SAND2007-1333C

Recent Advances in Engineered Surfaces, Nanostructured Coatings & Novel Deposition Techniques

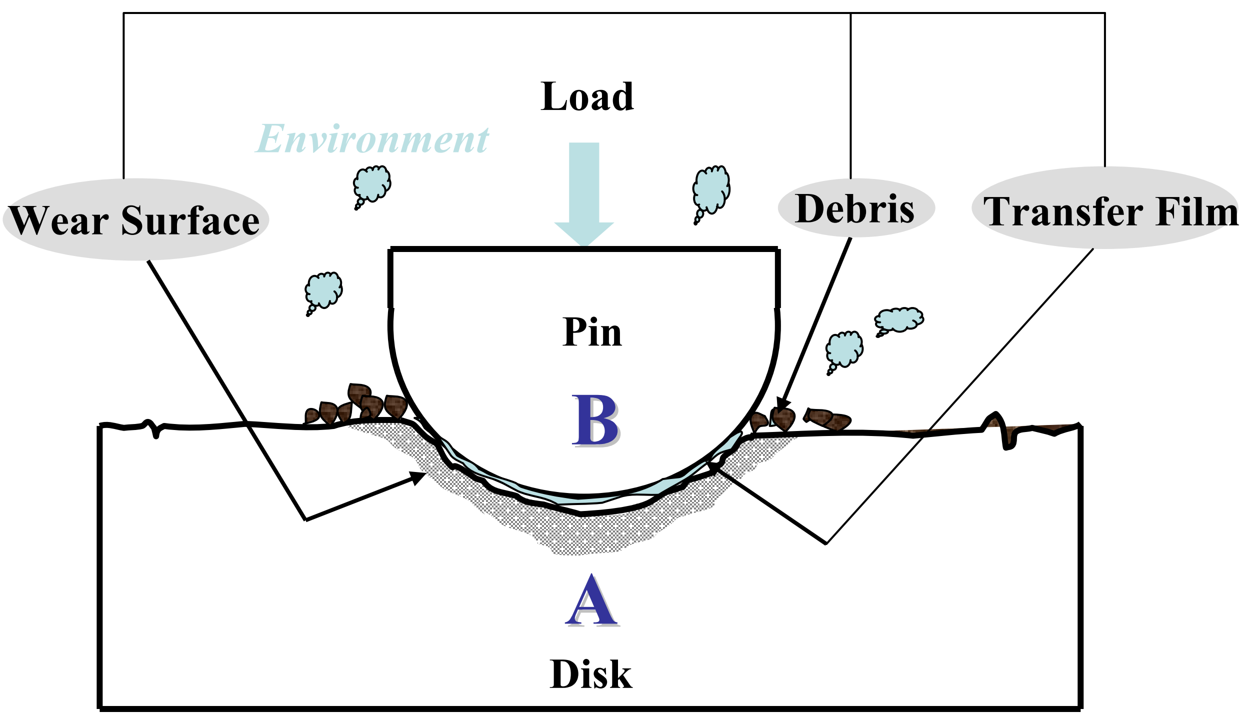
S. V. Prasad
Sandia National Laboratories
Albuquerque, NM
(svprasa@sandia.gov)

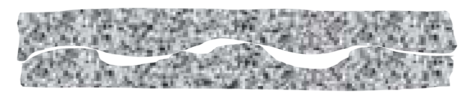
Next Generation Materials for Defense 2007
Institute for Defense and Government Advancement
March 29, 2007, Arlington, VA

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

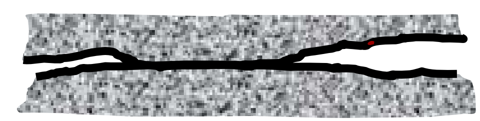
Sandia National Laboratories

Tribology is a systems property

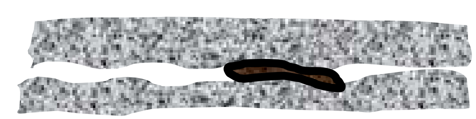




Mechanical Interlocking
(Surface Morphology)



Adhesion



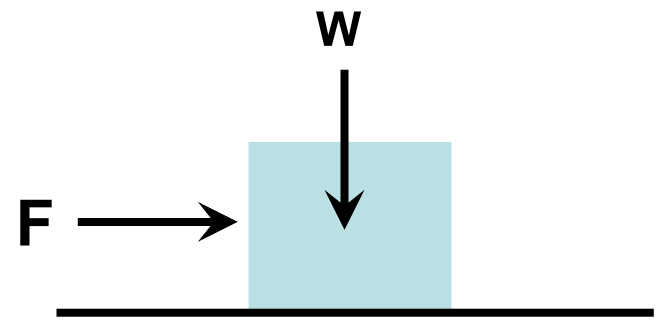
Debris Entrapment

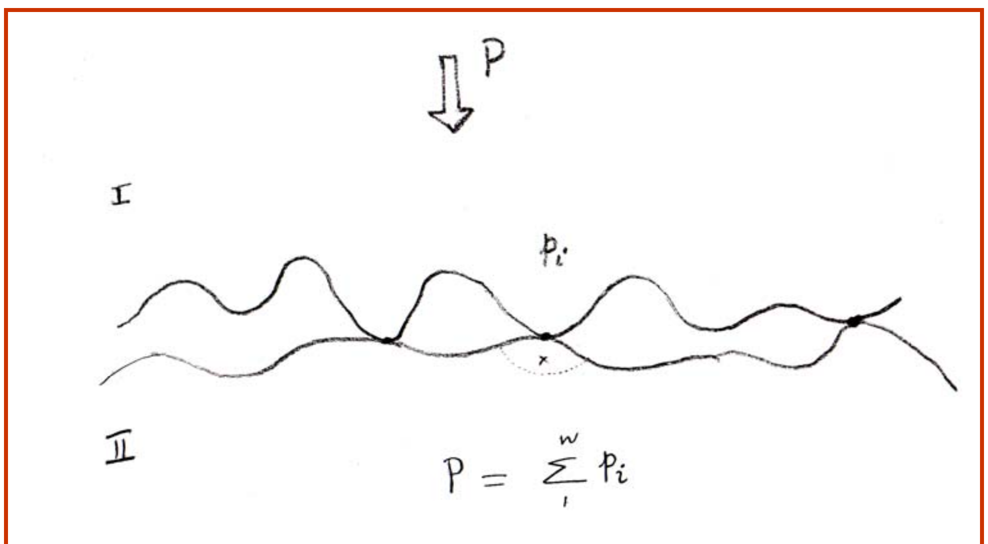
Recognize the limitations of the laws of friction

Guillaume Amontons (1663-1705)

Unaware of da Vinci's (1452-1519) recorded observations

- Friction force is proportional to normal force
- Magnitude of friction force does not depend on the apparent area of contact





- Engineering surfaces are not atomically flat
- Contact will be at asperity level
- Surface composition typically differs from the bulk
- Sliding contact results:
  - Plastic deformation
  - Diffusion
  - Fracture initiation
  - Tribochemistry and Environmental reactions

Sandia National Laboratories

Tribomaterials

Major Examples

- Materials for Bearings
- Friction Materials
- Abrasion-Resistant Materials
- Metal-Cutting Tools
- Biomedical Materials

Friction and Wear

Materials for Tribological Applications must also have a
"Precise Balance of Physical and Mechanical Properties"
(thermal expansion, damping capacity, conformability, strength, stiffness and fatigue life)

It is practically impossible to meet these diverse requirements with single phase materials. Materials strategies include:

- Composite Materials
- Engineered Surfaces
- Coatings

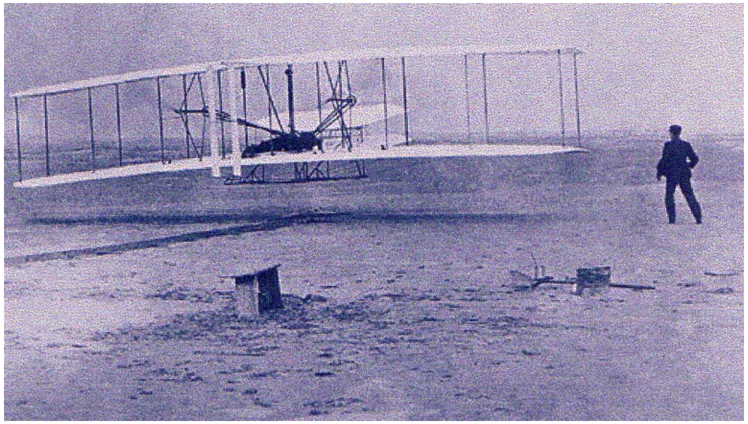
Outline

- Historic Example
  - Development of Wright Brothers' Engine
- Materials by Design
  - Metal-Matrix Composites (MMCs)
  - Polymer-Derived Ceramics (PDCs)
- Solid Lubricants, Thin Films and Coatings
  - Transition metal dichalcogenides (MoS_2, WS_2)
  - Diamond-Like Carbon
- Tribological Issues in MEMS
- Atomic Layer Deposition

Sandia National Laboratories

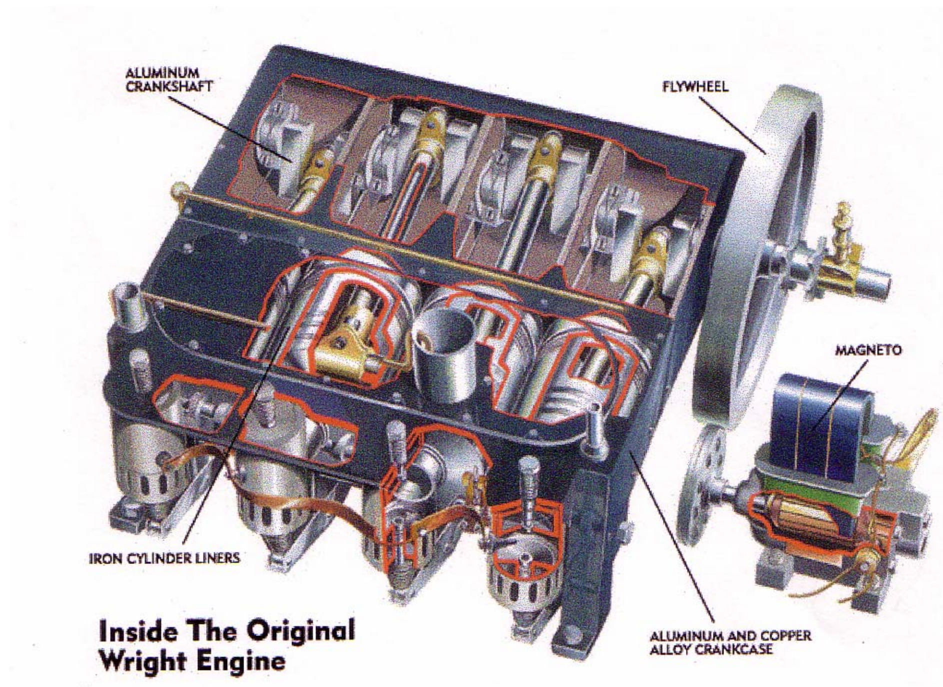
Historical Perspective: The Saga of Wright Brothers' Engine Development

1903



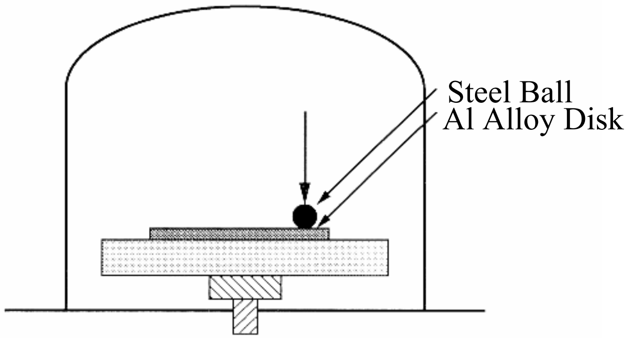
Mr. Charles Taylor (Mechanic)
Considered replacing CI with Al-Cu

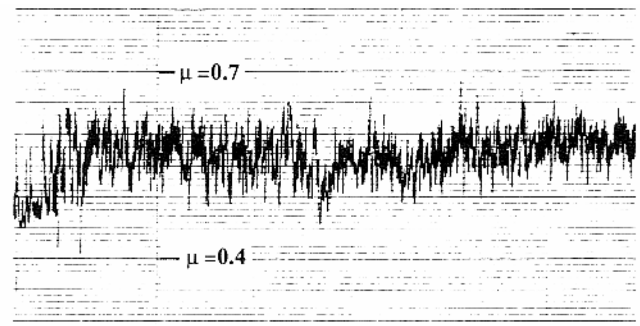
- The Brothers needed an Engine with 8 HP weighing <180 lbs



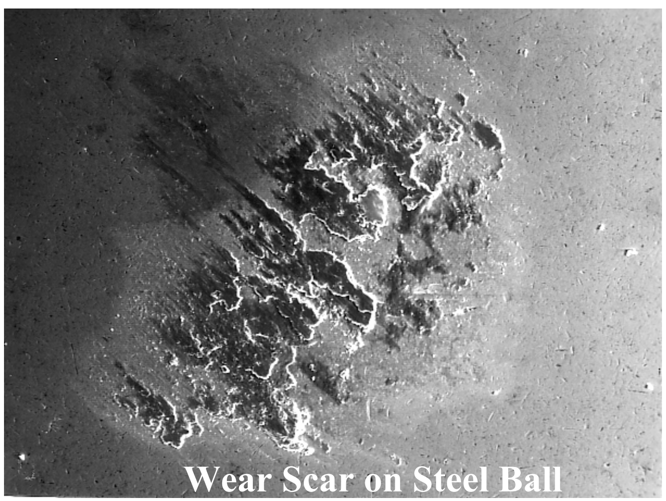
- 16 HP-12HP 178 lbs
- The Brothers used the extra weight allowance to strengthen the wings and frame
- But Al has a tendency for seizure and galling in the absence of complete fluid film lubrication

Aluminum has poor resistance to seizure and galling

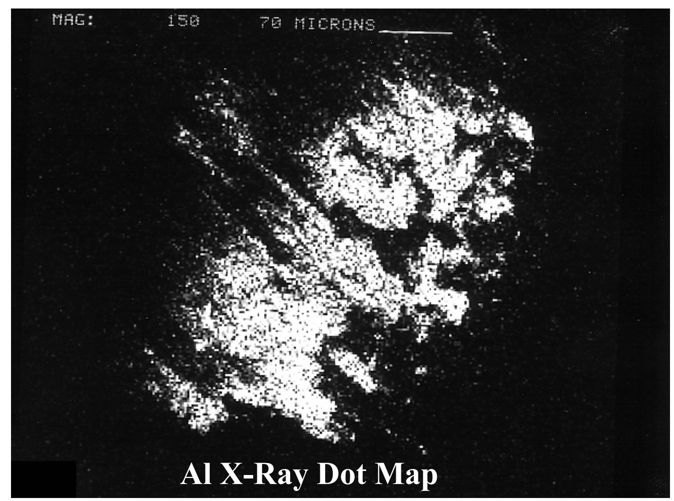




- **In the absence of external fluid lubrication, aluminum has a tendency to adhere to the hard counterface, creating an interface of weak nature. Note the transfer of aluminum to the steel counterface during a ball-on-disk test. Friction is of stick-slip type with a coefficient of 0.5 to 0.6.**



Wear Scar on Steel Ball

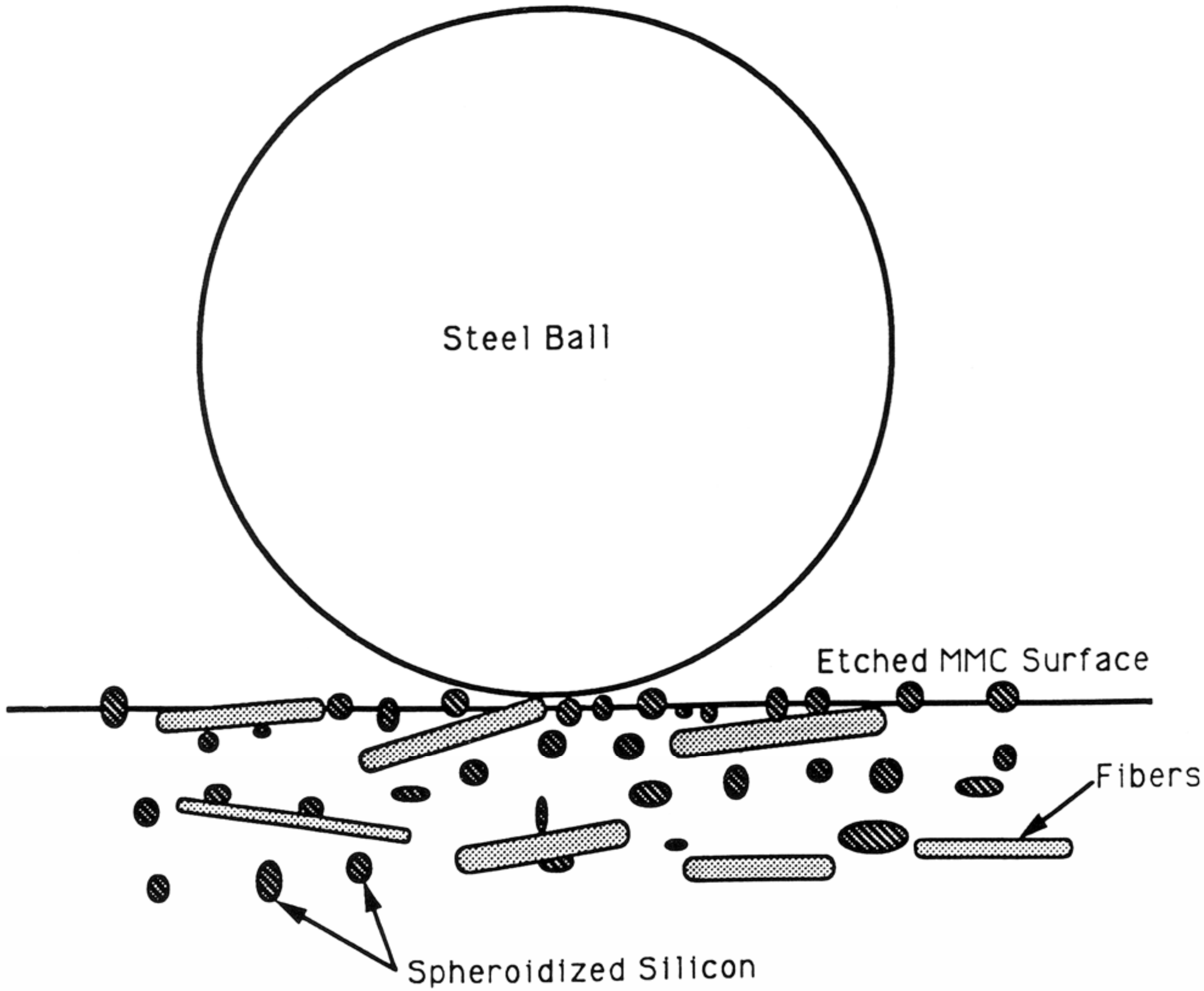


Al X-Ray Dot Map

Mr Taylor's solution: Use thin cast iron liners in Al-Cu crankcase

Sandia National Laboratories

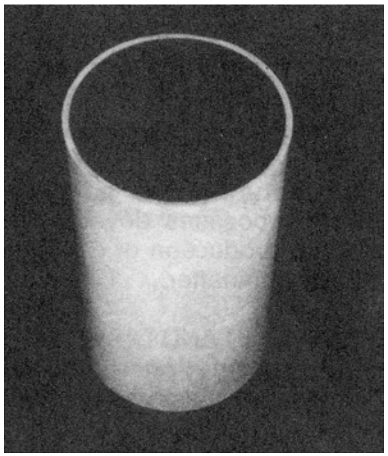
Engineered Surfaces for Precise Balance of Tribological and Physical Properties



S. V. Prasad and K. R. Mecklenburg, Wear 162 (1993) 47-56

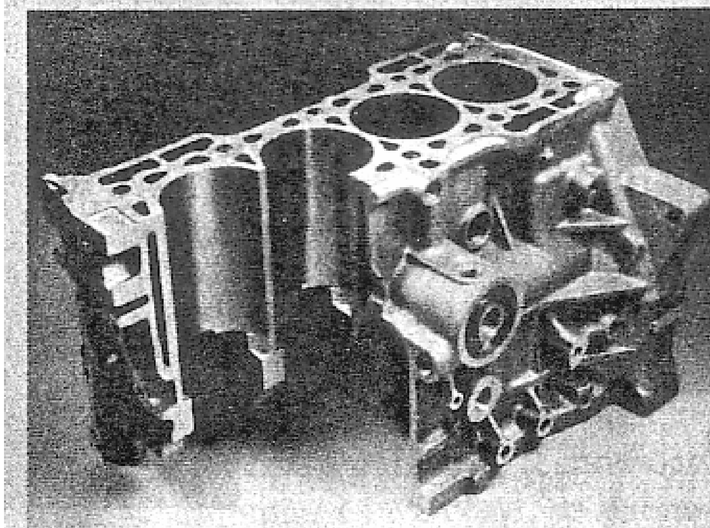
Sandia National Laboratories

Integrally Cast MMC Cylinder: Honda Corporation



Preform

A porous hybrid material made out of Short alumina and Carbon fibers



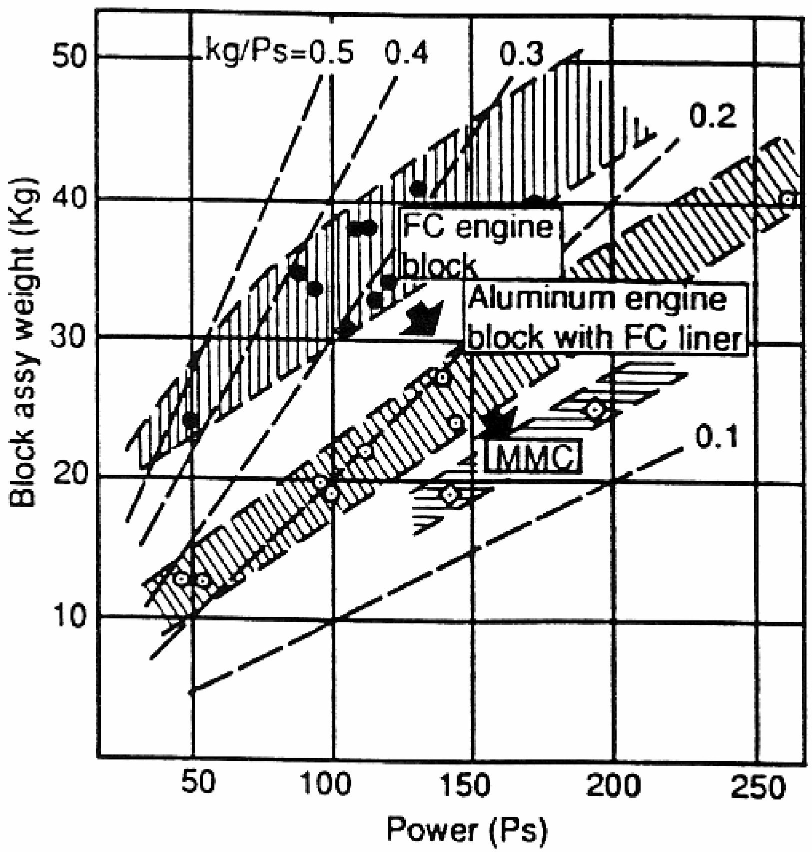
The integrally cast metal-matrix composite cylinder walls of the engine save weight and space, while improving its durability and ability to dissipate heat.

- Ceramic "preform" production
- Pressure casting process
- Honing

M. Ebisawa et. al, "The Production Process for MMC Engine Block", SAE 910835

Sandia National Laboratories

Relationship between Power and engine block weight



The new engine block features higher performance, further compactness and weight reduction compared to cast-iron engine blocks and those made out of Al alloy with cast-iron liners

M. Ebisawa et. al, "The Production Process for MMC Engine Block", *SAE 910835*

Commercial Applications of Al MMCs

Manufacturer	Component & Composite
Duralcan, Martin Marietta, Lanxide	Pistons, Al/SiC_p
Duralcan, Lanxide	Brake rotors, calipers, liners, Al/SiC_p
GKN, Duralcan	Propeller shaft, Al/SiC_p
Nissan	**Connecting rod, Al/SiC_w**
Dow Chemical	Sprockets, pulleys, covers, Mg/SiC_p
Toyota	Piston rings, Al/Al_2O_3 (saffil) & Al/$Boria_w$
Dupont, Chrysler	Connecting rods, Al/Al_2O_3
Hitachi	Current collectors, Cu/graphite
Associated Engineering, Inc.	Cylinders, pistons, Al/graphite
Martin Marietta	Pistons, connecting rods, Al/TiC_p
Zollner	Pistons, Al/fiberfrax
Honda	**Engine blocks, Al/Al_2O_3 – C_f**
Lotus Elise, Volkswagon	Brake rotors, Al/SiC_p
Chrysler	Brake rotors, Al/SiC_p
GM	Rear brake drum for EV-1, driveshaft, engine cradle, Al/SiC_p
MC-21, Dia-Compe, Manitou	Bicycle fork brace and disk brake rotors, Al/SiC_p
3M	Missile fins, aircraft electrical access door, Al/$Nextel_f$
Knorr-Bremse; Kobenhavn	Brake disc on ICE bogies, SiC/Al
Alcoa Innometalx	Multichip electronic module, Al/SiC_p
Lanxide	PCB Heat sinks, Al/SiC_p
Cercast	Electronic packages, Al/graphite foam
Textron Specialty Materials	PCB heat sinks, Al/B

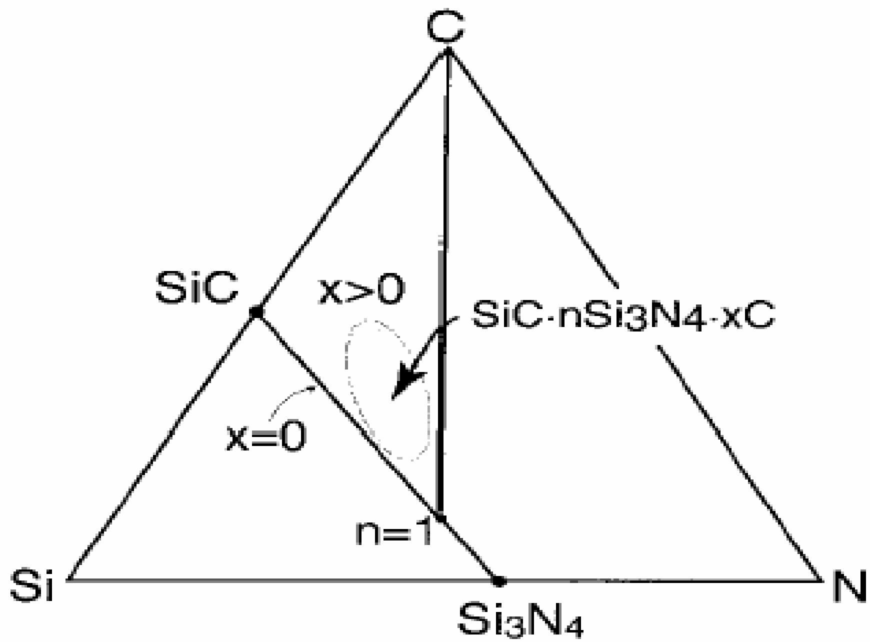
S. V. Prasad and R. Asthana, Tribology Letters 17 (2004) 445-453

Sandia National Laboratories

Polymer-Derived Ceramics

Work in collaboration with the University of Colorado at Boulder
Professor Rishi Raj

Composition diagram and the properties of SiCN PDC materials



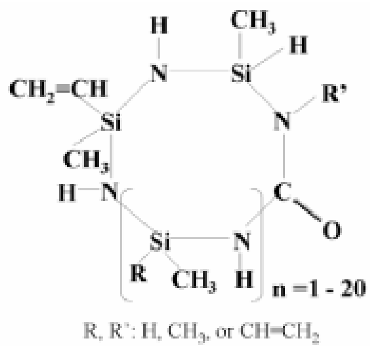
	SiCN	SiC	Si_3N_4
Density (g/cm^3)	2.35	3.17	3.19
E Modulus (GPa)	150	405	314
Poisson's Ratio	0.17	0.14	0.24
CTE (x 10^{-6}/K)	~ 3	3.8	2.5
Hardness (GPa)	25	30	28
Strength (MPa)	1100	418	700
Toughness ($MPa.m^{1/2}$)	3.5	4 - 6	5 - 8
Thermal Shock FOM*	2300	270	890
Creep rate at 1350 °C (s^{-1})	< 10^{-8}	~ 10^{-9}	~ 10^{-9}
Oxidation rate at 1350 °C ($cm/hr^{1/2}$)	~ 10^{-5}	~ 10^{-5}	~ 10^{-5}

* strength/(E-modulus.CTE)

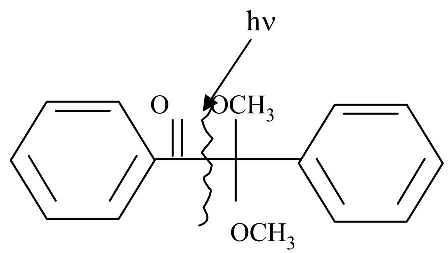
Raj et. al.

Sandia National Laboratories

Fabrication route for polymer-derived ceramics



Ceraset



2,2 Dimethoxy-2-Phenyl-Acetophenone (DMPA)

Ultrahigh Temp Ceramic MEMS

Pyrolyze

Cross-Link to Net-Shape

Liquid Precursor → High Temperature Polymer MEMS

Polymer Micromachining

Micro-casting

SiCN MEMS

Polysilazane MEMS

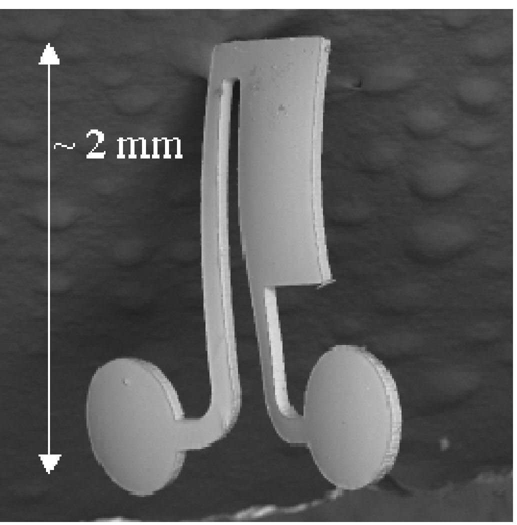
Cast in SU8 molds, followed by de-molding

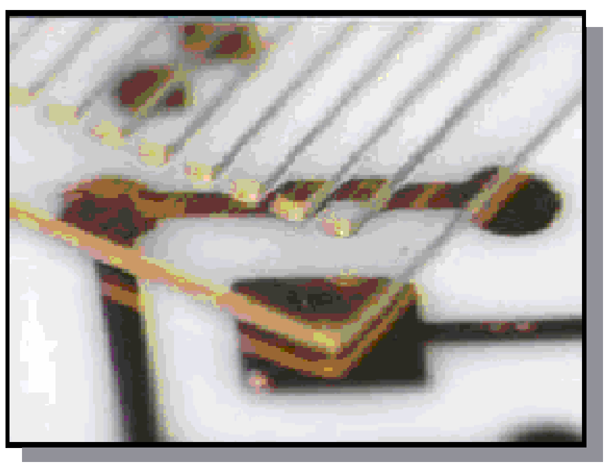
Direct Photopolymerization

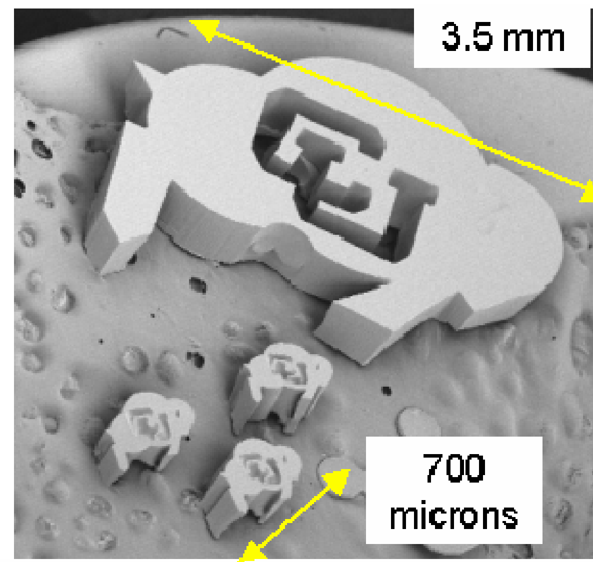
SiCN MEMS

Polysilazane MEMS

Treat precursor as a negative photoresist

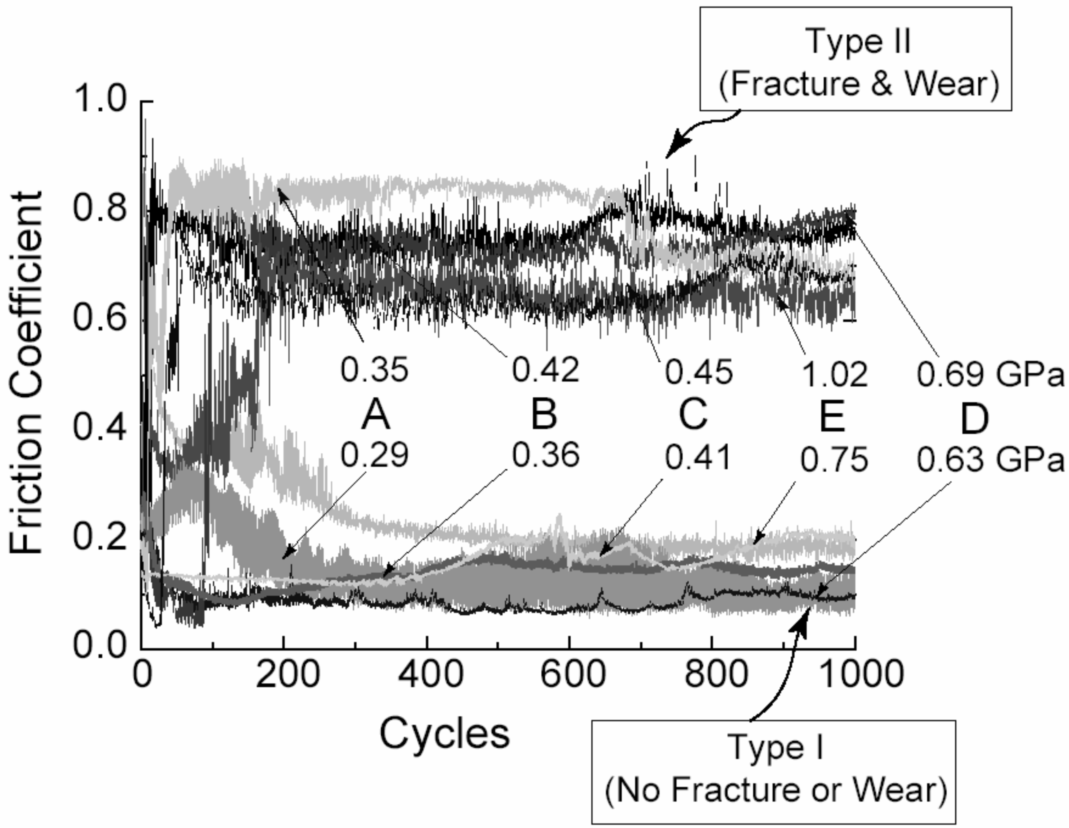




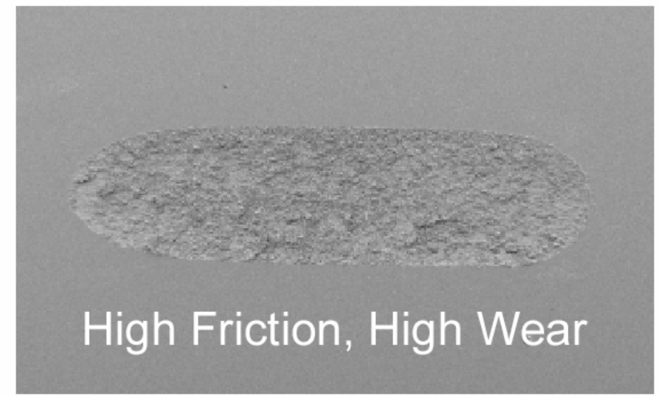


Preceramic polymer buffaloes, 500 microns thick

Friction behavior in dry nitrogen



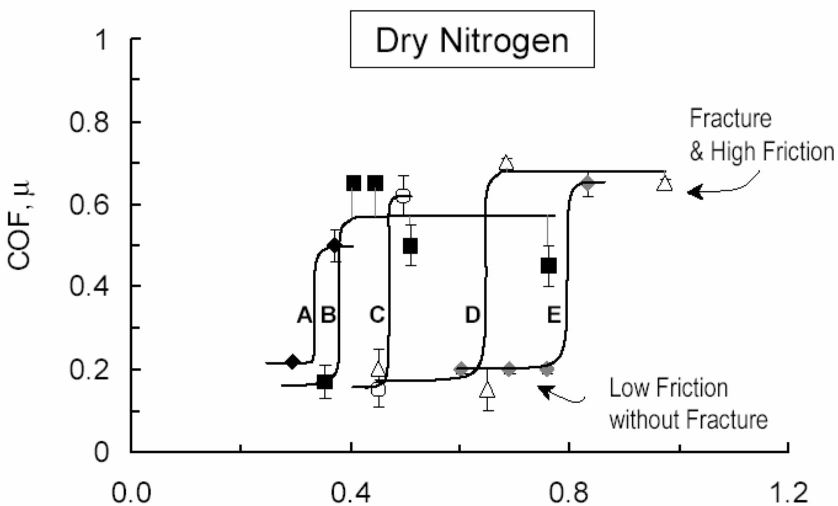
Type II: 097 GPa, μ~0.7

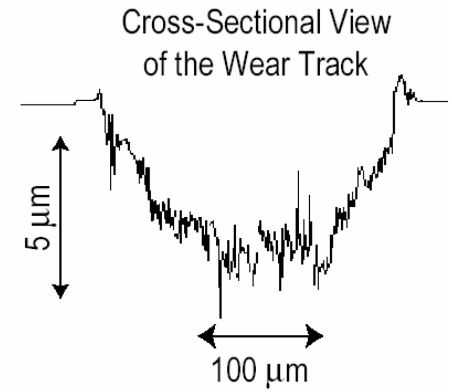


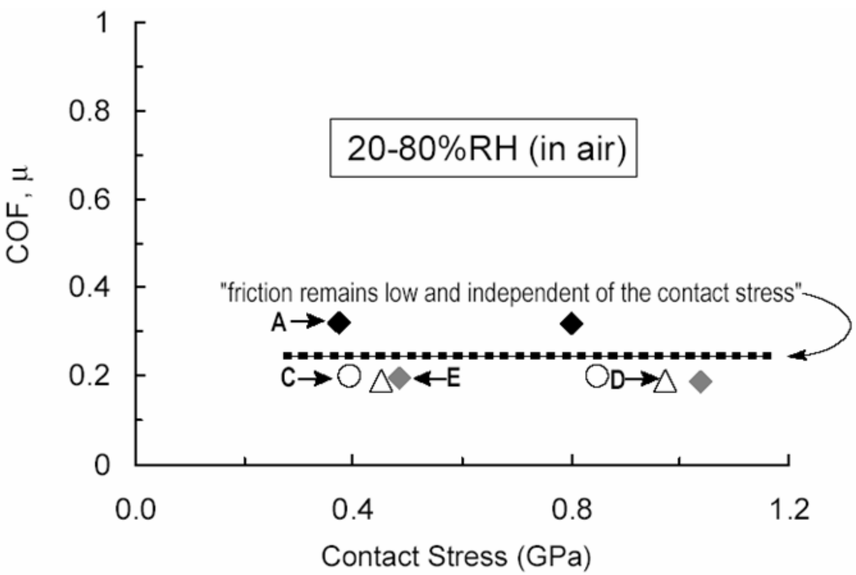
200 μm

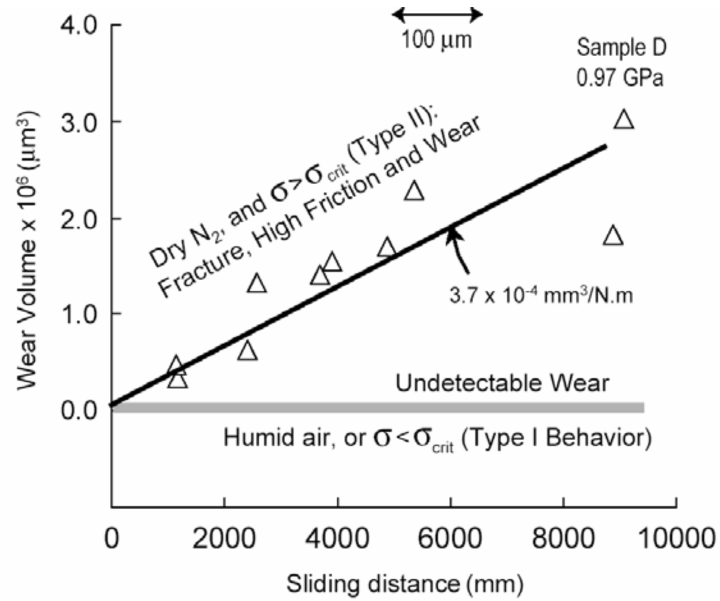
Type I: 0.36 GPa, μ~0.2

Environmental effects on friction and wear transitions



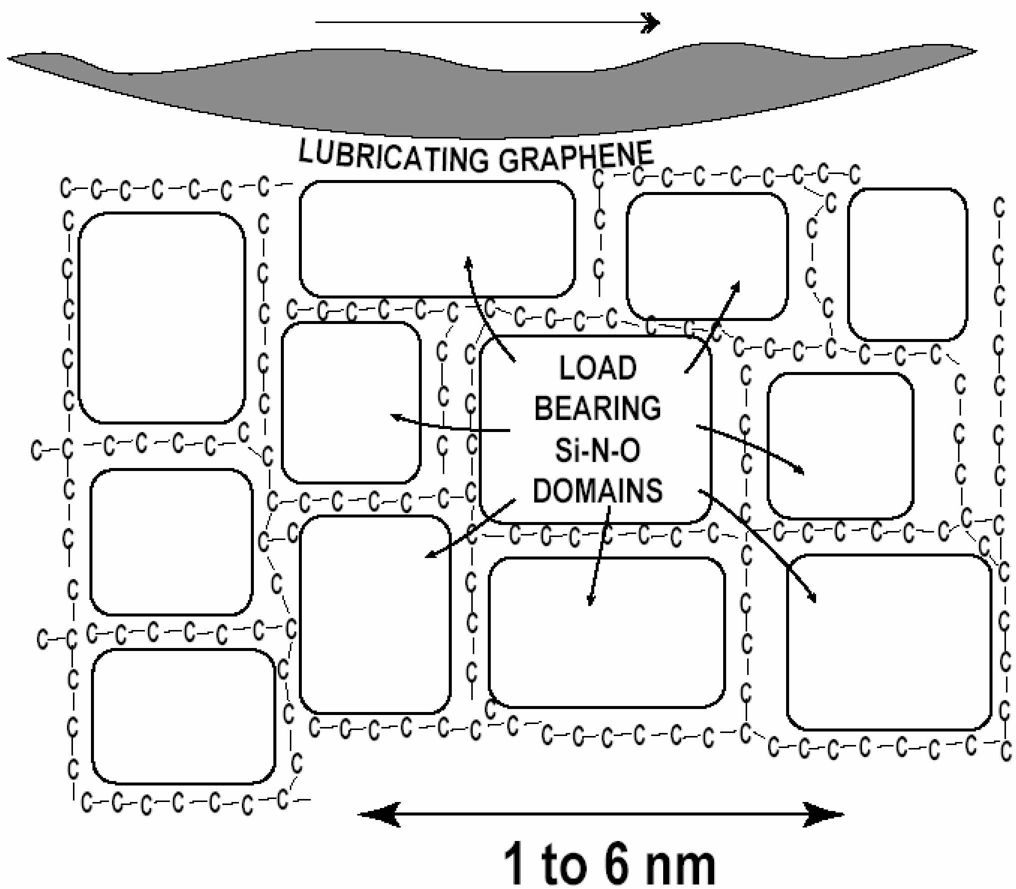






Laboratories

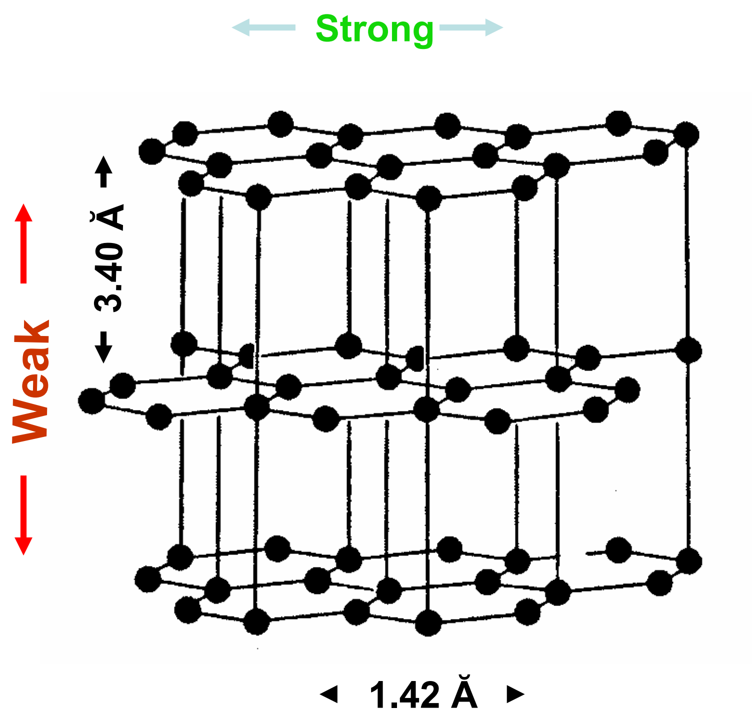
Schematic depiction of dual-phase structure in SICNO



Sandia National Laboratories

Solid Lubricants

Lubrication by graphite



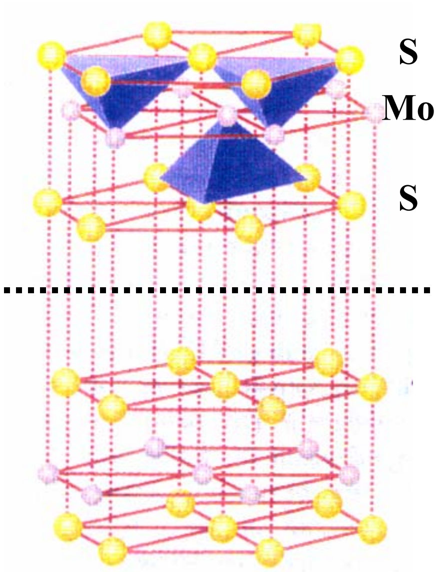
Graphite

Element C (four valence electrons) can exist in different allotropic forms

- sp^2 bonding configuration (crystalline graphite as shown in the right): basal planes held with strong covalent bonds, while the planes are held with weak Van der Waals forces. This gives rise to interlamellar mechanical weakness. Other sp^2 kinds include: carbon-carbon composites, unhydrogenated carbon, etc.
- sp3 bonding in diamond
- Hydrogenated carbon with various degrees of sp^2/sp^3 bond ratios that are commonly known as diamond-like carbon.

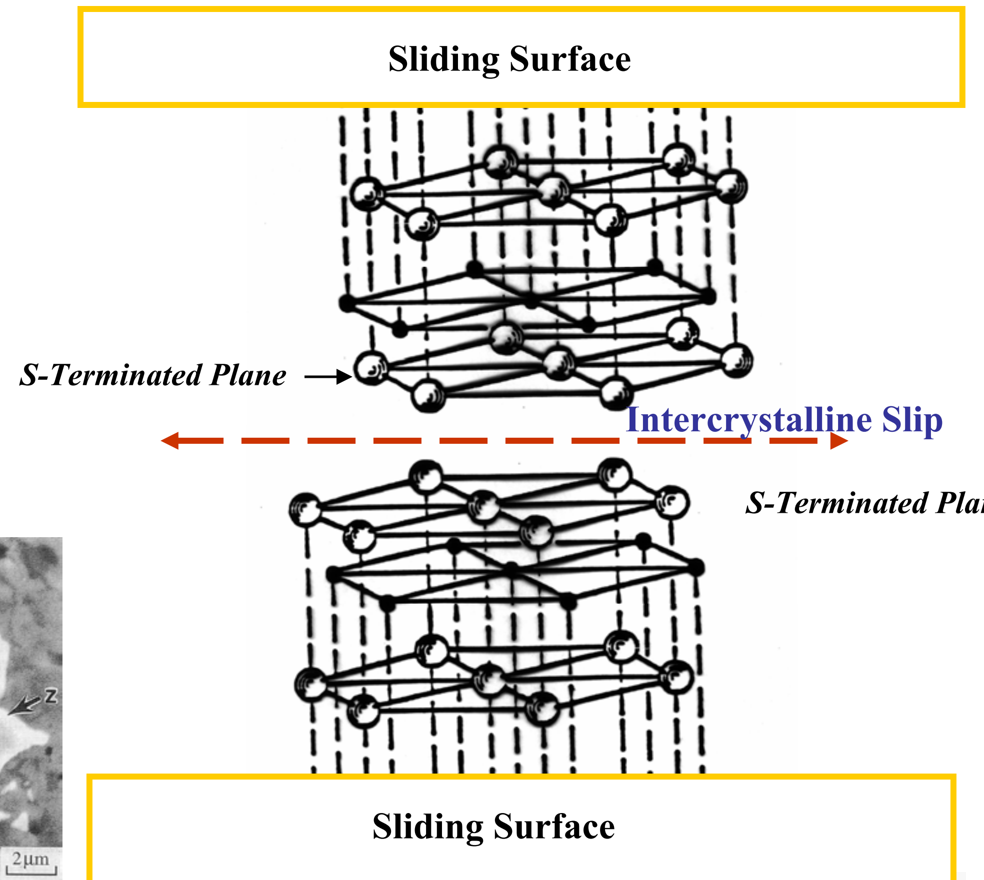
Graphite needs moisture or adsorbed gases in the environment (>100 ppm) (they either act as intercalants, or passivate the dangling covalent bonds) to lubricate.
In vacuum, graphite exhibits high friction and wear—a phenomenon known as "dusting", first observed in the late 1930's when graphite brushes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

Transition metal dichalcogenides (MoS_2, WS_2)

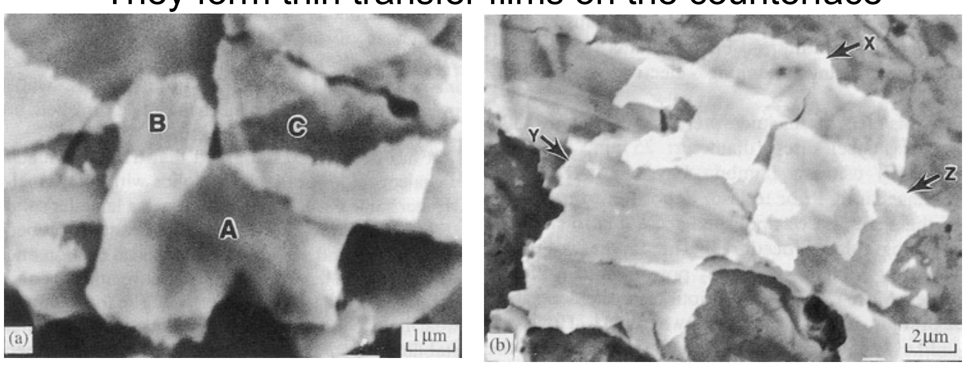


Mo/W Disulfide

Extremely low COF (0.01-0.05) and long wear life (millions of wear cycles for a micron thick MoS_2 film), **but only in dry environments**.



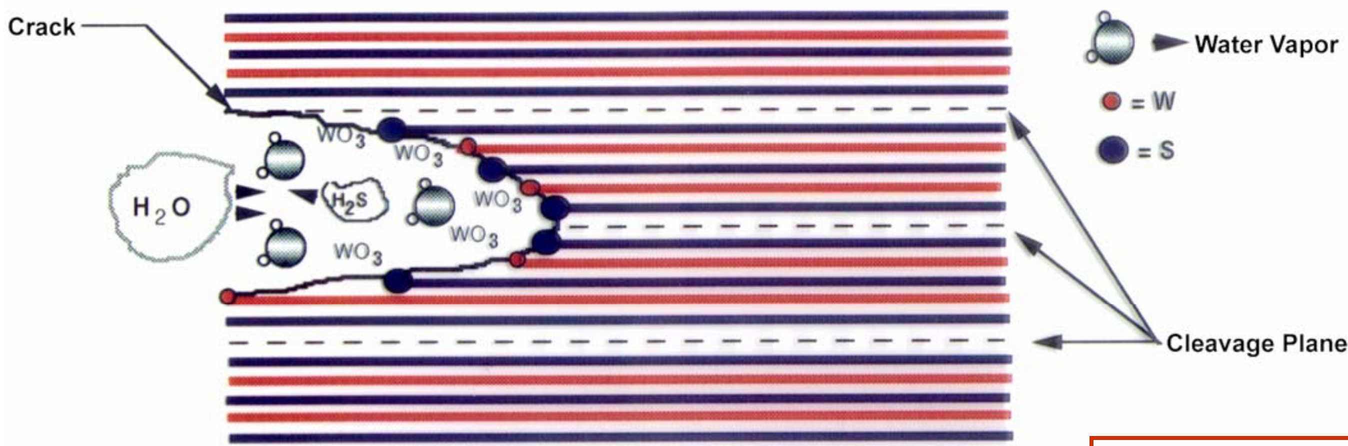
They form thin transfer films on the counterface

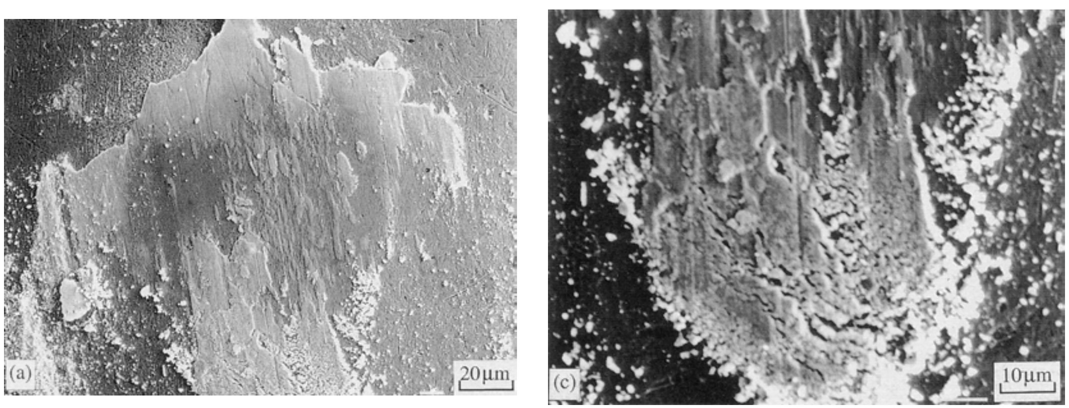


S. V. Prasad and J. S. Zabinski, *J. Mater. Sci. Lett*. 12 (1993) 1413-1415

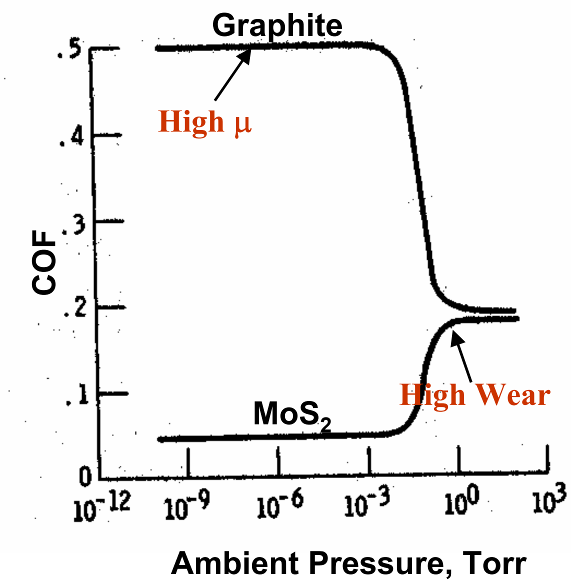
Sandia National Laboratories

Oxidize in humid environments, losing their ability to lubricate





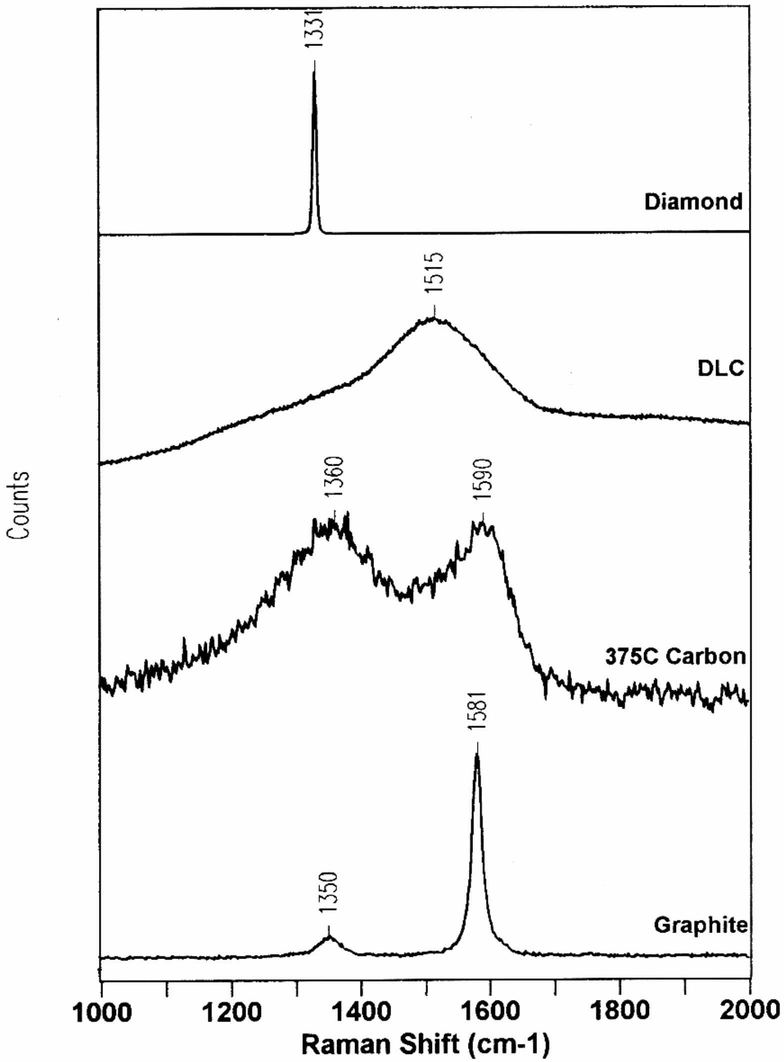
Typical transfer films (WS_2) in humid air

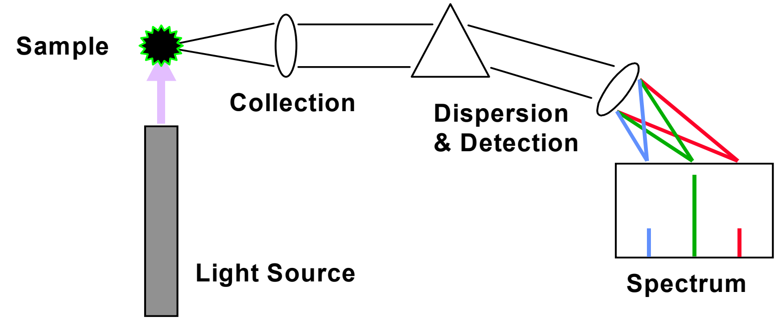


S. V. Prasad, J. S. Zabinski and N. T. McDevitt, Tribology Transactions, 38 (1995) 57-62

Sandia National Laboratories

Carbon can exist in different forms





Argon laser: 458 nm wavelength
Spot size: 1 μm (Microscope Accessory)

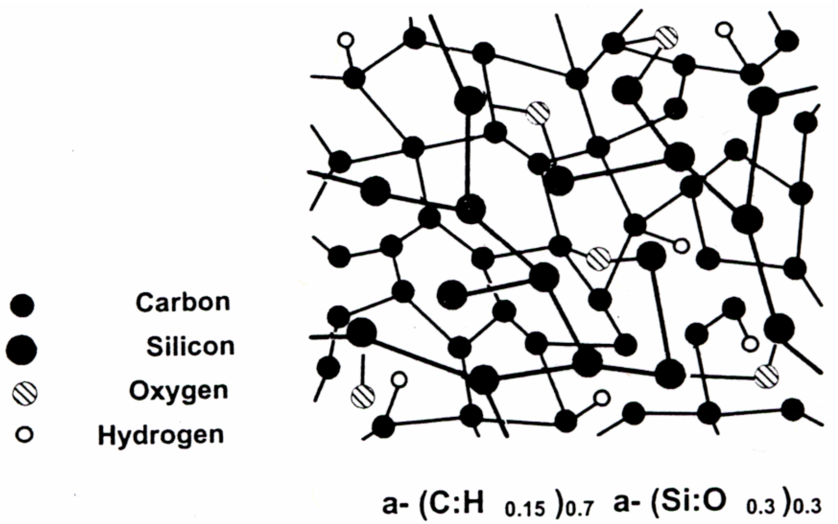
D. R. Tallant et. al, *Diamond and Related Materials* 4 (1995) 191-199

Sandia National Laboratories

Diamond like nanocomposite (DLN) coatings were produced by PECVD (Source: Bekart Advanced Coating Technologies)

Plasma Enhanced CVD

Ployphenylmethylsiloxane precursor



Schematic of DLN atomic structure.

Interpenetrating random networks DLC (a-C:H) and glass like a-Si:O

- Conformal coatings could provide coverage of sidewalls
- Substrate temperatures do not typically exceed 150 to 200 ºC

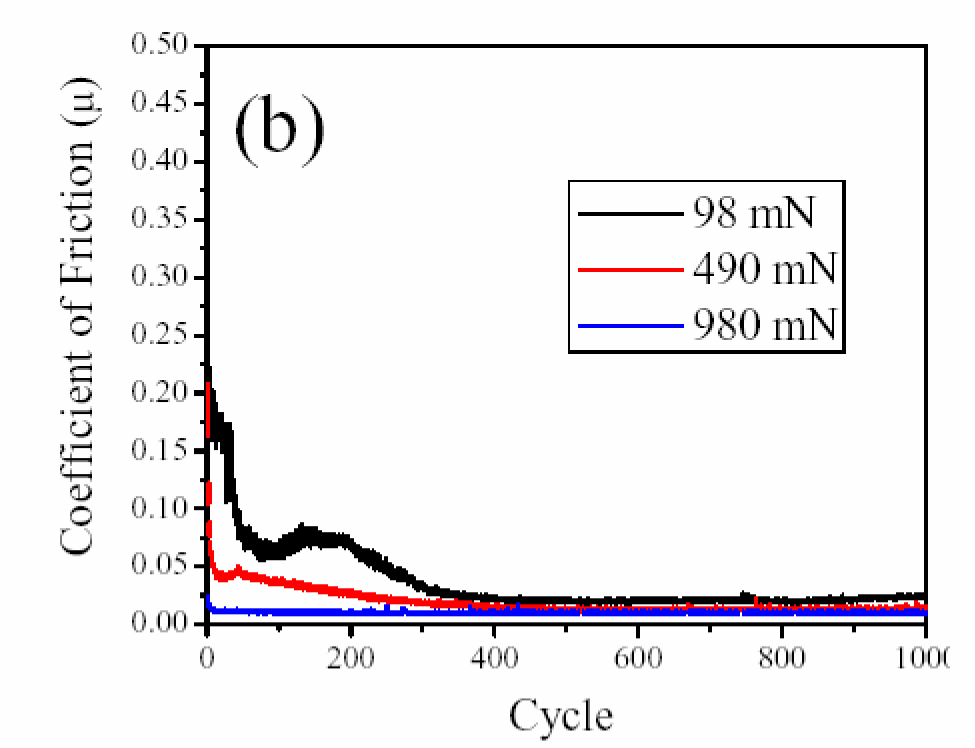
Hardness: 9-17 GPa
Modulus: 90-140 GPa

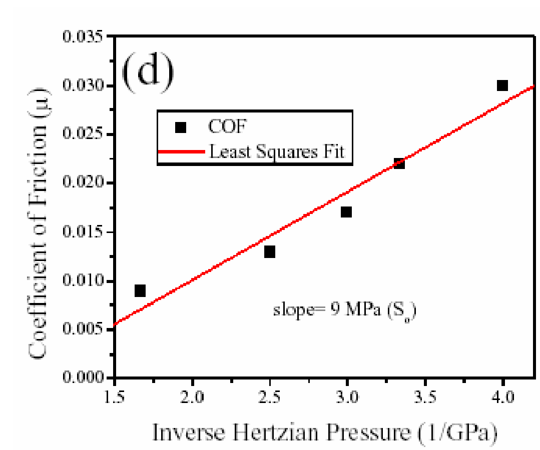
V. F. Dorfman, *Thin Solid Films*, 212 (1992) 267-273

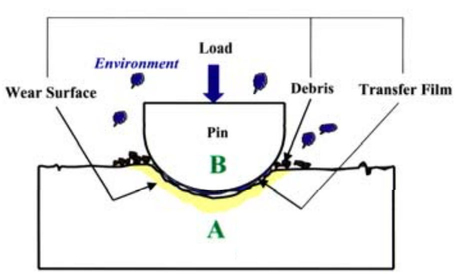
D. J. Kester, C. L. Brodbeck, I. L. Singer and A. Kyriakopoulos, *Surface and Coatings Tech*. 113 (1999) 268-273.

C. Venkatraman, C. Brodbeck and R. Lei, *Surface and Coatings Tech*. 115 (1999) 215-221.

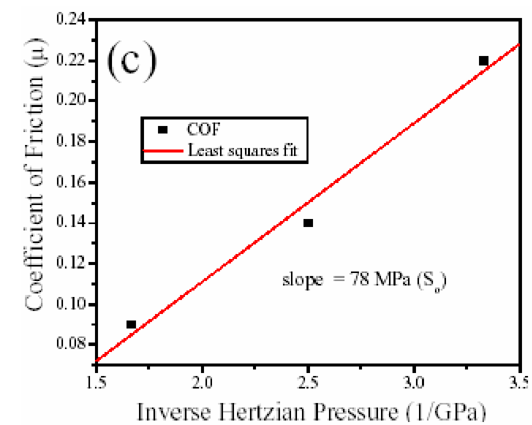
Many solid lubricants exhibit is non-Amontonian friction behavior





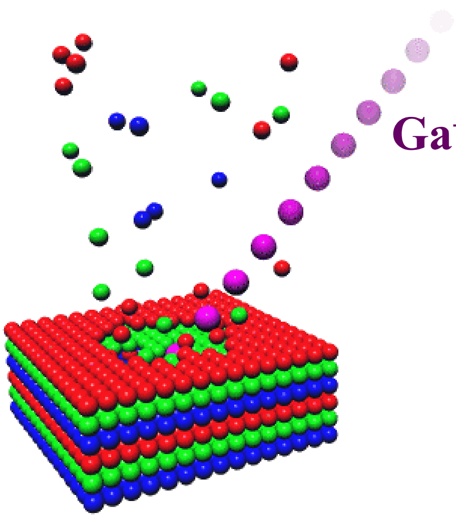


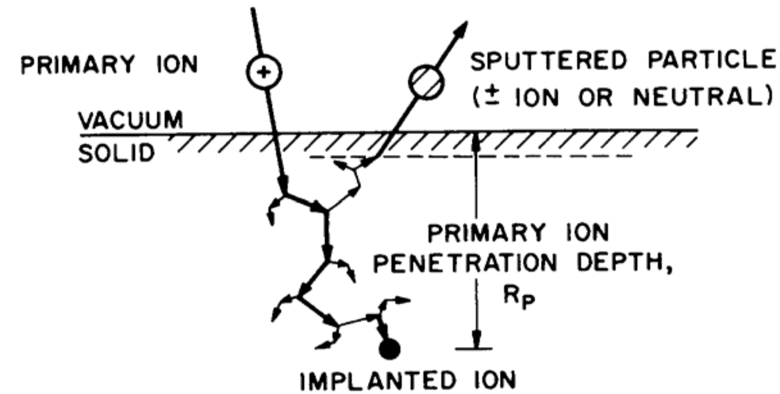
$$\mu = S_o/P + \alpha$$

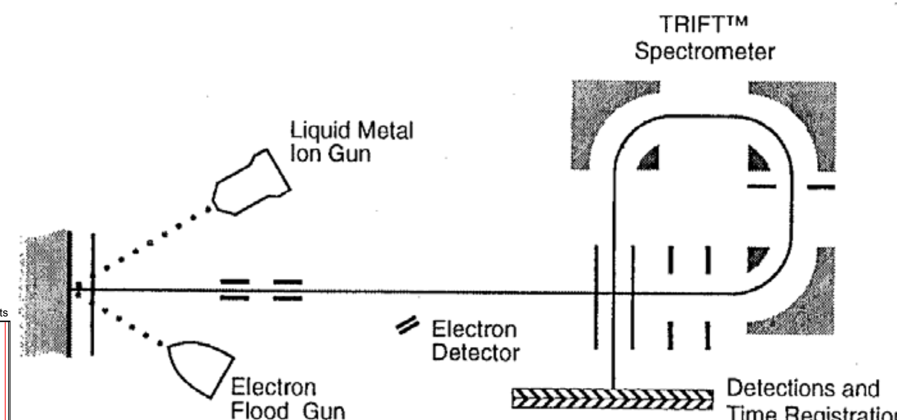


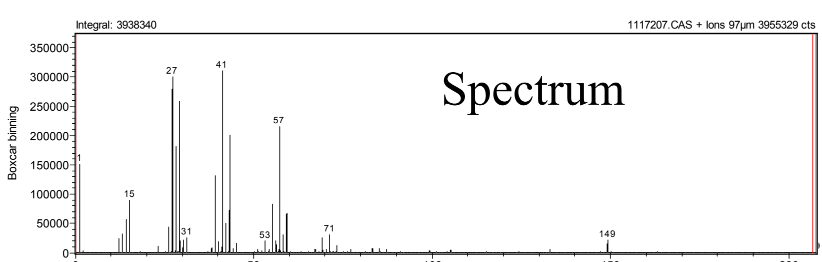
Time-of-Flight Secondary Ion Mass Spectrometry

+/- Ions and Neutrals ejected from surface (Elemental and Molecular)





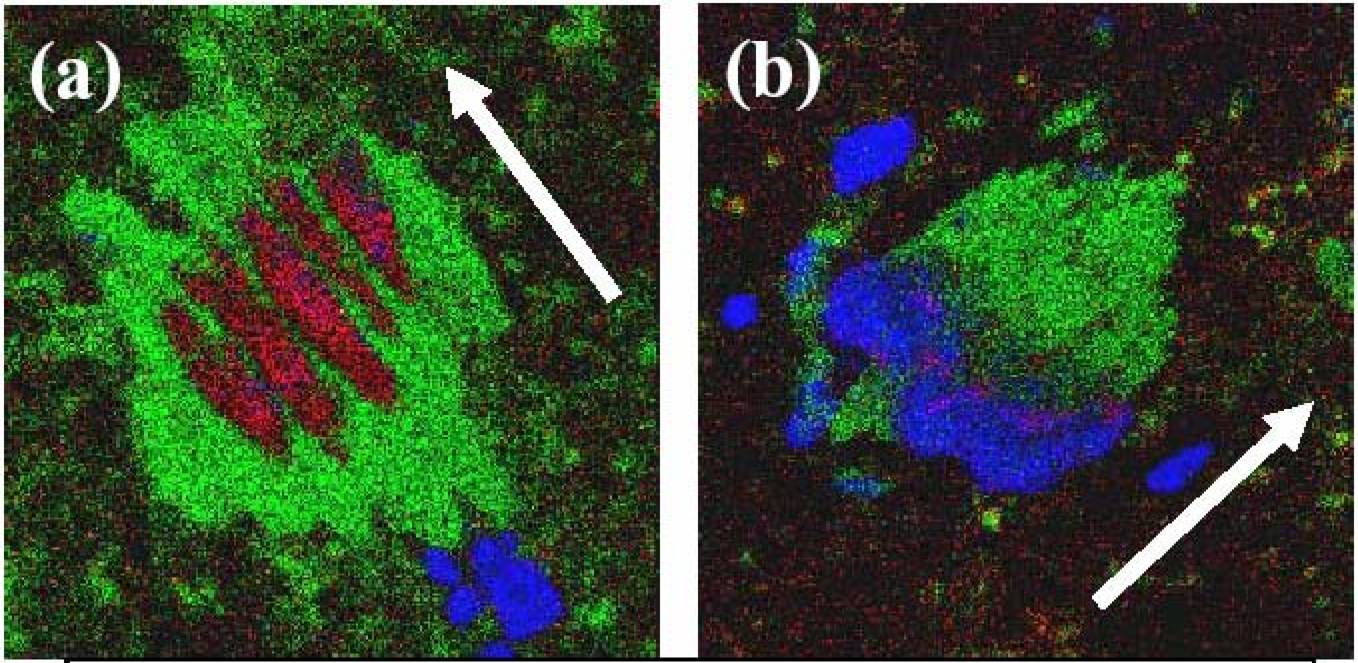




National Laboratories

Spectral Imaging and Multivariate Analysis

Wet   Dry

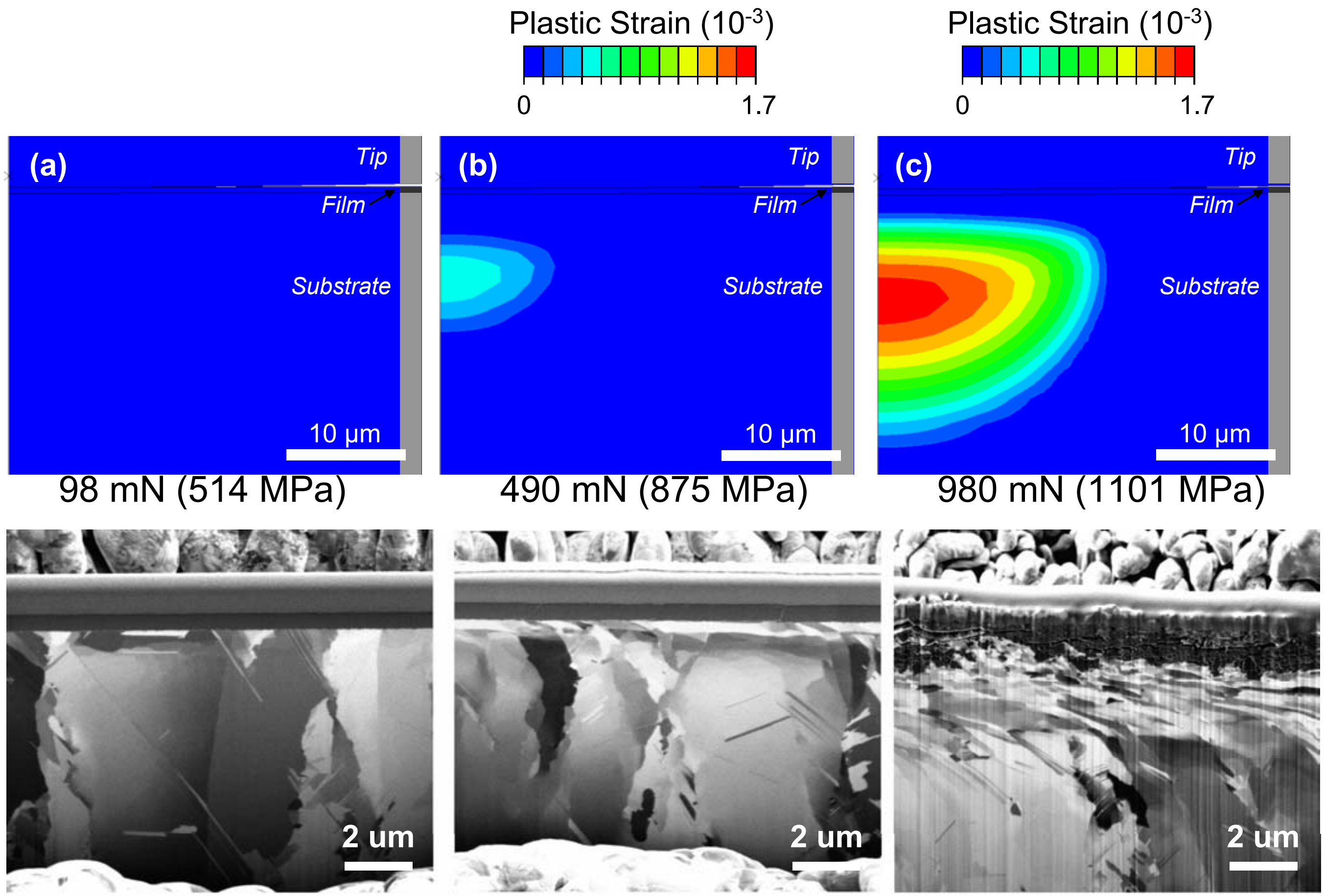


Red: SiO_2 ($O + Si + SiO_2 + SiO_3$)

Green: Long Range Carbon (C_1 to C_4 fragments)

Blue: Hydrogenated Carbon ($CH + CH_2 + C_2H$)

FEA and FIB can reveal the onset of substrate plastic deformation



Generation of plastic strain under 1/8" Si_3N_4 ball on DLN-coated Ni at peak contact stresses of (a) 507 MPa [98 mN], (b) 864 MPa [490 mN] and (c) 1088 MPa [980 mN].

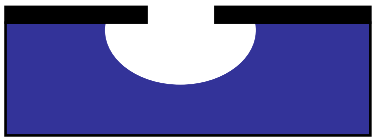
Sandia National Laboratories

Tribological issues in MEMS

Microelectromechanical Systems (MEMS)

A variety of fabrication methods can be used to construct microsystems

anisotropic

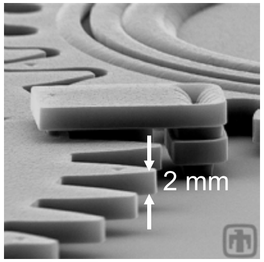


isotropic

Bulk Micromachining

- subtractive process; pattern and etch
- well established for Si; also done in GaAs

SNL

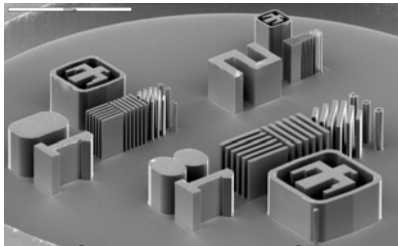


Surface Micromachining

- additive process; structural (Si) and sacrificial (SiO_2) layers
- dissolve sacrificial layers to free structures

Lithographie, Galvanoformung und Abformung (LIGA)

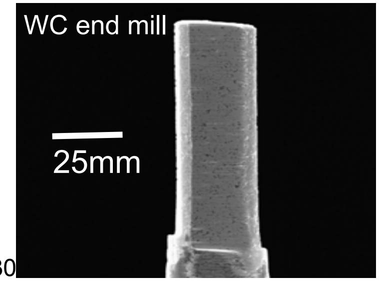
- plate or press into thick polymer mold
- micron to centimeter scale parts

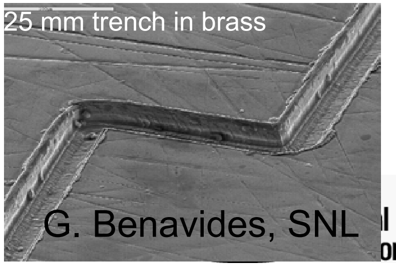


T. Christenson, SNL

Meso-Machining

- subtractive process; push machining methods to micron scale
- micro-milling, micro-EDM, plunge EDM

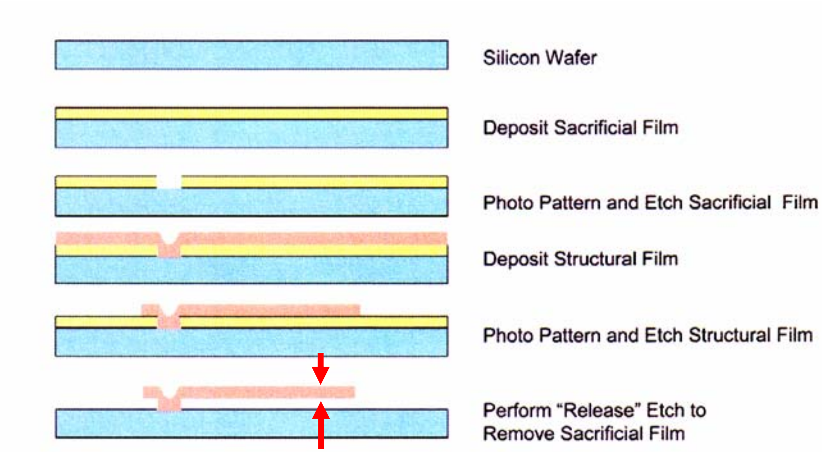


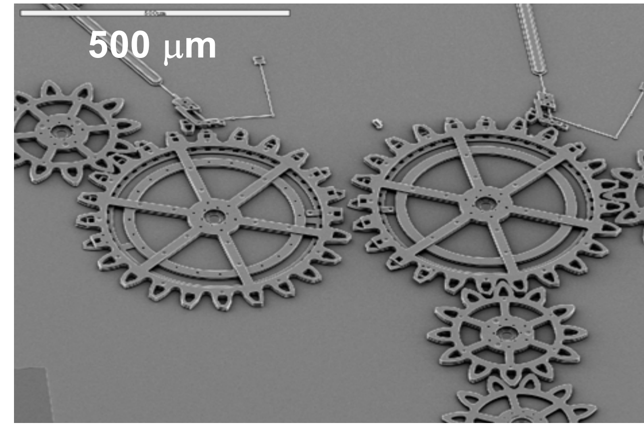


G. Benavides, SNL

Surface Micromachined (SMM) Silicon Devices

Microfabrication with silicon leverages decades of process knowledge
Mature fabrication equipment and processes

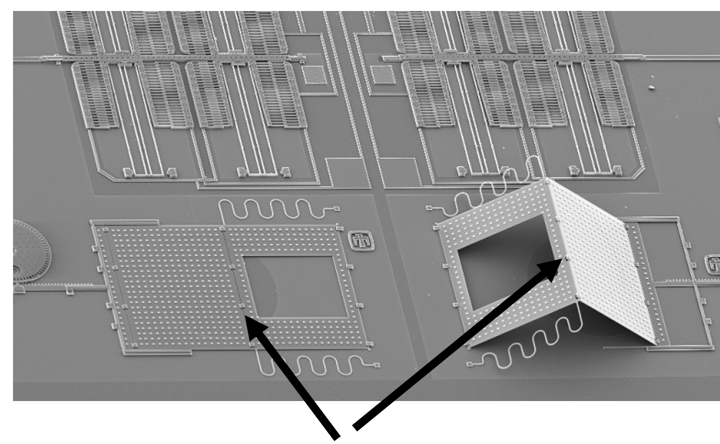




actuators, guides and gears used to achieve motion

In-process adhesion (stiction) is no longer a significant barrier to successful device fabrication and initial operation

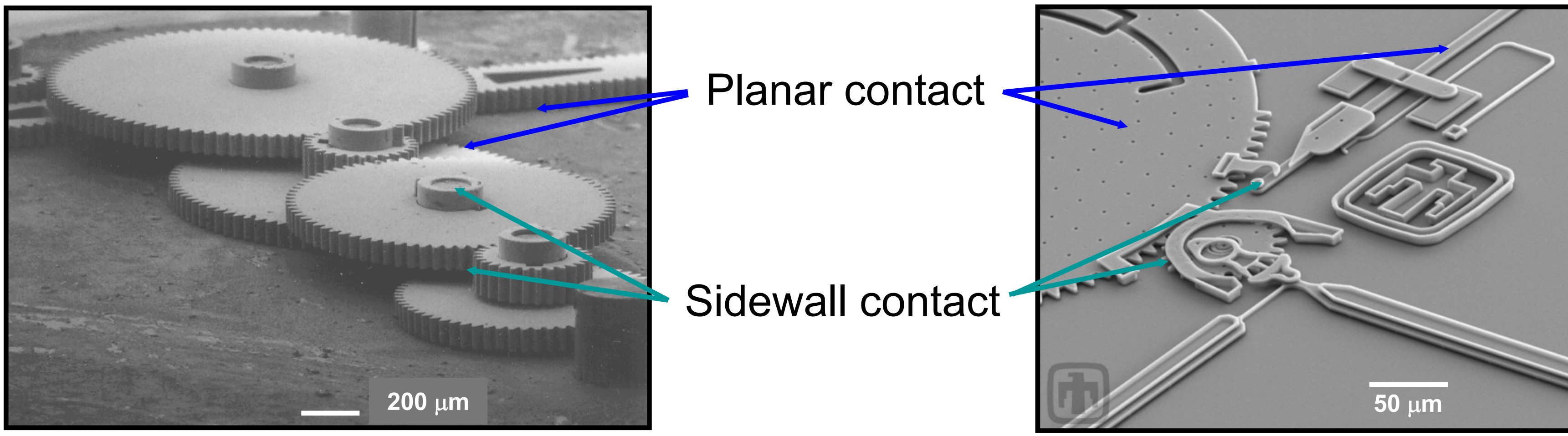
- **Dynamic Interfaces (Tribology)**
- **Dormancy and Materials Aging**
- **Surfaces (Buried/Hidden)**



Pop-up Mirrors

Sandia National Laboratories

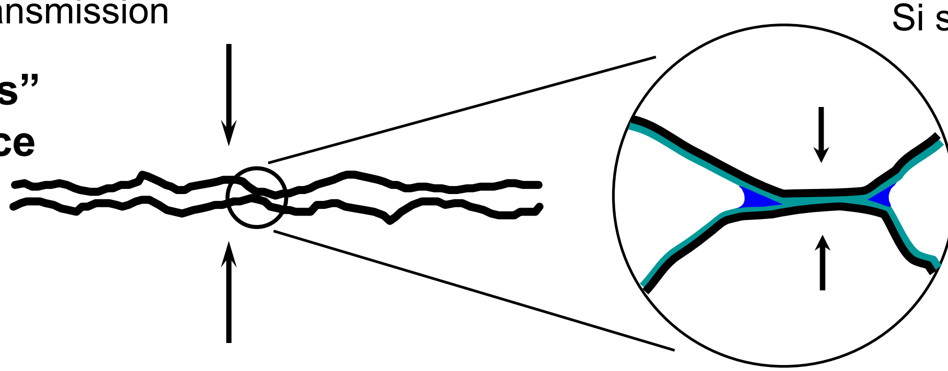
Microsystems frequently contain rubbing surfaces



Electroformed Ni transmission

Si surface micromachined lock

"Macromachines"
applied force
inertia



"Micromachines"
applied force
capillary
electrostatic
Van der Waals

Surface interactions dominate as machine scale is reduced

dormancy ↔ ***friction, wear*** → ***reliability***

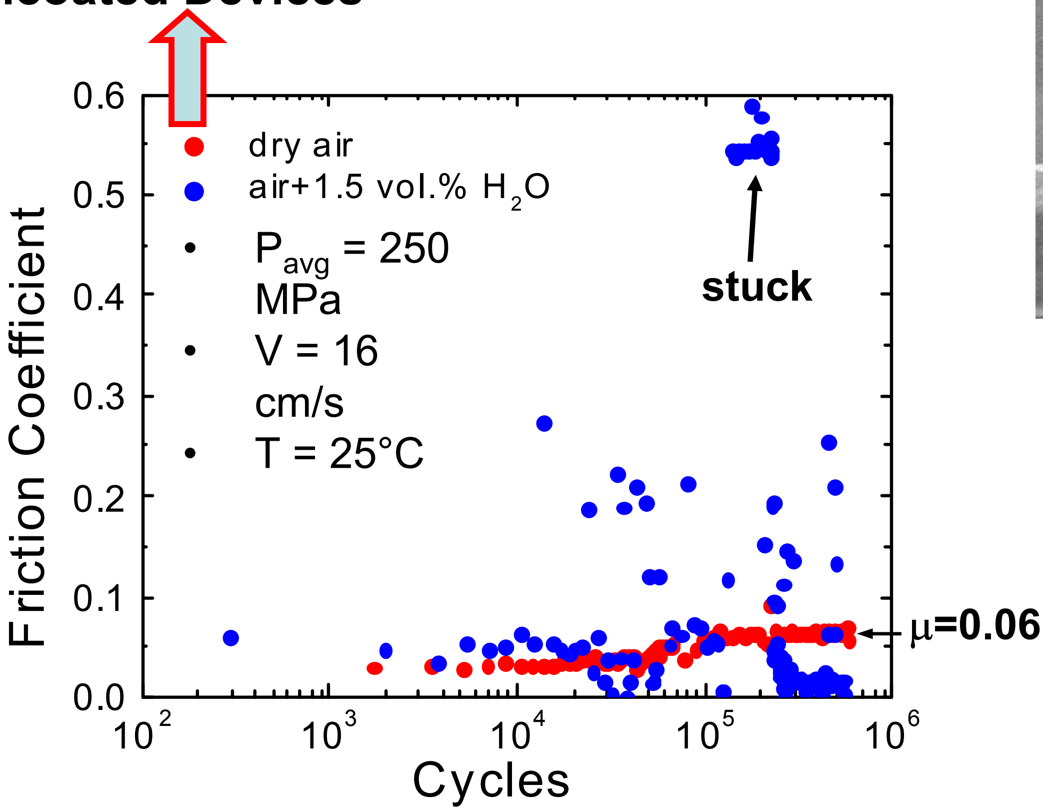
Apply novel, small scale experimental techniques to study tribology.

Sandia National Laboratories

Friction evolution in FTS-coated devices exhibits a strong dependence on the presence of water vapor

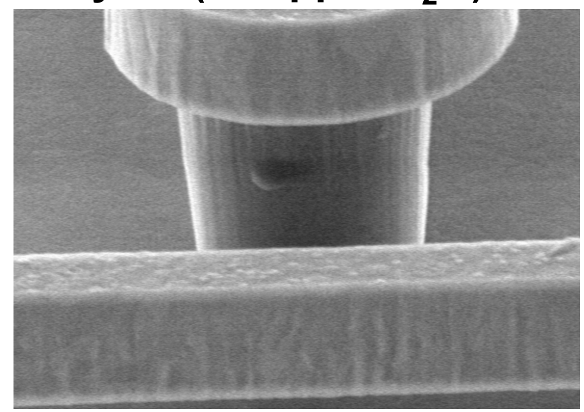
Lubricated with
Perfluorodecyltrichlorosilane (FTS)
$CF_3(CF_2)_7(CH_2)_2SiCl_3$

Uncoated Devices

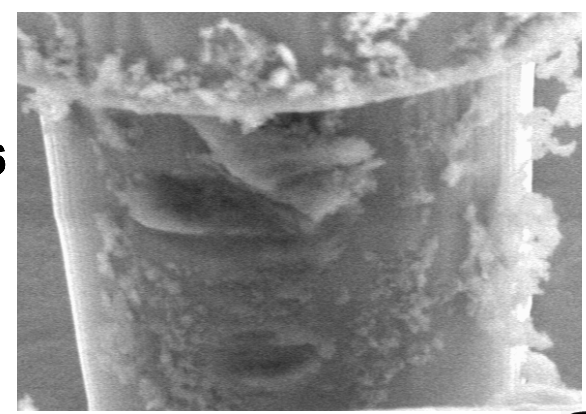


Courtesy: M. T. Dugger (mtdugge@sandia.gov)
Romig AD, Dugger MT, McWhorter, Acta Materialia 51 (2003) 5837

dry air (100 ppm H_2O)

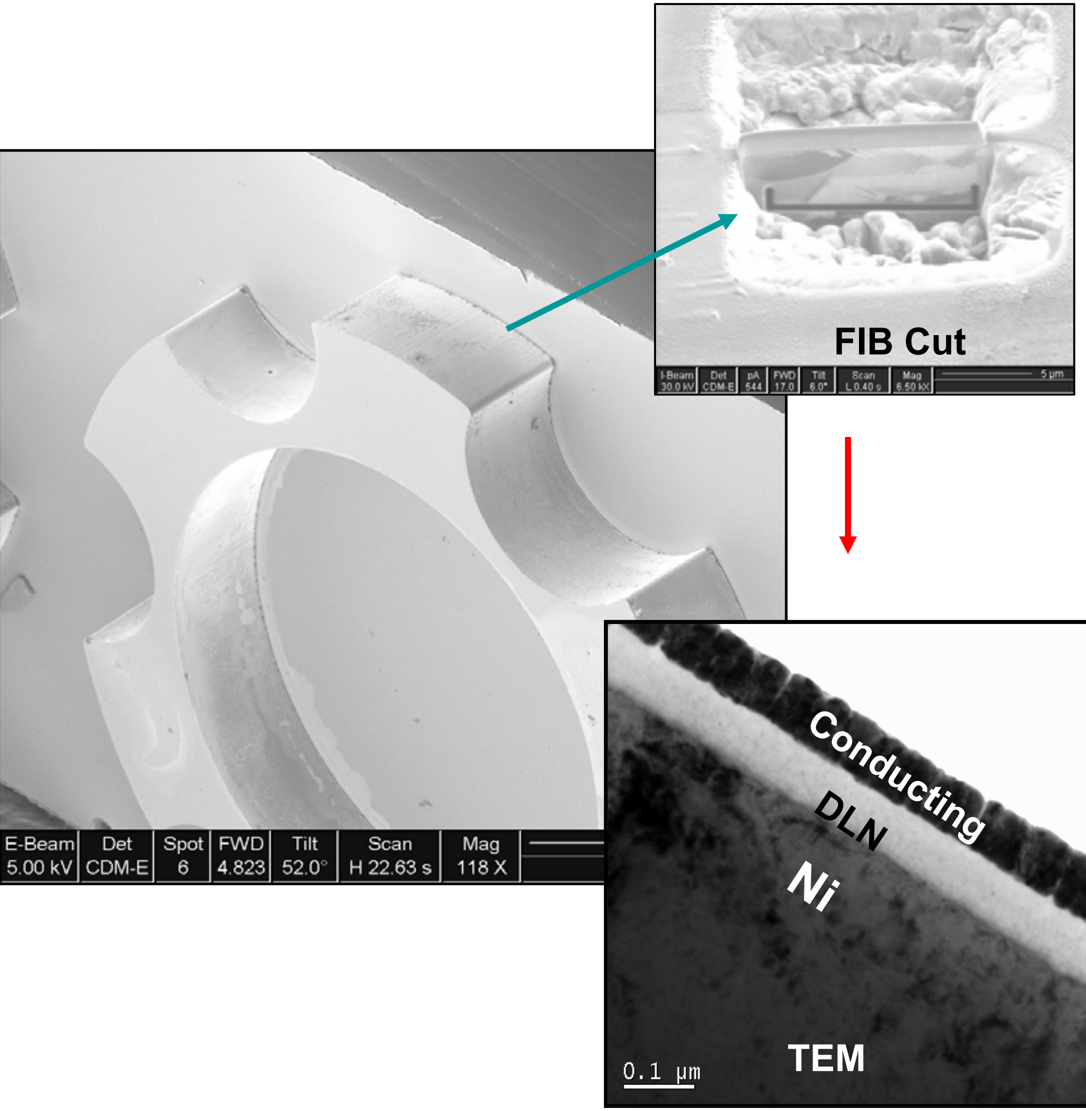


air+1.5 vol.% H_2O (40%RH)

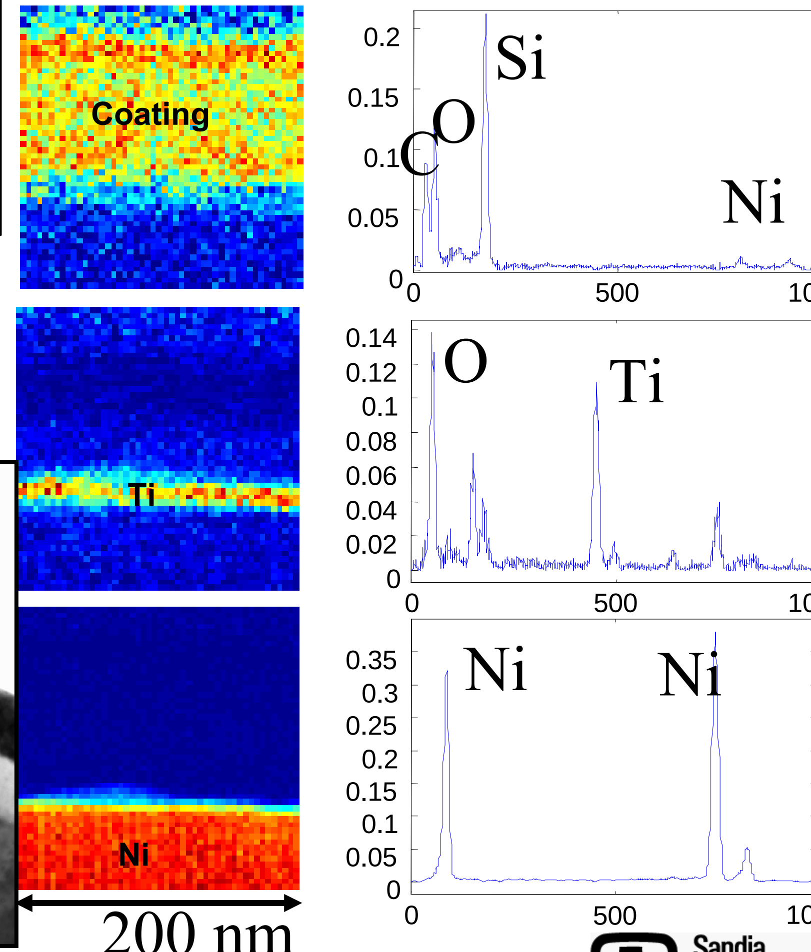


Sandia National Laboratories

Novel techniques are necessary to characterize the chemistry and coverage on the sidewalls of miniature parts



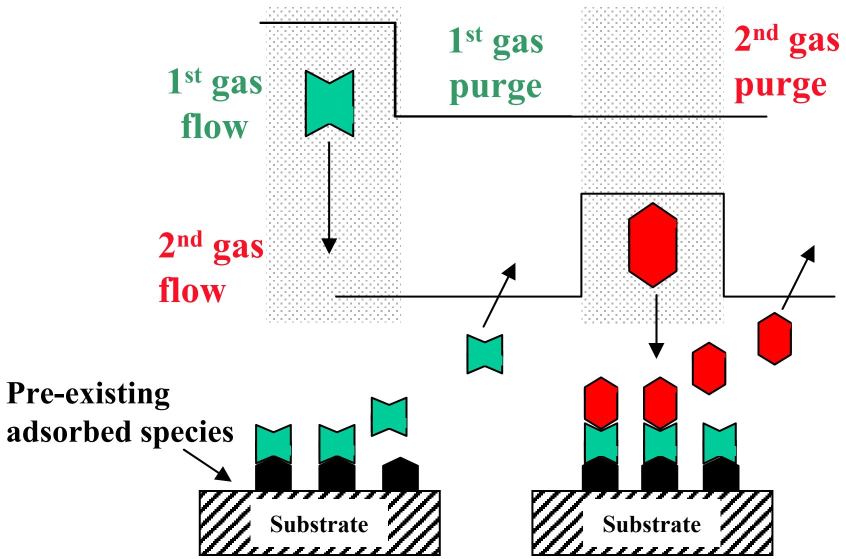
X-ray Spectral Image Analysis



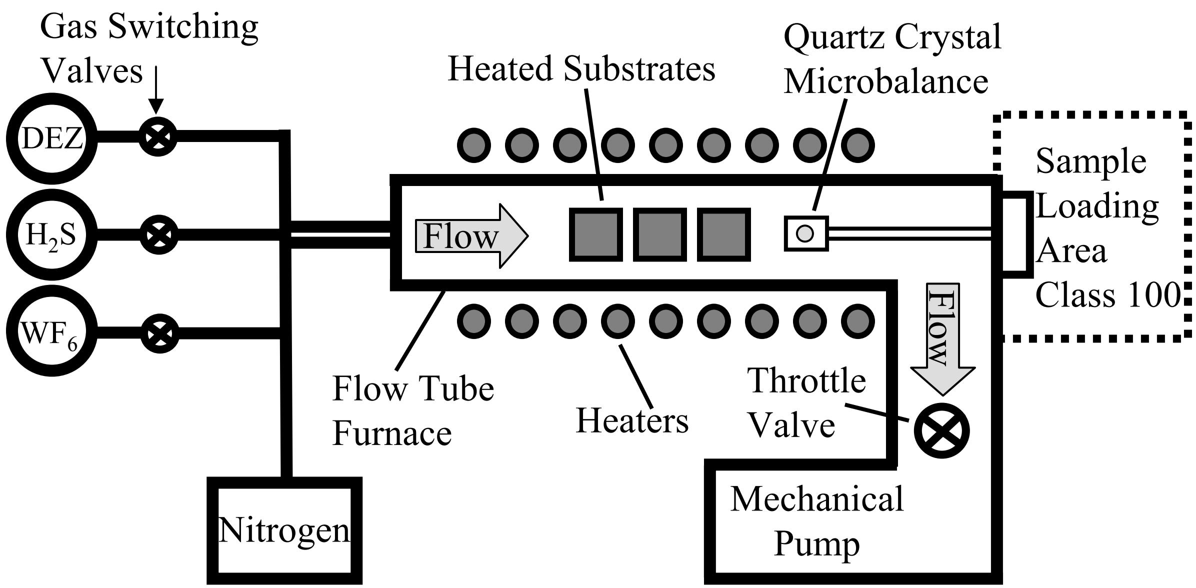
Atomic Layer Deposition (ALD)

Atomic Layer Deposition for Tribological Coatings

Atomic Layer Deposition (ALD) is based on sequential introduction of gaseous precursors and selective chemistry



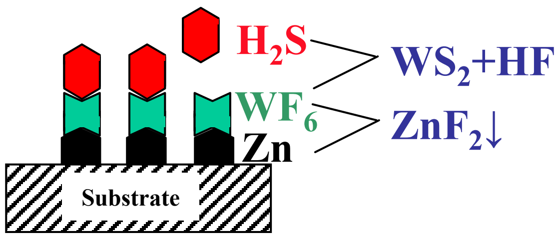
Schematic illustration of the ALD reactor for the synthesis of WS_2 films



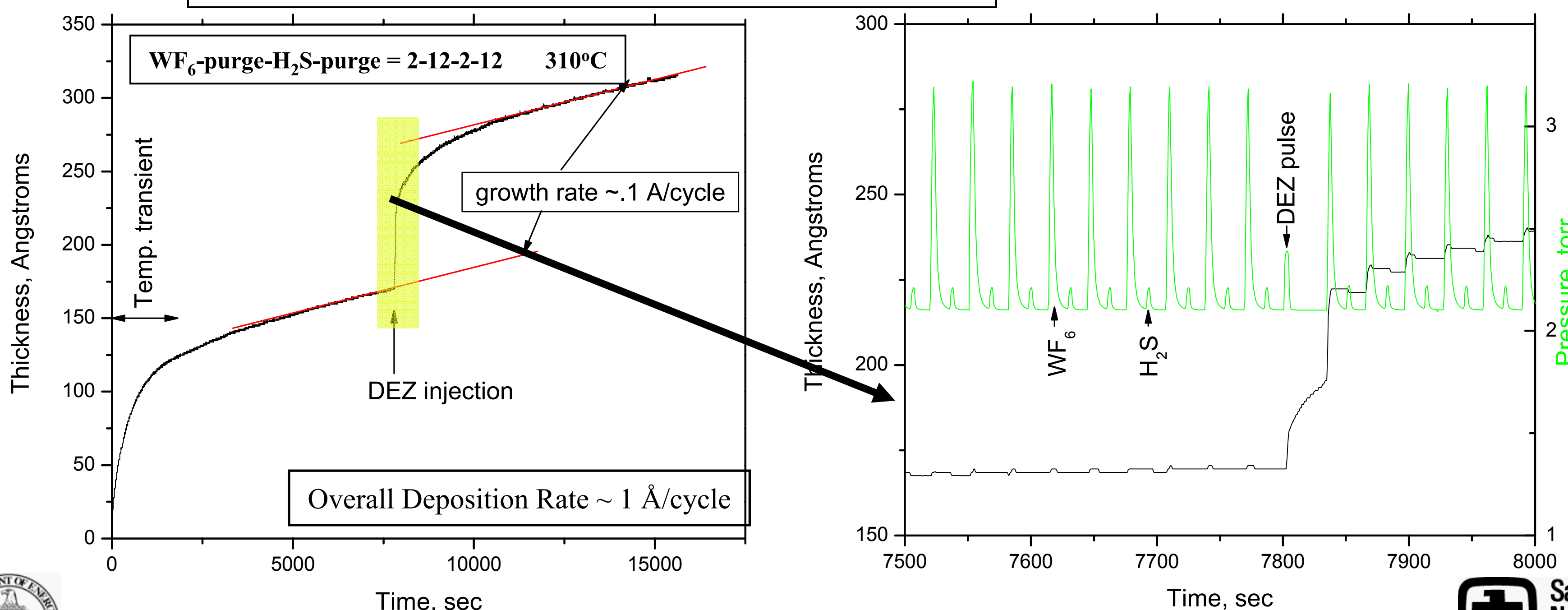
Quartz Crystal Microbalance Provides *in-situ* Process Diagnostics

ALD WS_2 is based on the CVD reaction: $WF_6 + H_2S \rightarrow WS_2 + HF$

Zn catalyzed adsorption and reaction of WF_6 greatly increases WS_2 growth rate:

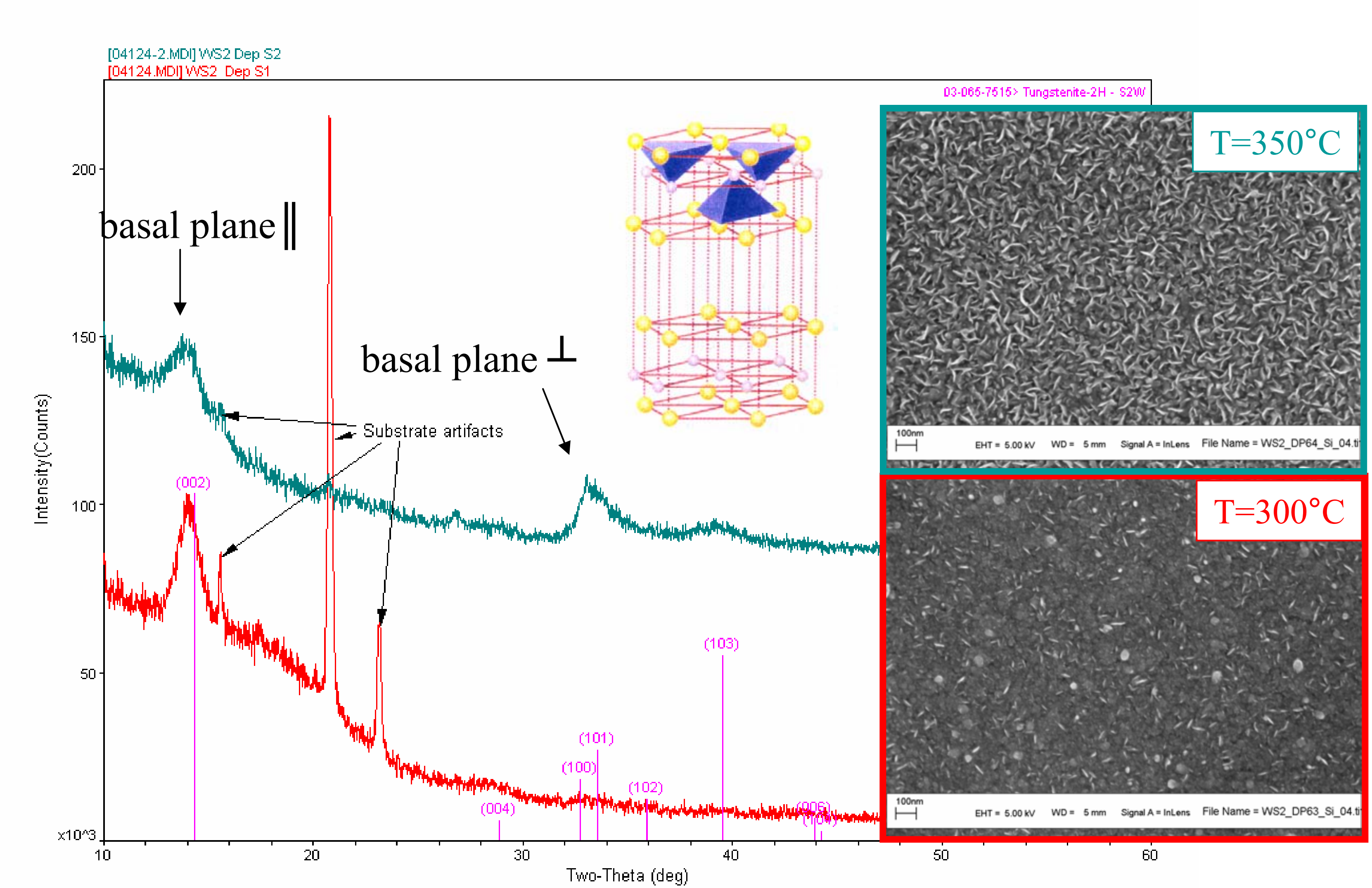


Recipe: 1 cycle of DEZ followed by 50 cycles of WF_6+H_2S



T.W. Scharf, et al. *Journal of Materials Research*, 19, 3443 (2004).

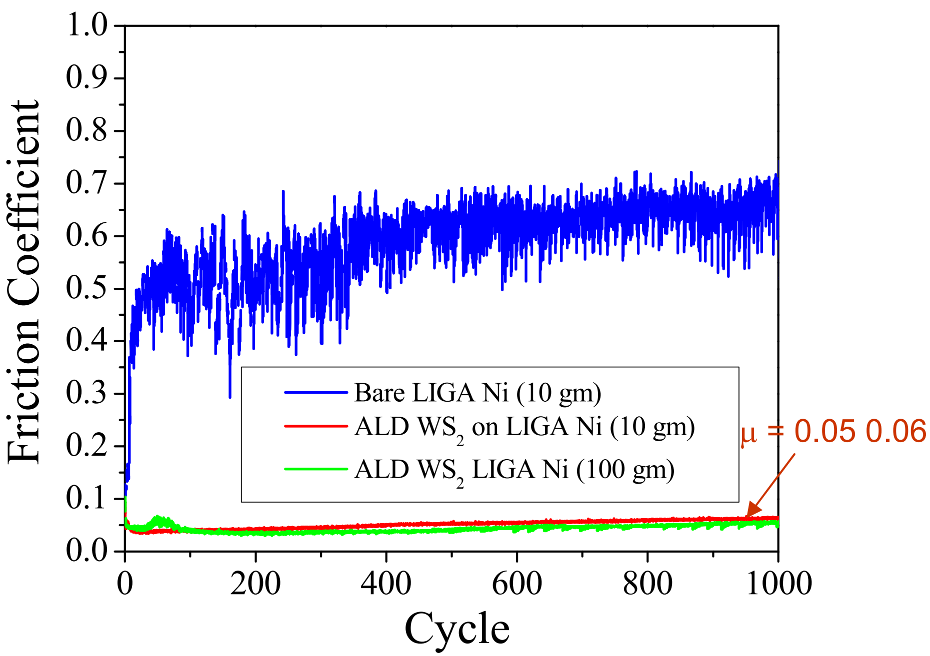
Crystallographic texture of ALD WS_2 is growth temperature dependent



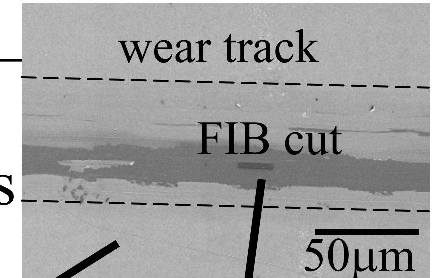
Basal plane preferred orientation effects as function of T

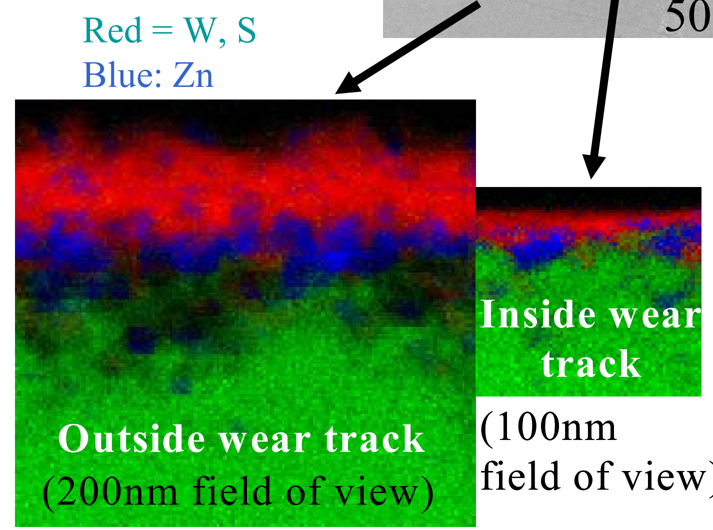
Tribology of ALD WS_2 Films

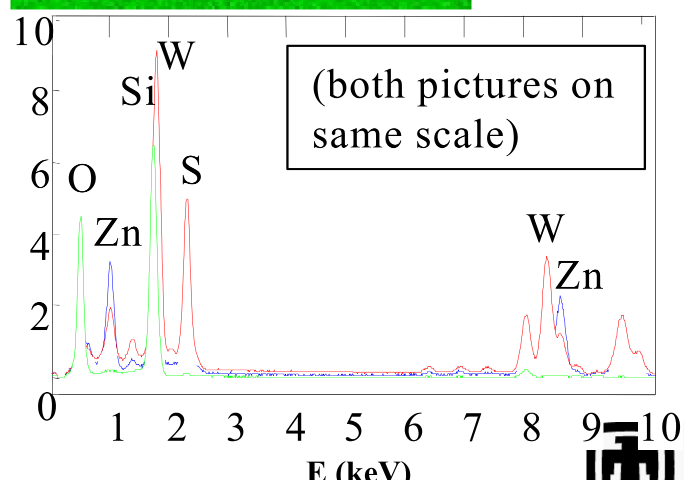
Friction



Spectral Images



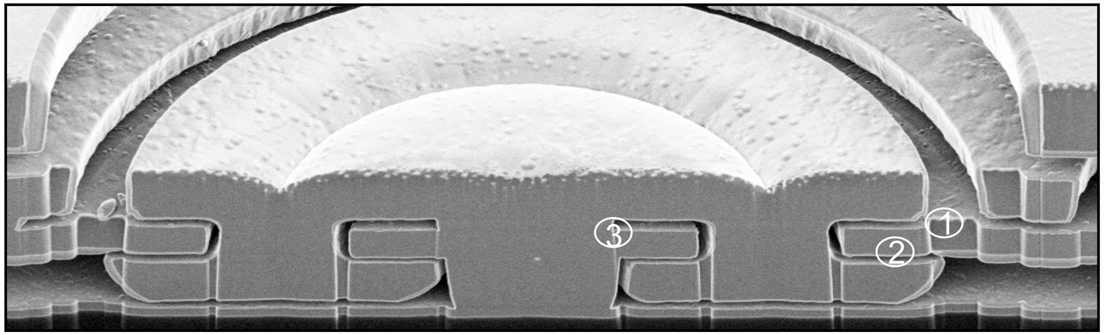




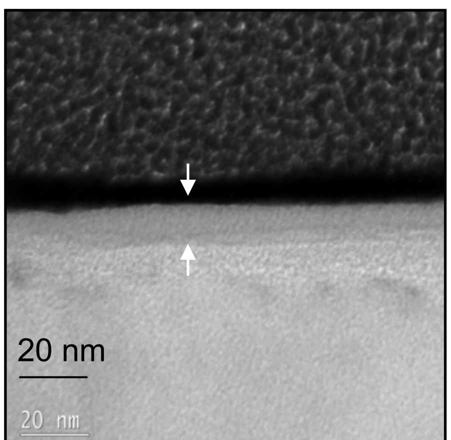
- We are able to grow ALD WS2 films on a variety of substrates: Si, SiO_2, Au, Stainless Steel, LIGA Ni
- Some of the wear taking place is a result of film material being transferred to the rubbing counterface (Si_3N_4).

Sandia National Laboratories

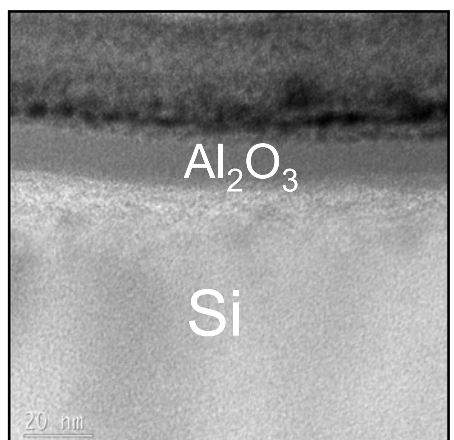
ALD conformally coats very high aspect ratio structures and buried interfaces



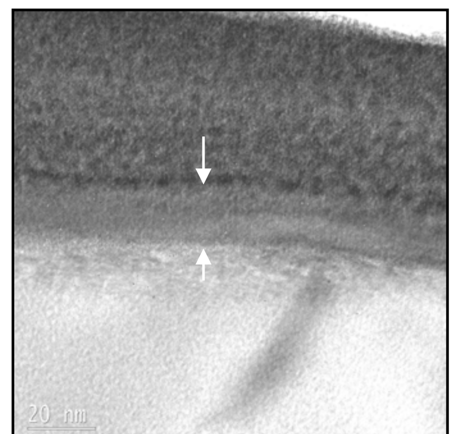
1. Gear top exposed



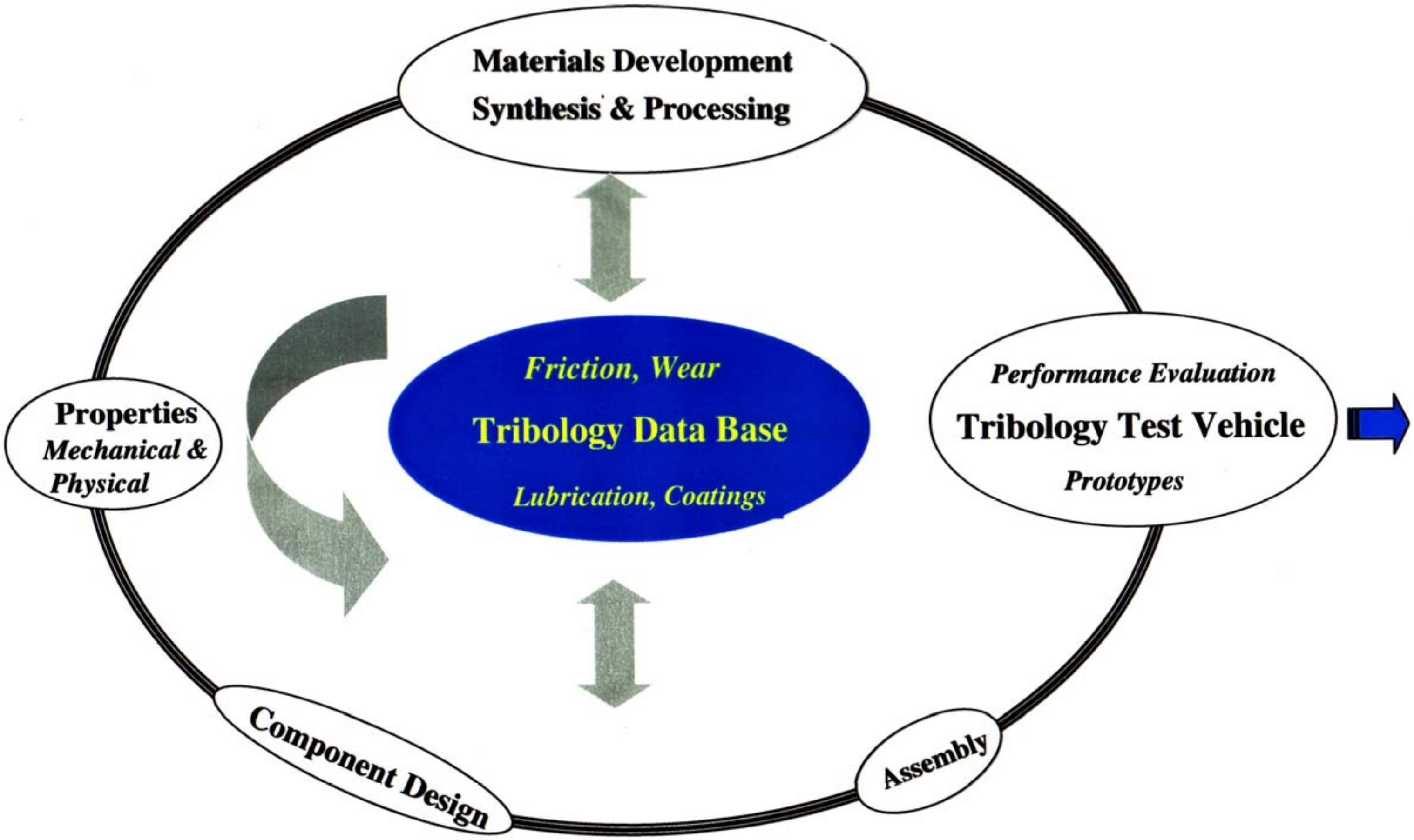
2. Gear bottom shadowed



3. Hub interior aspect ratio ~100



Concluding Thoughts: Systems Approach



Sandia National Laboratories

Acknowledgements

- MEMS
  - Mike Dugger
- PDCs
  - Rishi Raj (UC Boulder)
  - Tsali Cross (Currently with Intel Santa Clara)
- Coatings
  - Chandra Venkatraman & Cindi Ackerman (Bekeart Coatings)
  - Tom Scharf (Currently with University of North Texas)
  - John Jungk (Currently with Ball Aerospace)
- MMCs
  - Rajiv Asthana (University of Wisconsin-Stout)
  - Pradeep Rohatgi (University of Wisconsin-Milwaukee)