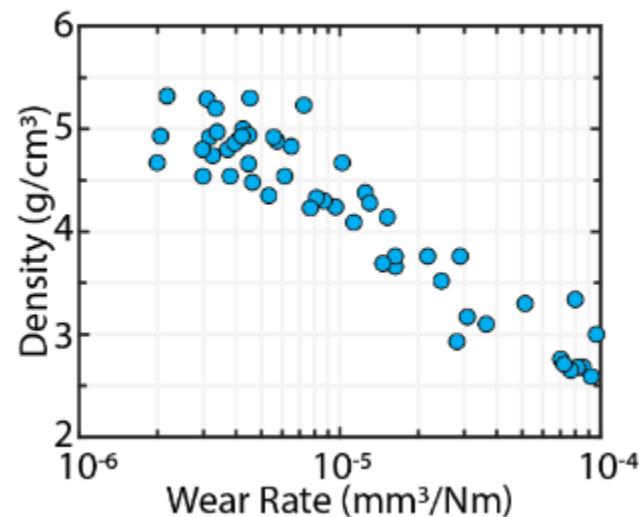
A representative 2D slice through the wear track.



Friction vs Density

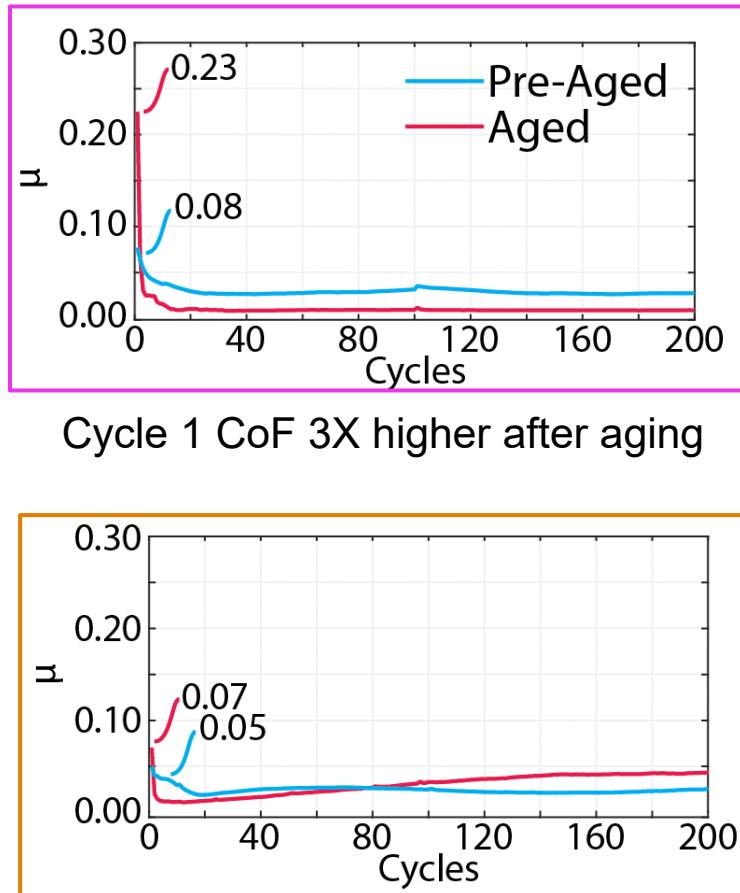
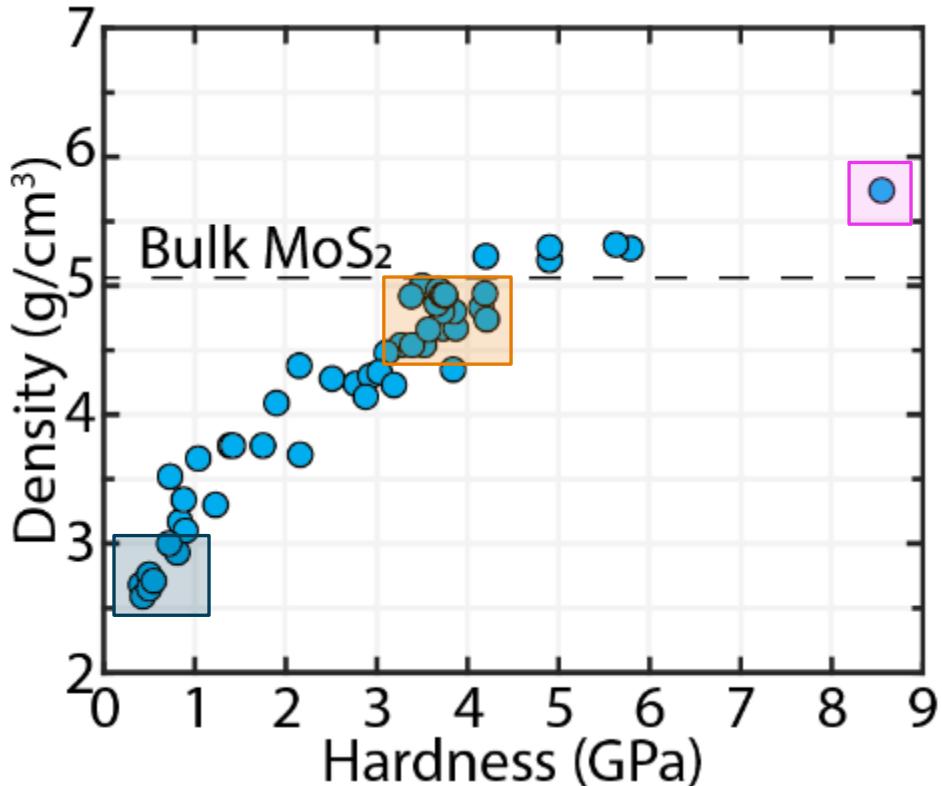


Wear vs Density



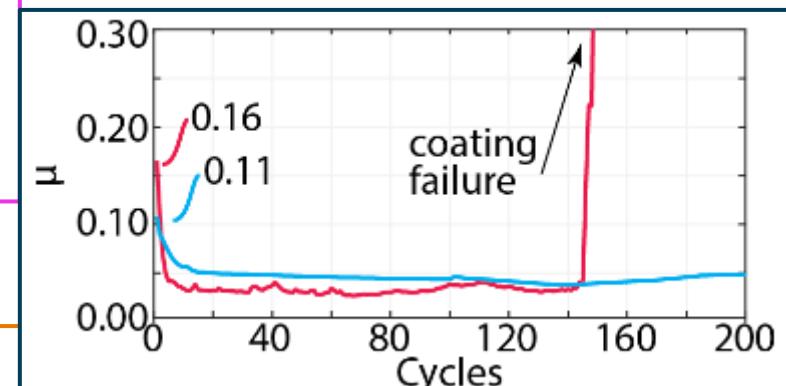
Friction behavior alone is not sensitive to density; wear rate tracks well with density

INITIAL FRICTION AFTER AGING



Negligible change in friction after aging

Oxidative Aging Exposure:
48 hours @ 300°C in dry air



Higher initial friction and early onset film failure after aging

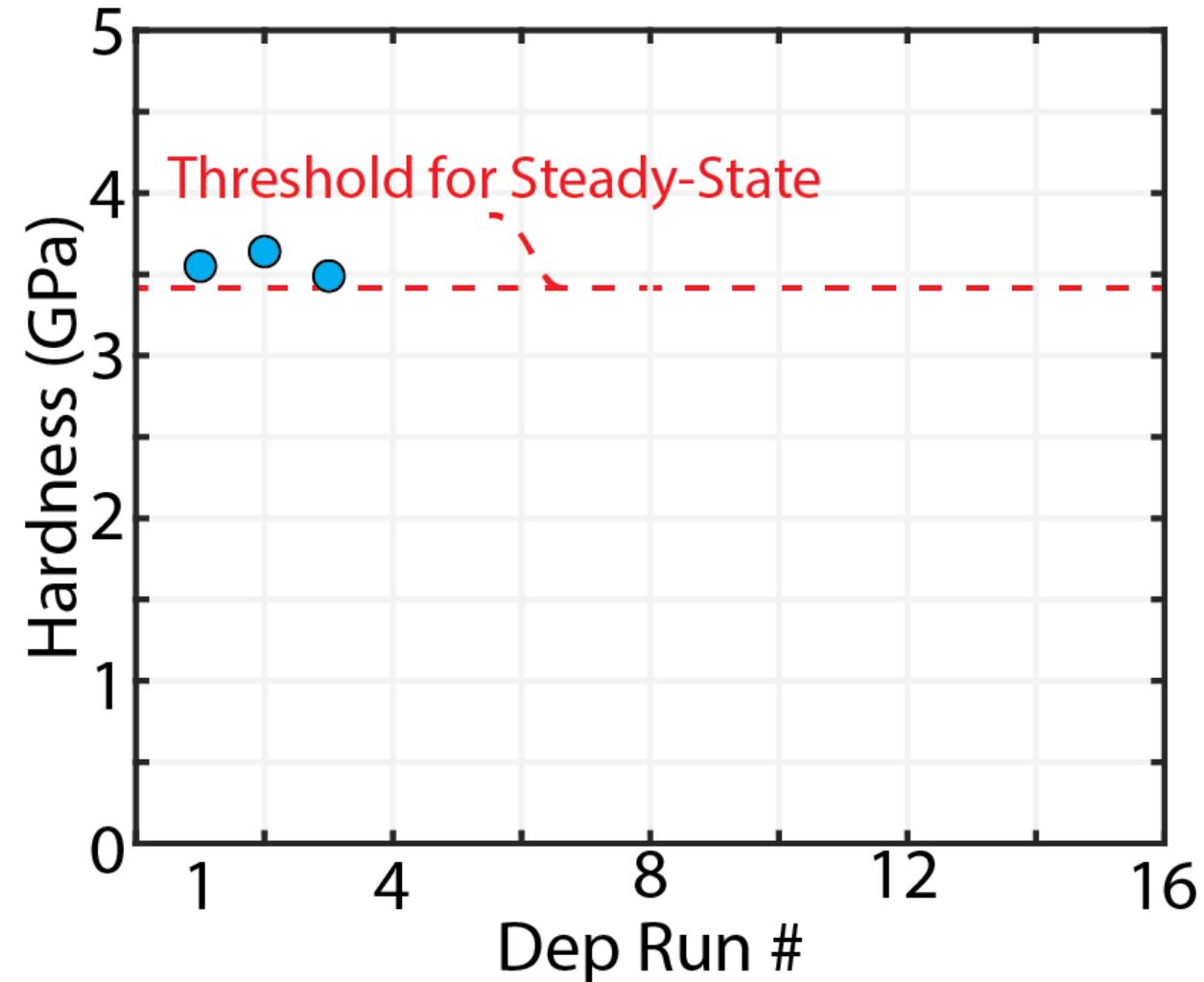
Friction behavior confirms simple, yet powerful hypothesis:

Hardness can rapidly assess density, a surrogate for structural characterization to aid predictions of aging resistance and design of new materials

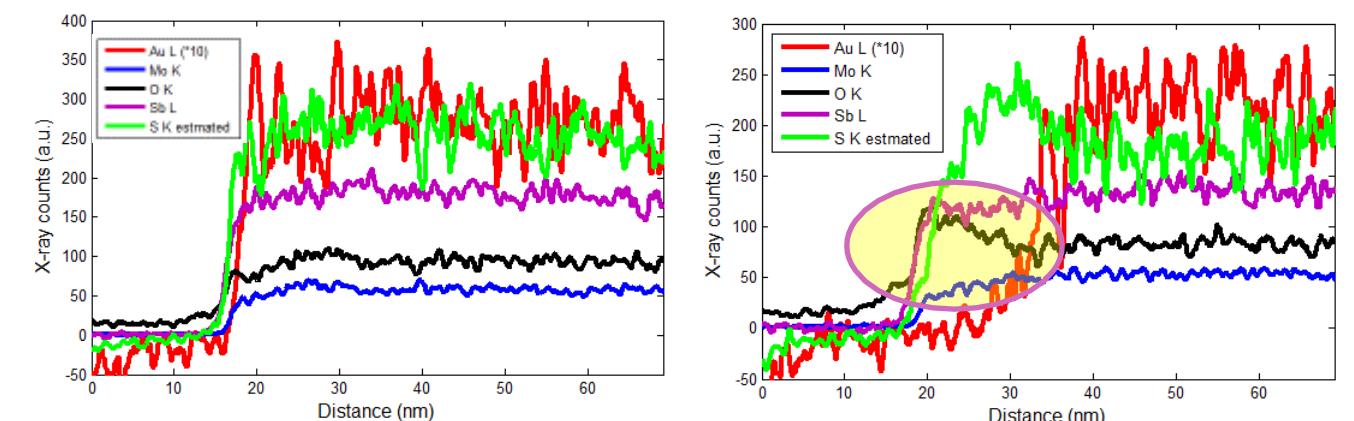
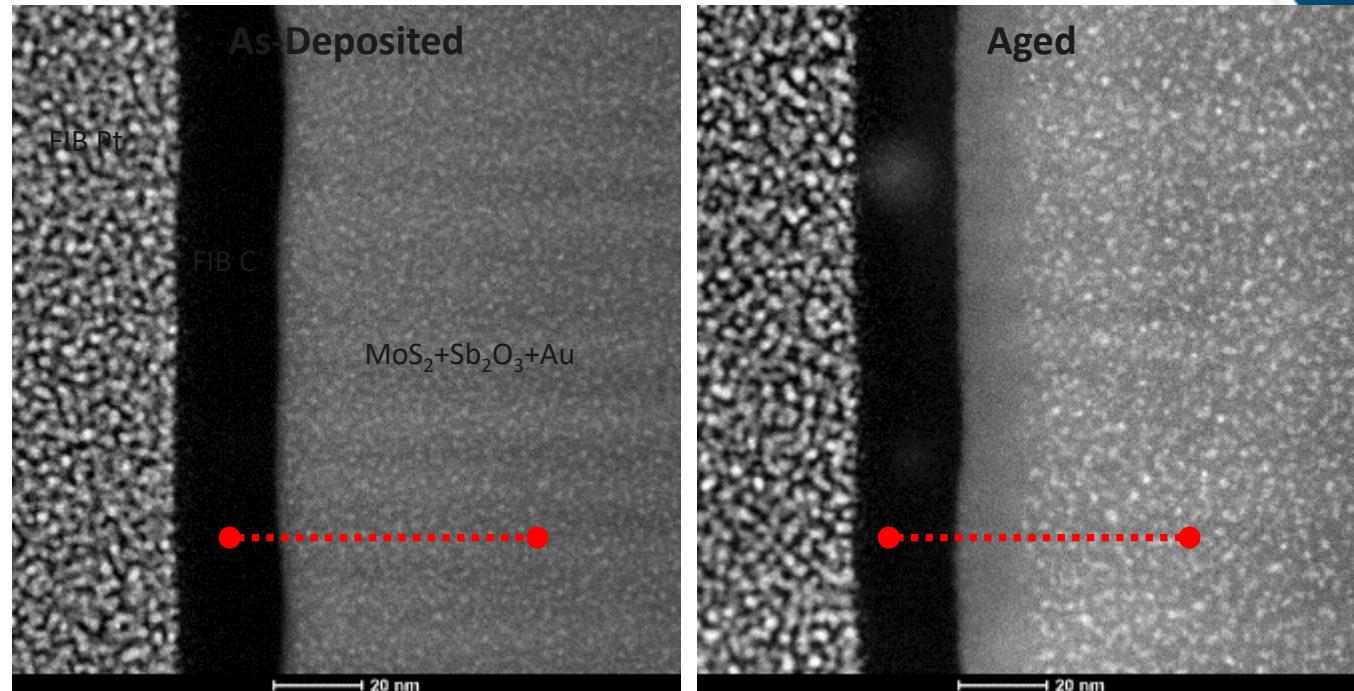
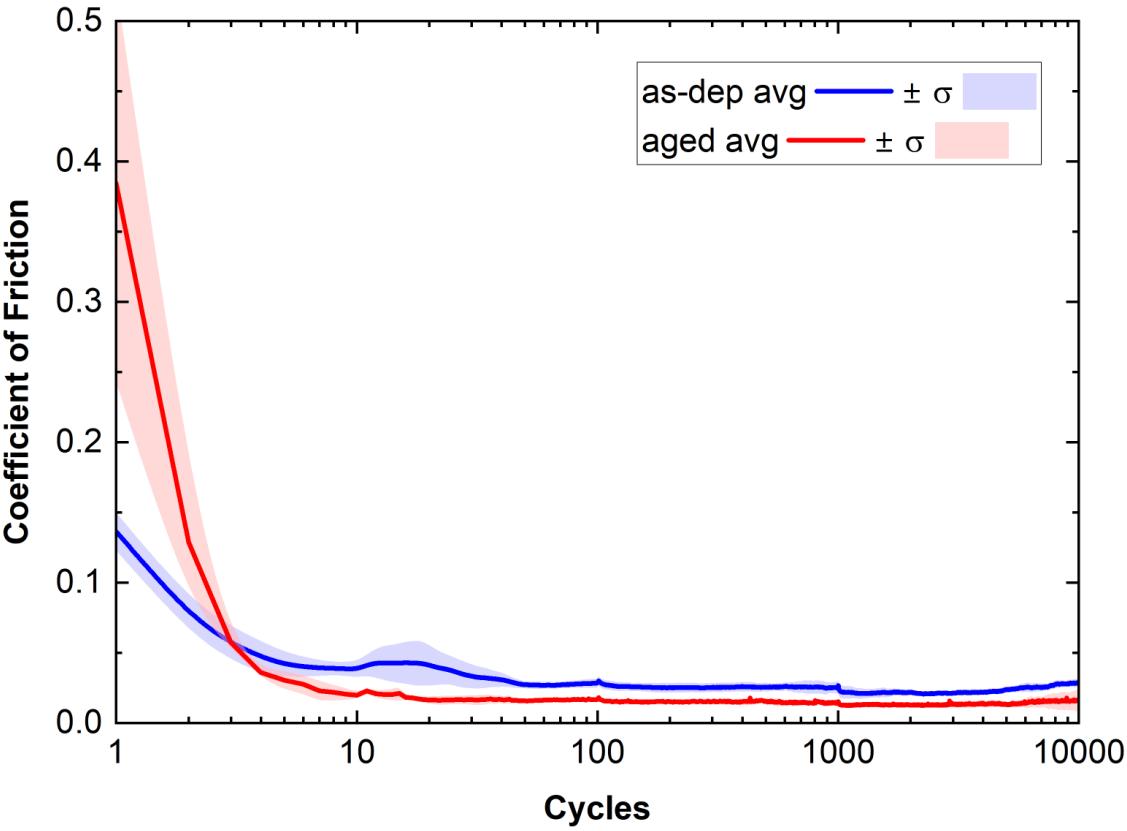
HARDNESS CAPTURES BATCH-TO-BATCH VARIATIONS



- We run the same deposition process multiple times:
 - 100W DC, 3 mtorr Ar, 1800 sec dep time
- Achieve a steady-state value for hardness for process (~3.5 GPa)
 - Confirmed this hardness indicated highly-dense film
- When chamber maintenance is performed, same process no longer yields same outcome
- We can use hardness to monitor when steady-state is achieved and condition chamber appropriately

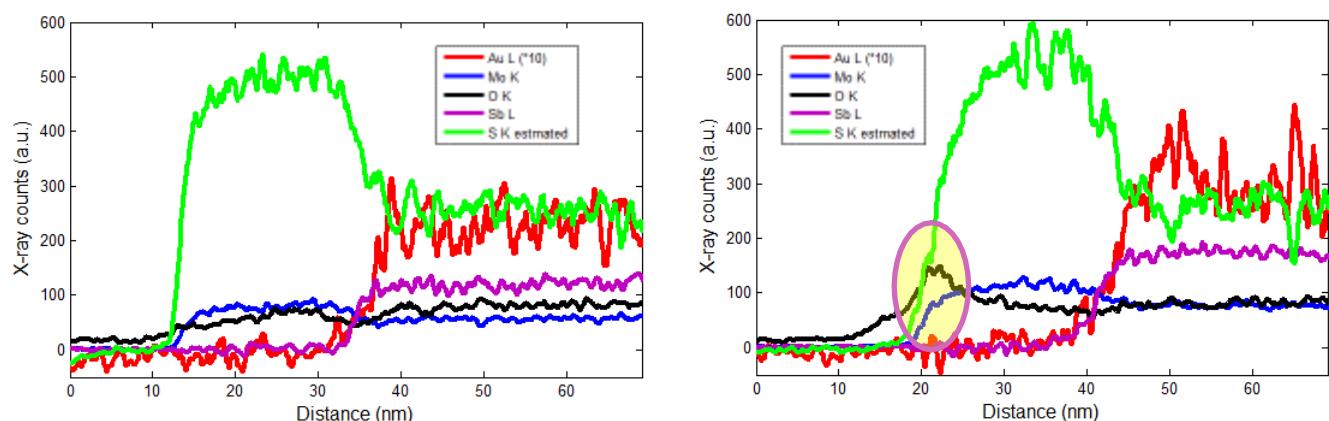
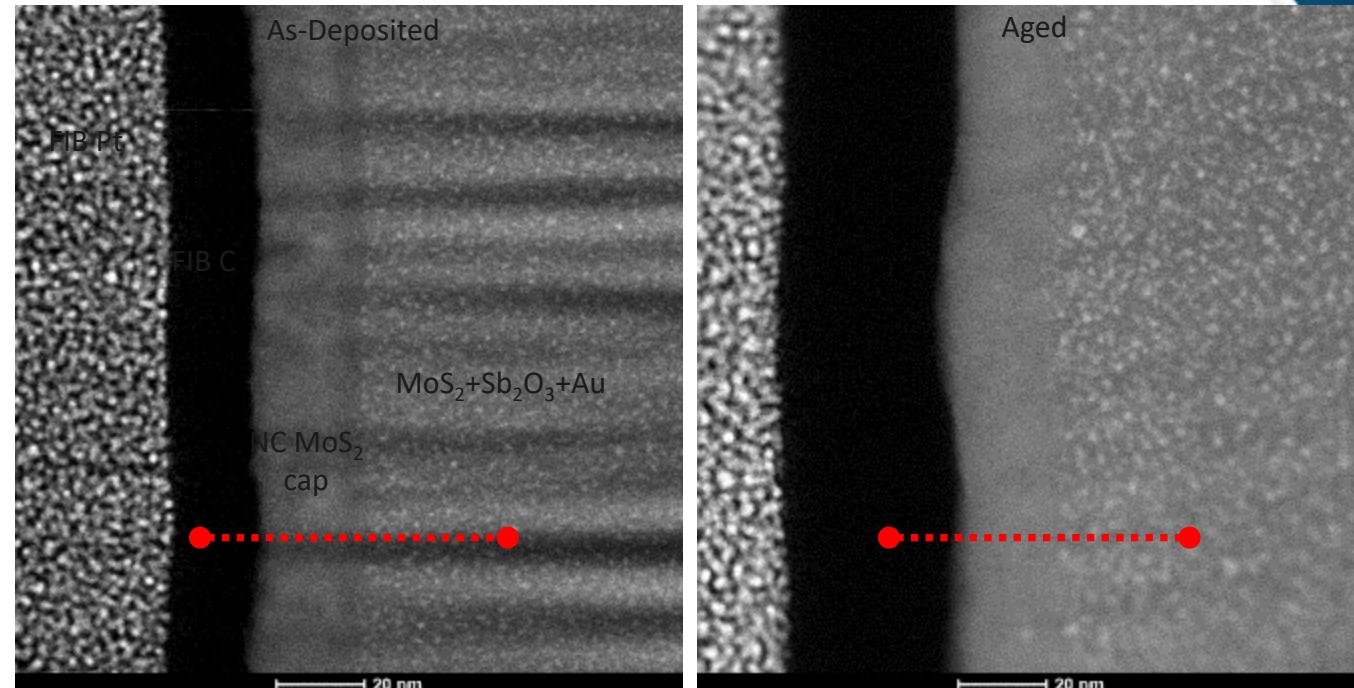
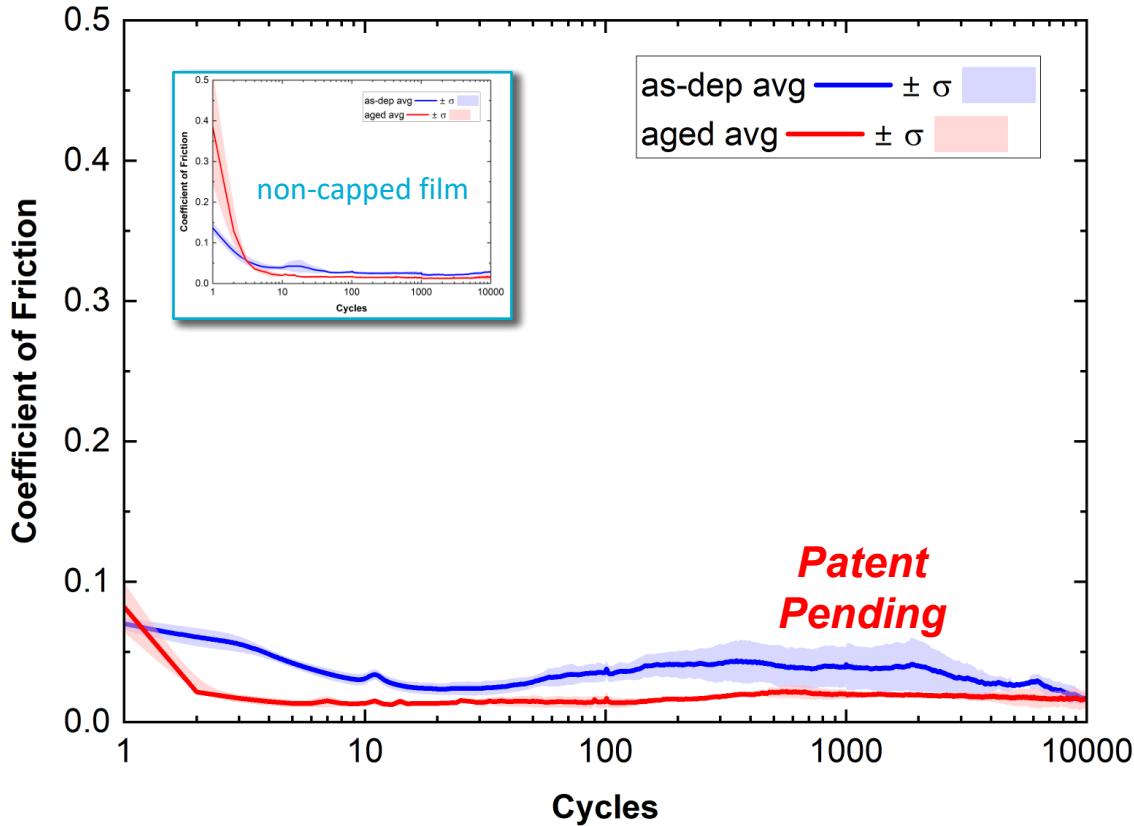


Behavior of Amorphous PVD MoS_2 Pre- and Post-Aging



- Aged film exhibits $\sim 3x$ increase in starting friction relative to as-deposited film
- Aging alters the structure (Au coarsening) and composition (O increase) of the top 15-20 nm of the film

Behavior of SNL PVD Multilayer Pre- and Post-Aging



- Starting friction is virtually unchanged in the aged film relative to the as-deposited film
- Oxygen is incorporated in top \sim 5 nm of the aged film



HAVING FUN WITH BUZZ WORDS

AUTOMATED HIGH THROUGHPUT TRIBOLOGY TOWARDS ML APPLICATIONS

ELECTRICAL CONTACT INDUSTRY IS VAST...

*wind turbine slip-rings
(sensors and blade pitch motors)*



PCB sockets

**ESTIMATED 150 METRIC
TONS (\$6.9B) OF GOLD
USED IN ELECTRICAL
CONTACTS PER YEAR**

Refs: *Gold Survey, Gold Fields Mineral Survey Ltd, 2011*
Gold Bulletin 2010, Vol. 43-3, C. Hagelüken and C.W. Corti,
Gold Bulletin 1986, Vol. 19-3, T.D. Cooke



cell phones

CPU sockets



RJ45 connectors



EV charging



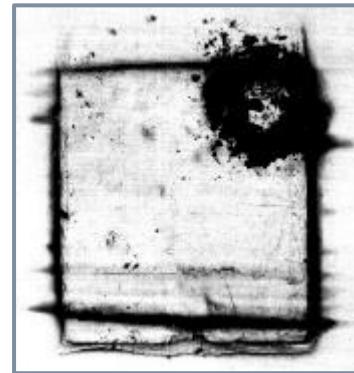
spacecraft slip-rings



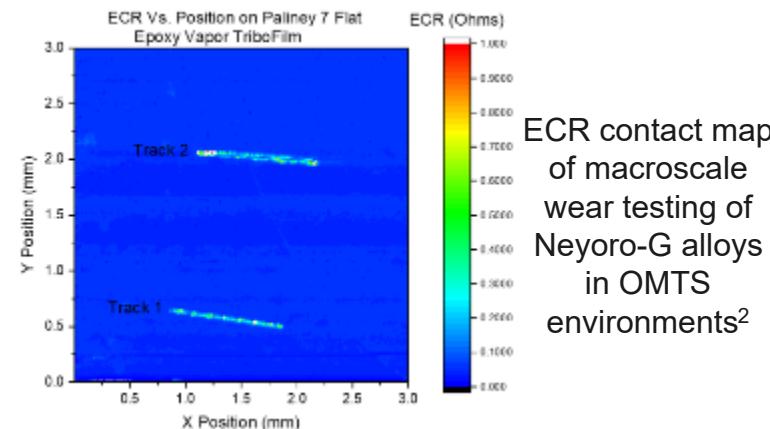
KNOWN ISSUES IN ELECTRICAL CONTACTS

- Noble metal alloys (Au, Pt, Pd, etc.) commonly used, yet suffer from:
 - Wear, galling & frictional losses.
 - Corrosion & oxidation.
 - **Tribopolymer formation.**
- Frictional polymerization, or tribopolymer (TP) formation in electrical contacts has been a known and recurring issue for nearly 70 years.
- Engineers struggle balancing contact stress/resistance requirements
 - Existing alloys too soft to displace organics at high stress
 - Still suffer from TP formation at all other contact pressures

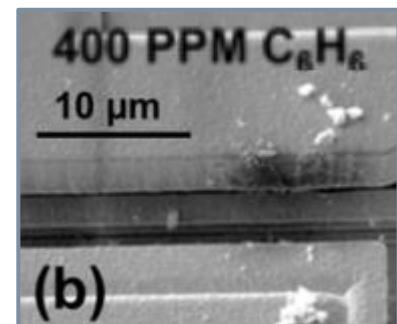
Need ultra-low wear, high hardness contact alloys to mitigate tribopolymer formation



Pd contact with inorganic film formation after 10^6 switches.¹



ECR contact map of macroscale wear testing of Neyoro-G alloys in OMTS environments²



Pt MEMS contact with tribofilm formation after switching in 400 ppm C₆H₆.³

¹ Hermance & Egan, *Bell Sys. Tech. Journal* 1958

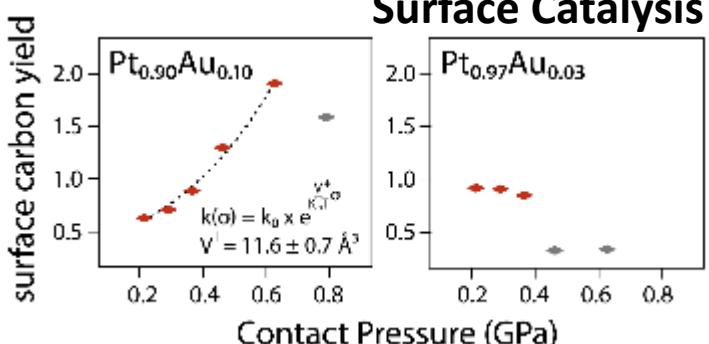
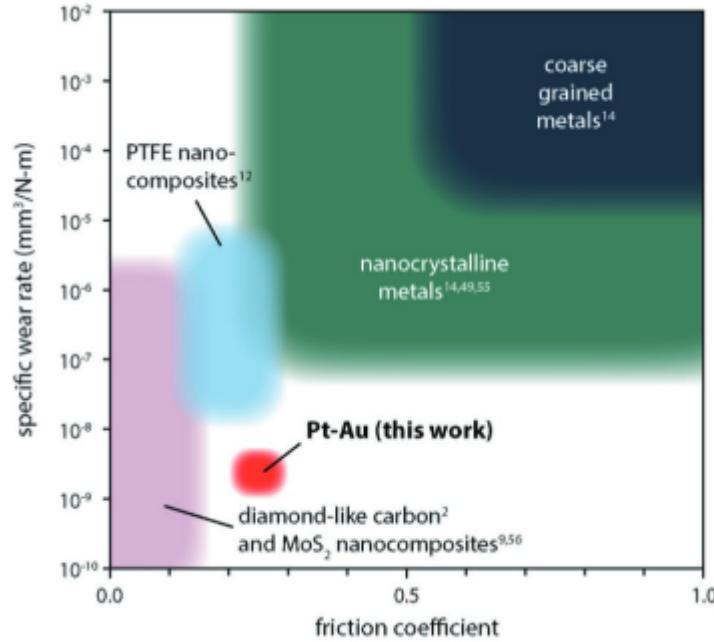
² Curry et al., *IEEE Holm Conf. Proc.* 2022

³ De Boer & Brand, *IEEE Holm Conf. Proc.* 2015

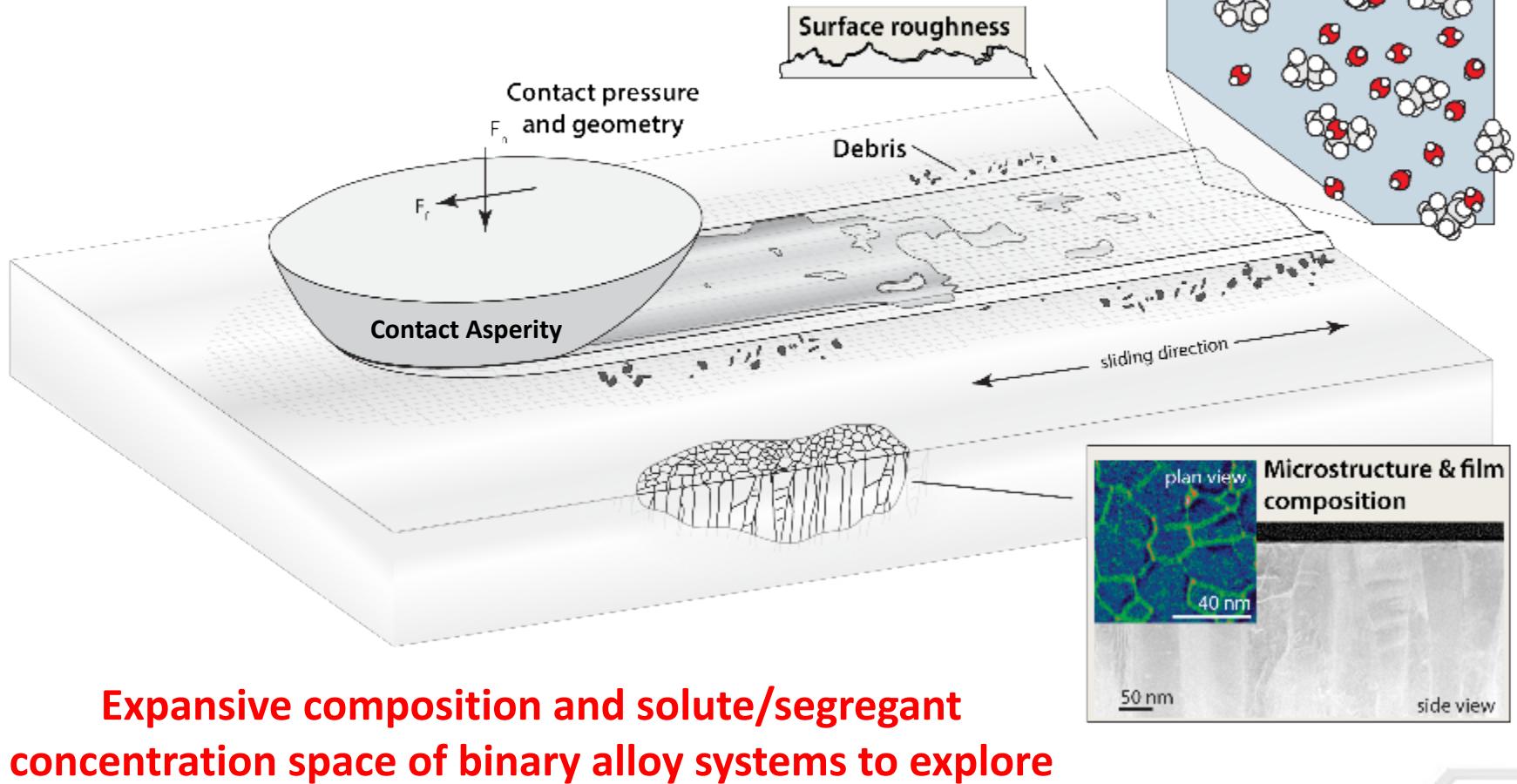
THE PROMISE OF HARD, WEAR-RESISTANT NC ALLOYS



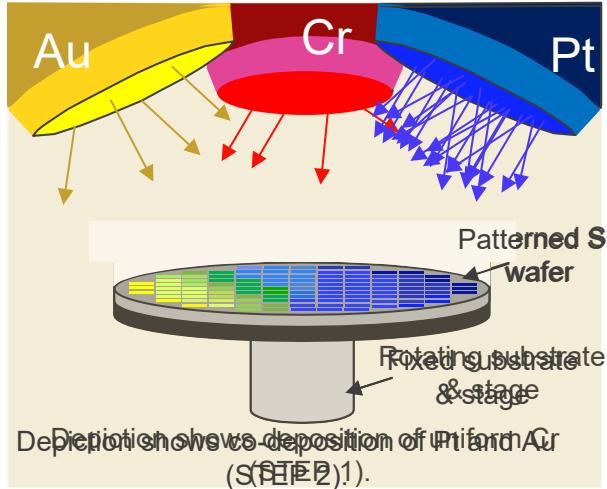
Pt-Au alloys exciting candidates for electrical contacts applications



Friction, wear and surface chemistry are all highly dependent on sliding system

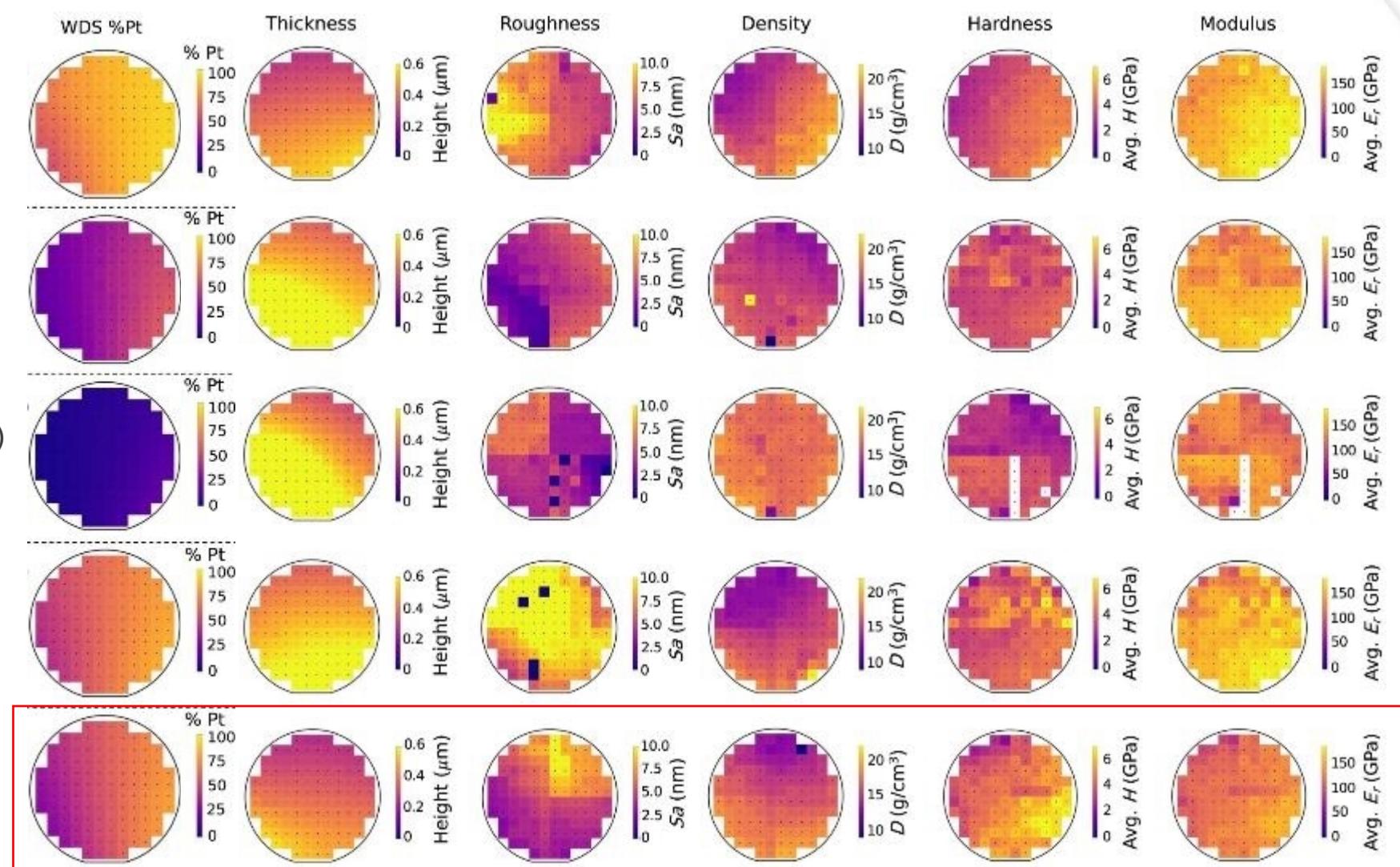


PVD COMBINATORIAL APPROACHES TO ALLOY DISCOVERY



Key Elements of combinatorial PVD

- 1.) Multiple operating sputter guns (co-dep)
- 2.) Stationary wafer in known position
- 3.) Varied working distance
- 4.) Patterned wafer w/ 112 designated 1 cm² areas



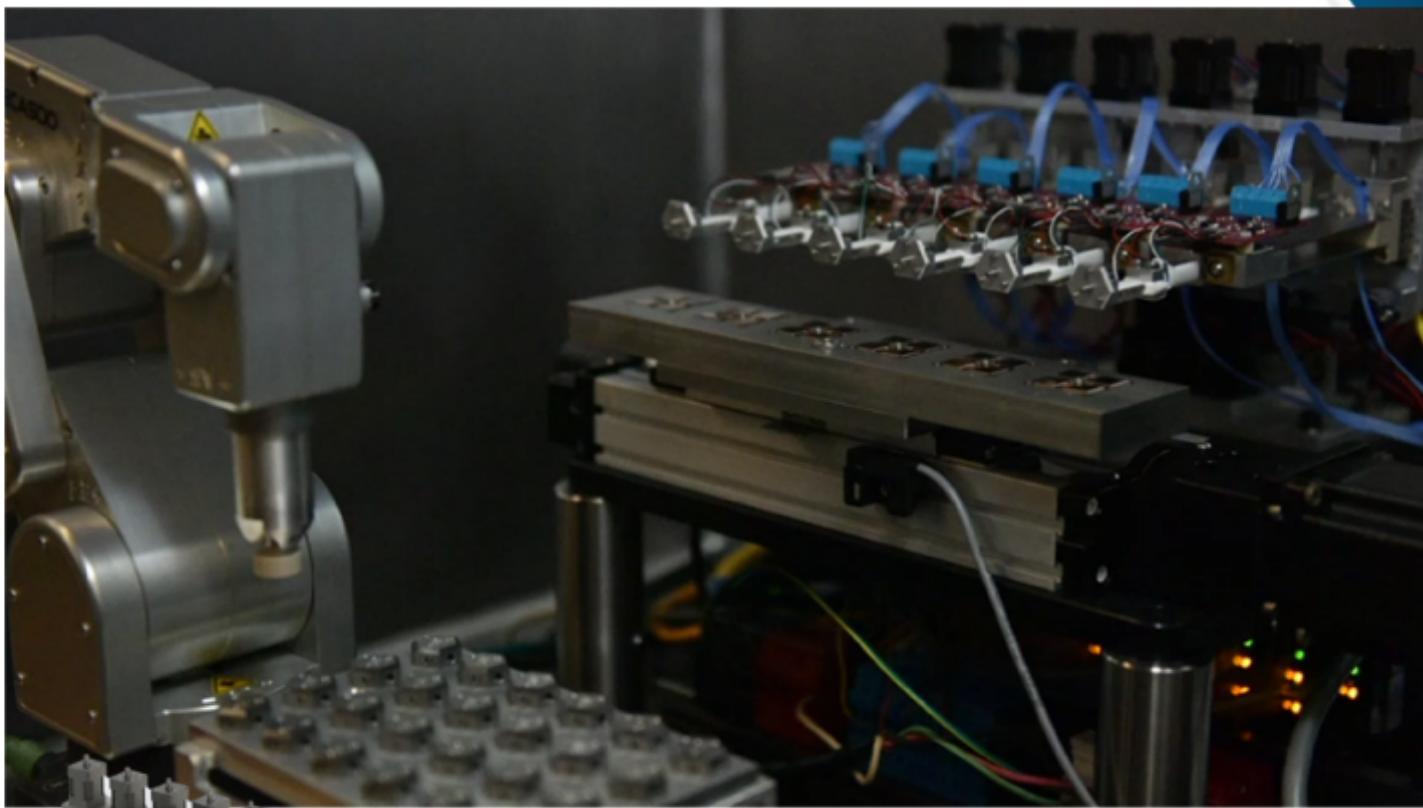
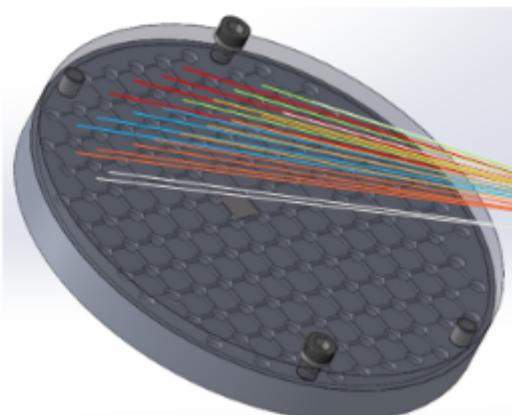
AUTOMATED HIGH THROUGHPUT TRIBOLOGY



Combinatorial wafer has 112 unique samples tested 3 times for repeatability

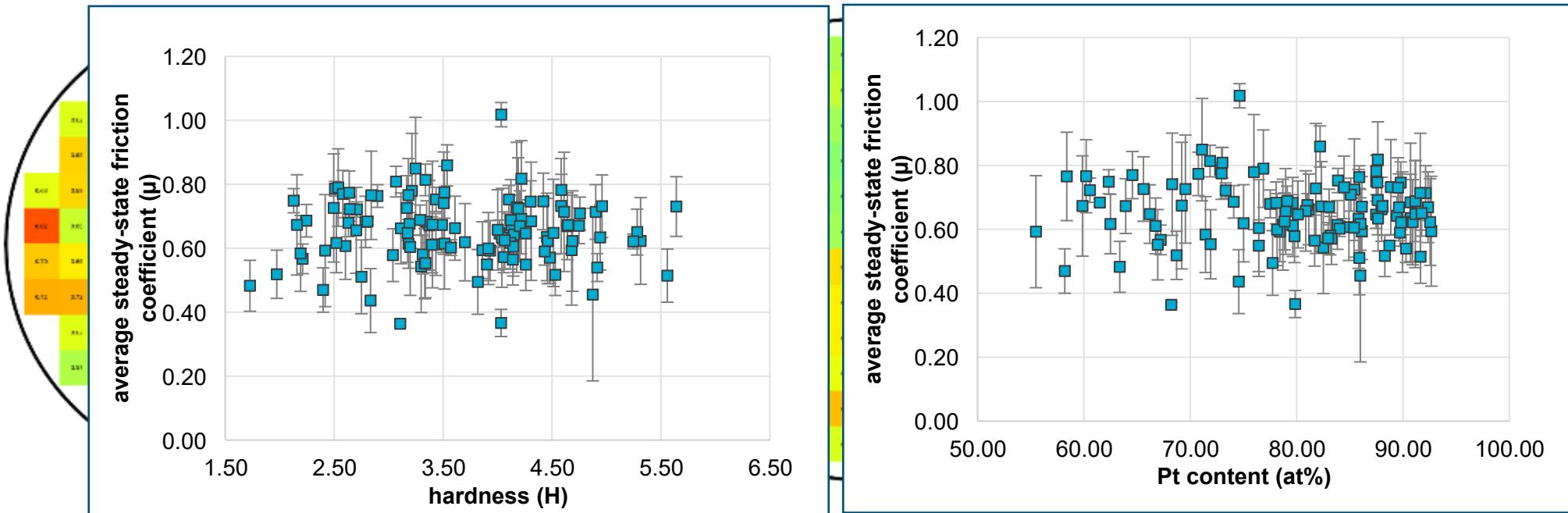
- New Hydra Capability
 - 6 parallel test heads; 4 samples/head; 3 pins/head
 - 72 experiments automatically changed via robotic arm

New Fixture allows for 112 sample combinatorial deposition array – tester fits 24 pieces at once

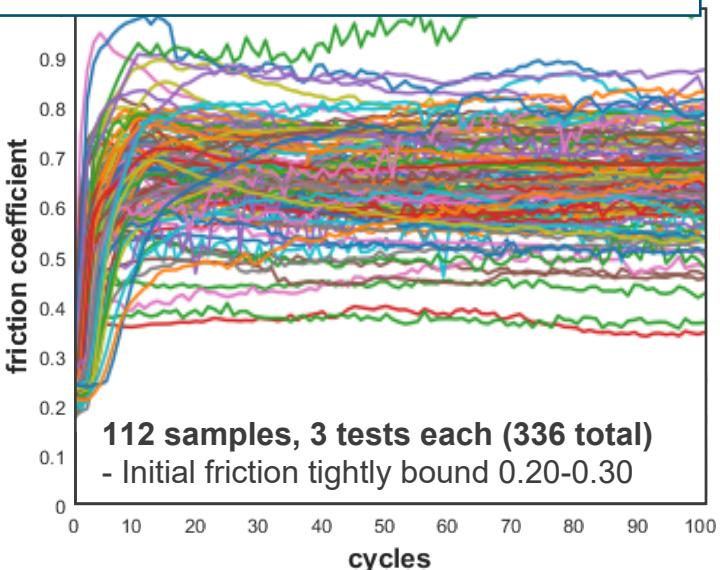


Routinely running 100's of experiments per day with new capabilities. Allows for engagement with many ML projects.

WAFER SCALE RESULTS – FRICTION IN AIR

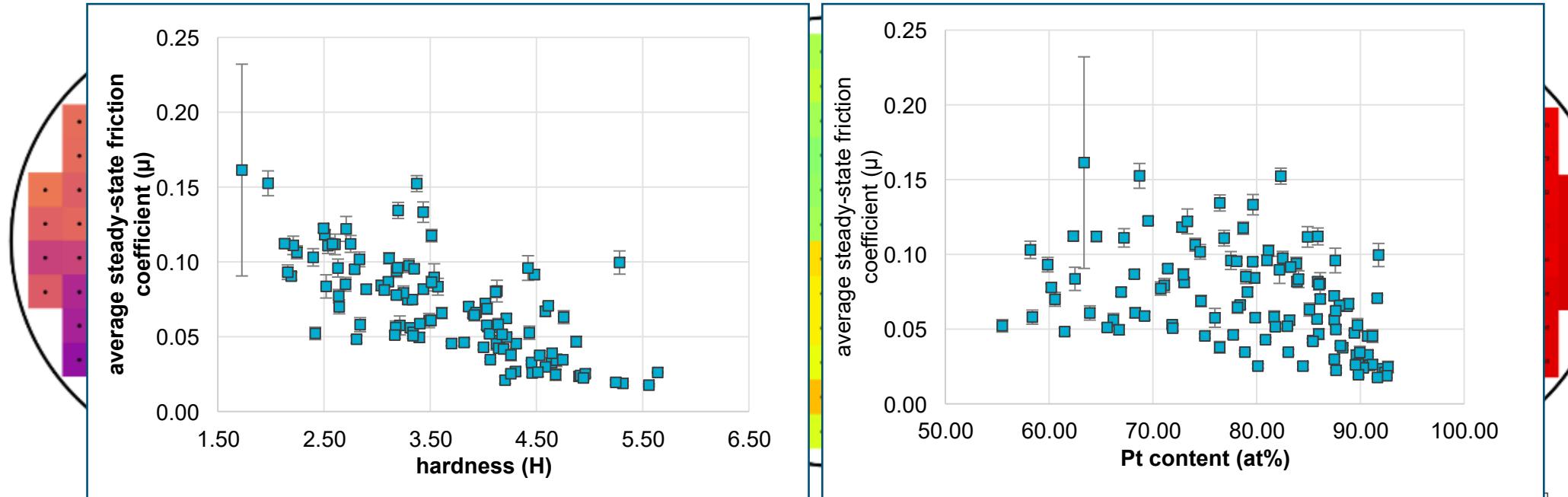


- No apparent trends with hardness and composition.

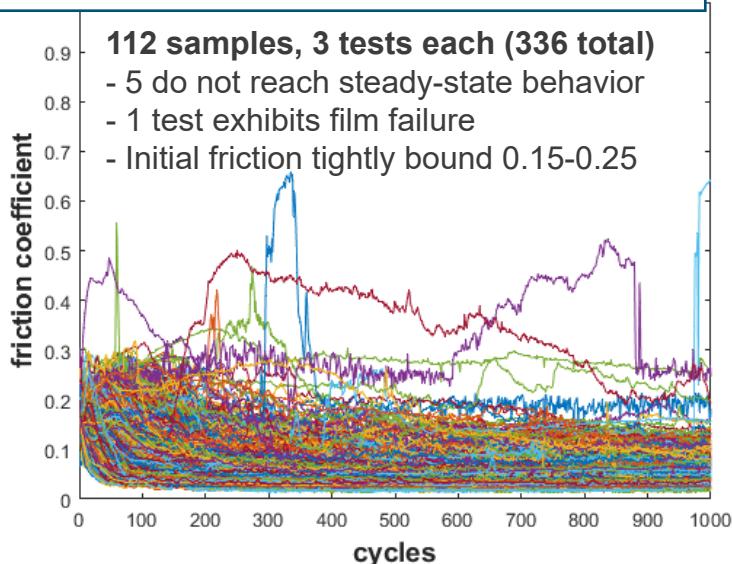


Friction Test Parameters	
2 mm Track Length	
4 mm/s sliding speed	
100mN Normal Force	
Lab Air	
100 Cycles	
Repeated 3x	
Run Time: 6 hours	

WAFER SCALE RESULTS – FRICTION IN DRY N₂



- Strong correlation between hardness and friction, with lower friction at higher hardness.
- High Pt content alloys tend to form low friction films, with more variability as Au content increases.



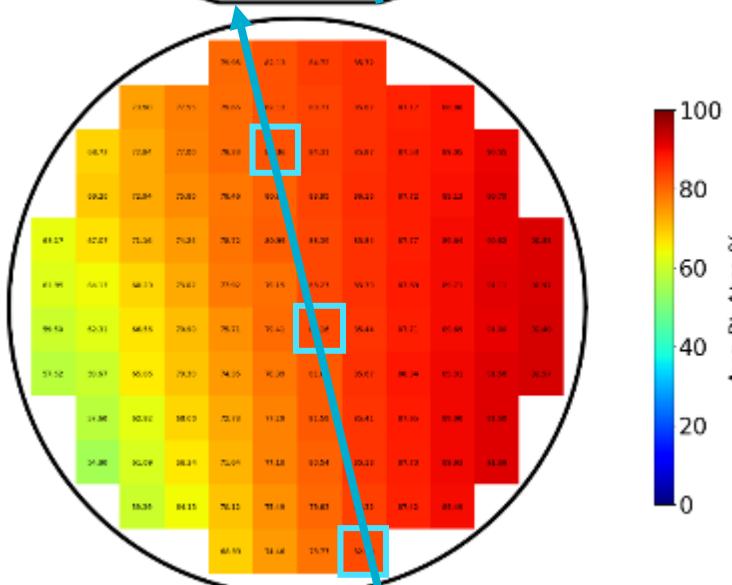
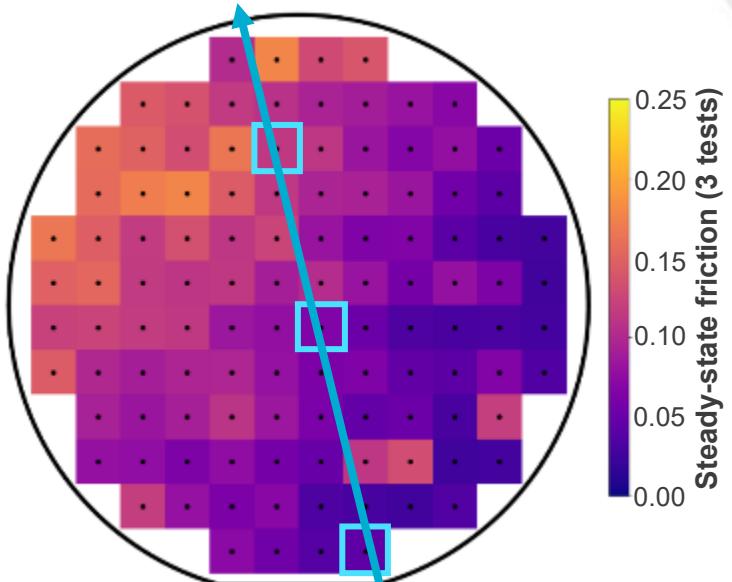
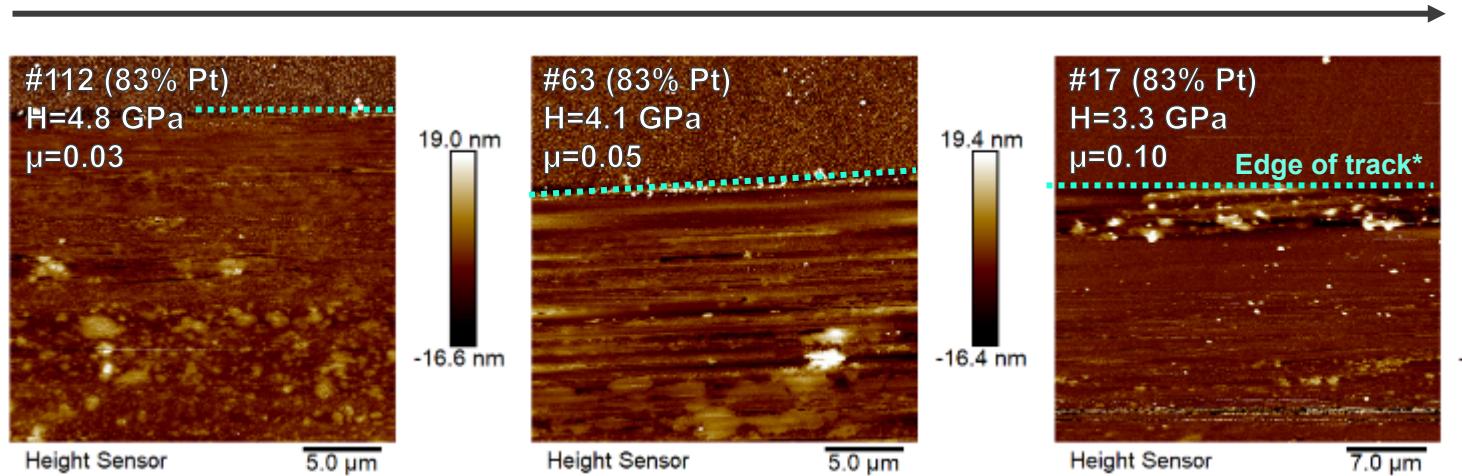
Friction Test Parameters	
2 mm Track Length	
4 mm/s sliding speed	
100mN Normal Force	
Dry N₂ environment	
1000 Cycles	
Repeated 3x	
Run Time: 3 days	

LET'S LOOK AT THE TRIBOFILMS



VARYING FRICTION, CONSTANT COMPOSITION (DRY N2)

increasing friction; **decreasing hardness**; constant Pt composition

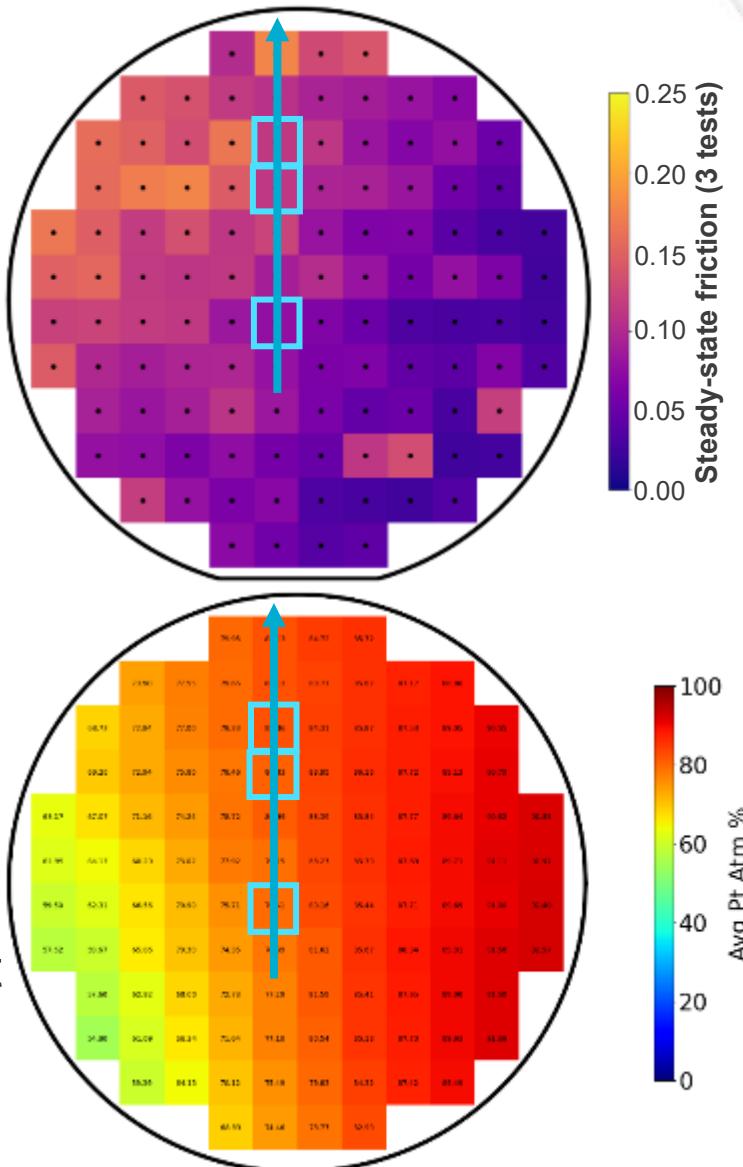
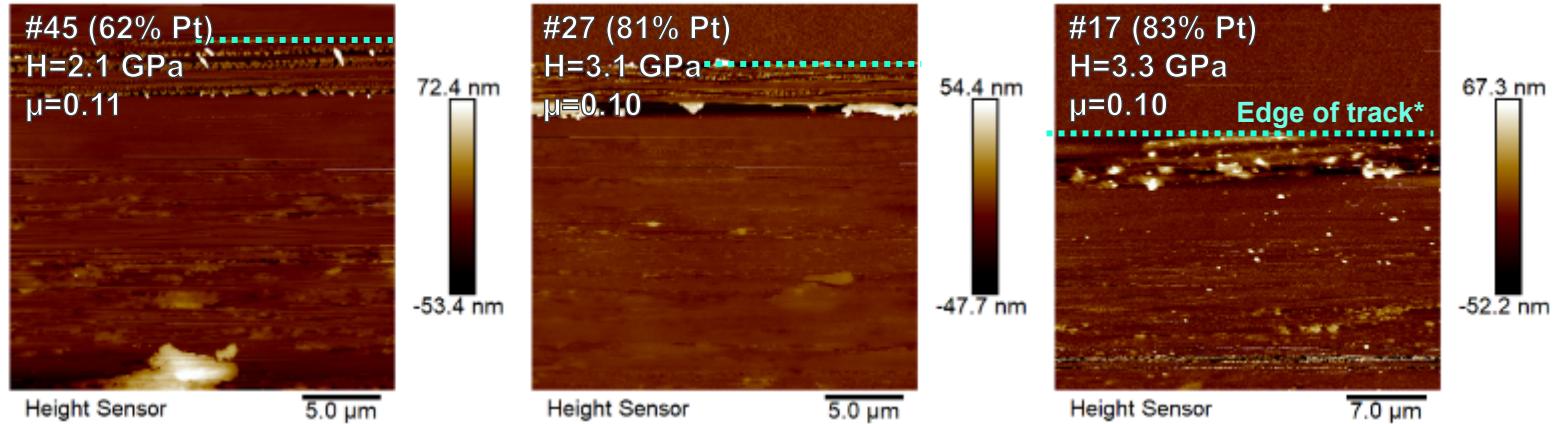


- Preliminary AFM shows patches of raised material (~20nm) in wear scars for low friction cases only, despite same % Pt.
 - Must consider density & thickness variations at play due to combinatorial deposition technique.
- Higher friction shows tribofilm pileup (~65nm) pushed to edges. **Similar result to previous AFM for lower hardness compositions.**

* all wear scars ~ 30-35 μm wide

LET'S LOOK AT THE TRIBOFILMS

HIGH FRICTION, SPANNING COMPOSITION (DRY N2)



- Lower hardness films at different compositions all exhibit debris pileup at track edges (~50-60nm) & high friction.
- Despite this, some instances of tribofilm within wear scar still exist (e.g., sample 45)

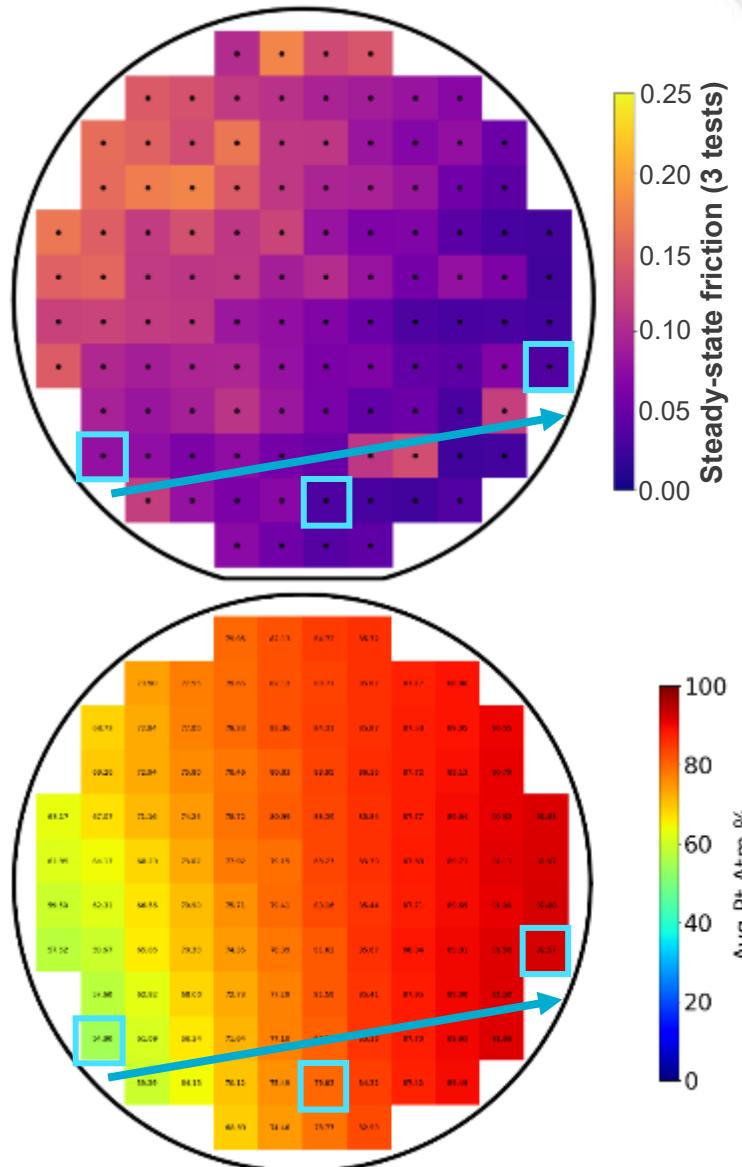
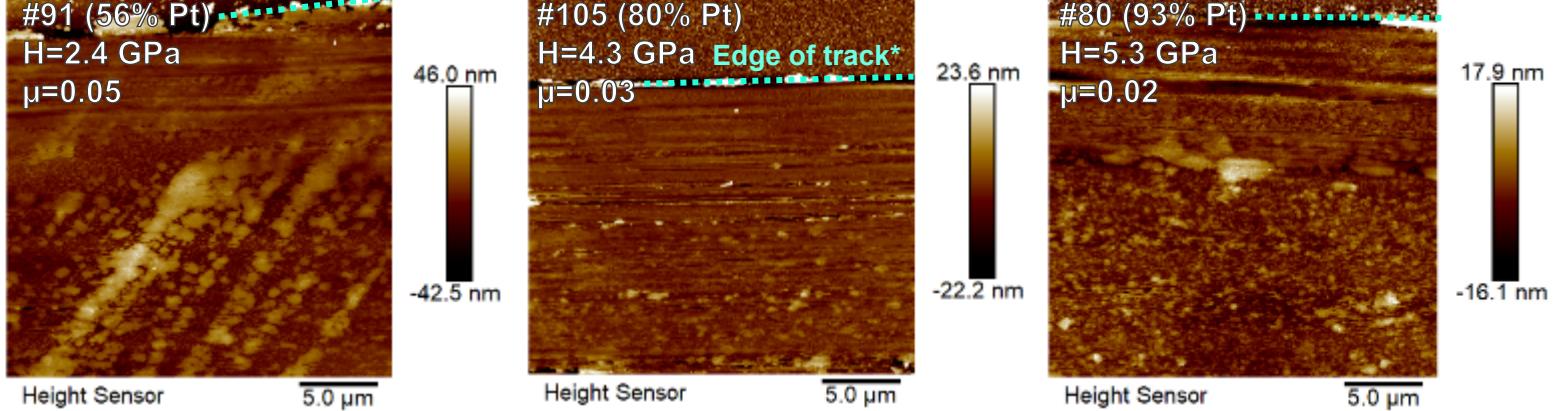
* all wear scars ~ 30-35 μm wide

LET'S LOOK AT THE TRIBOFILMS



LOW FRICTION, SPANNING COMPOSITION (DRY N2)

decreasing friction; increasing hardness; increasing Pt composition



- Tribofilms observed in wear scars for all cases (~20-40nm).
- High Au content wear scar (lower hardness, higher friction) exhibits formation in wear scar and at edges.

* all wear scars ~ 30-35 μ m wide



THANK YOU!
QUESTIONS?

APPENDIX