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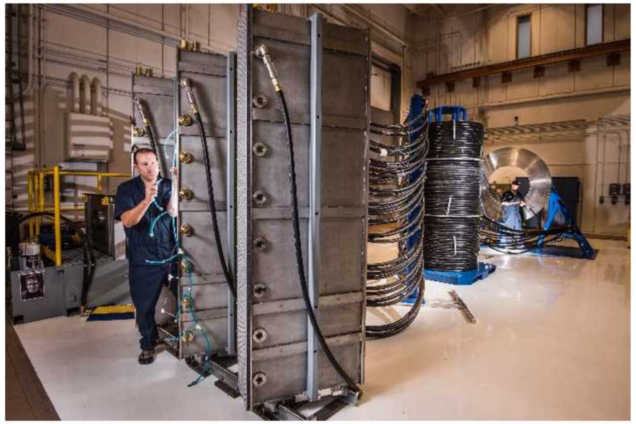

Solid Lubricants

Somuri V. Prasad

Materials, Physical, and Chemical Sciences Center

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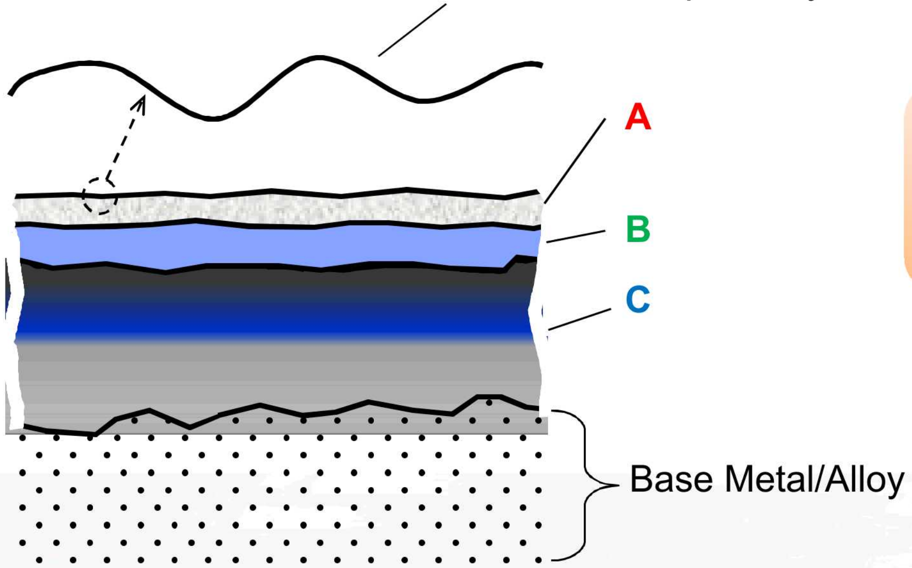
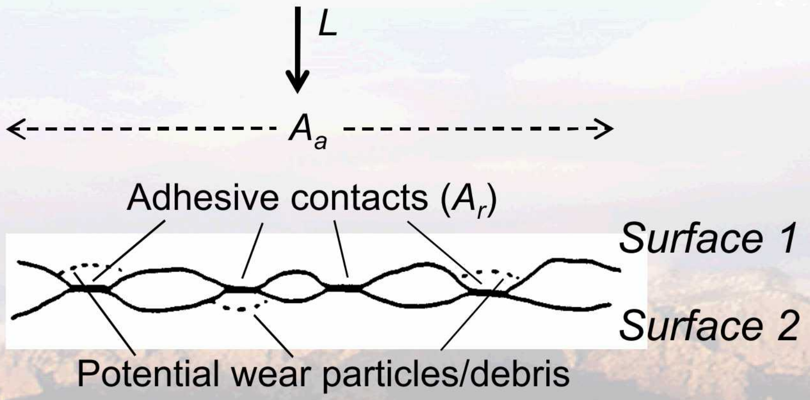
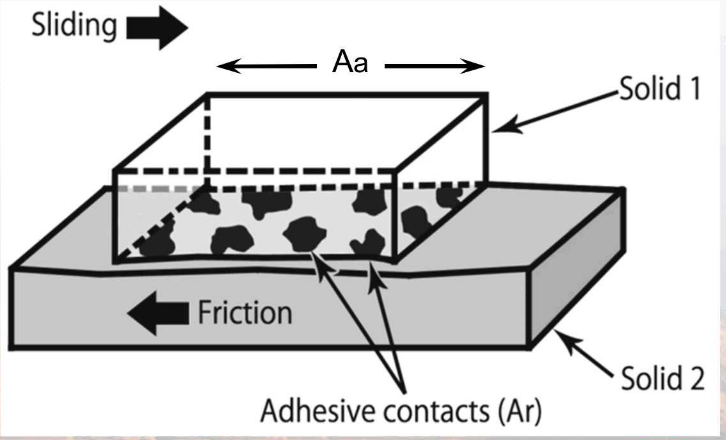
Nature of Metallic Surfaces

The real area of contact is a small fraction of the apparent area of contact.



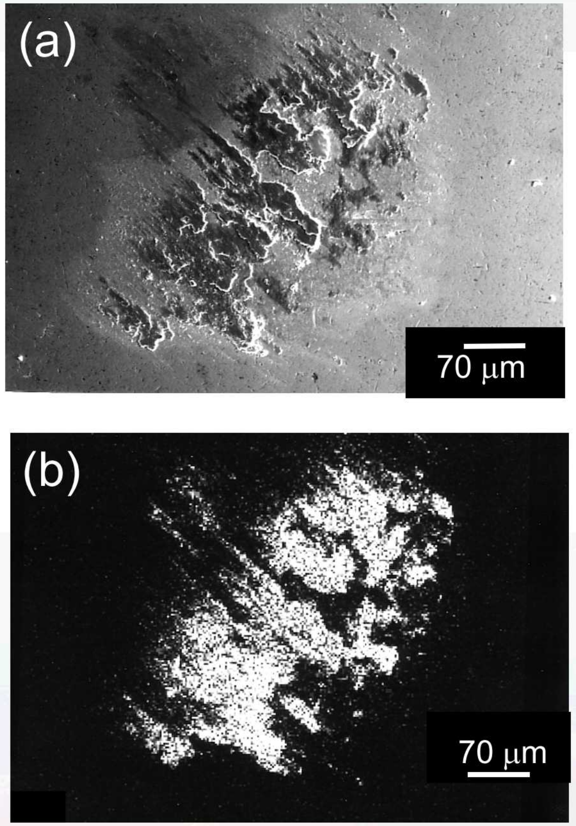
A: Physisorbed/Chemisorbed
B: Oxides (Chemically Reacted)
C: Deformed layers





T.W. Scharf , S.V. Prasad, Journal of Material Science (2013) 48:511-531

Generalized Compatibility Chart for Binary Metallic Contacts



Smearing of Al on a steel ball during a ball-on-disk wear test. SEM showing adhesive transfer of Al on steel ball (a) with corresponding X-ray map (b).

S. V. Prasad and K. R. Mecklenburg, Lubrication Engineering, 50 (1994) 511-518.

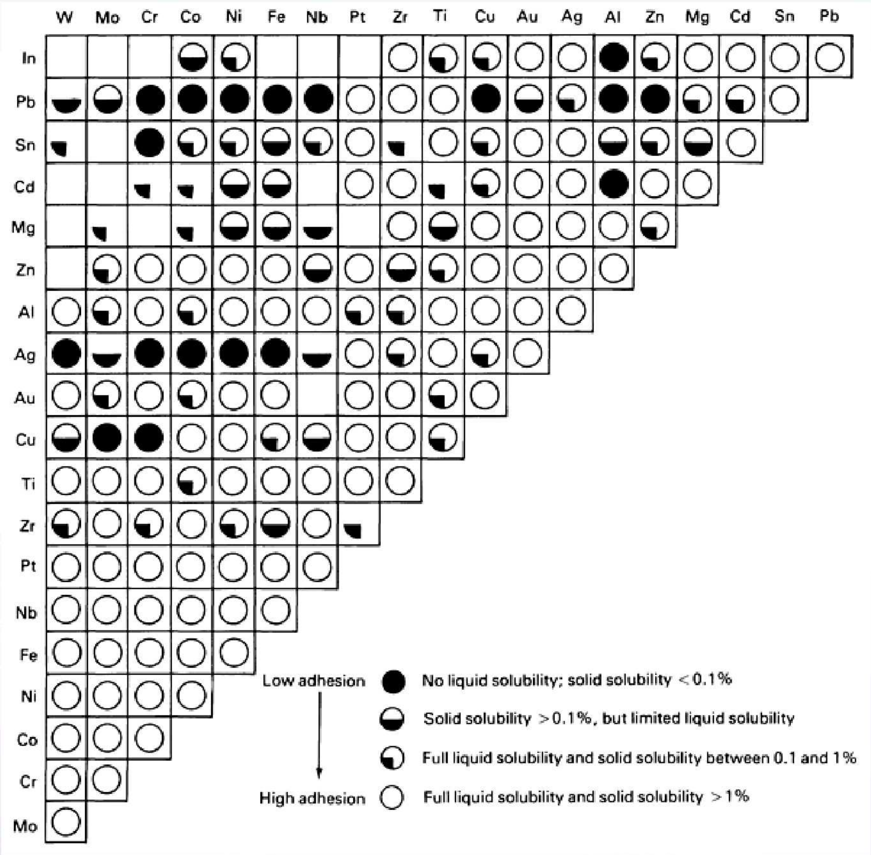


Chart indicates the degree of expected adhesion (and thus friction and wear) between the various metal combinations derived from binary equilibrium diagrams.

E. Rabinowicz (1971) ASLE Trans 14:198

Solid Lubricants

- *The majority of lubrication needs are still met by fluids and greases*
- *When the operating conditions are beyond the liquid realm (e.g., high temperature or vacuum), or situations where liquids cannot be introduced, attention turns to solids*

1. Carbon-based materials (graphite, DLCs, nanocrystalline diamond)
2. Transition metal dichalcogenides (MoS_2, WS_2)
3. Polymers (e.g., PTFE)
4. Soft Metals (Ag, Sn, Pb, In , Au)

Challenges in Appling Solid Lubricant Coatings

Buried Interfaces/Hidden Contacts

Handling of Micron-sized parts

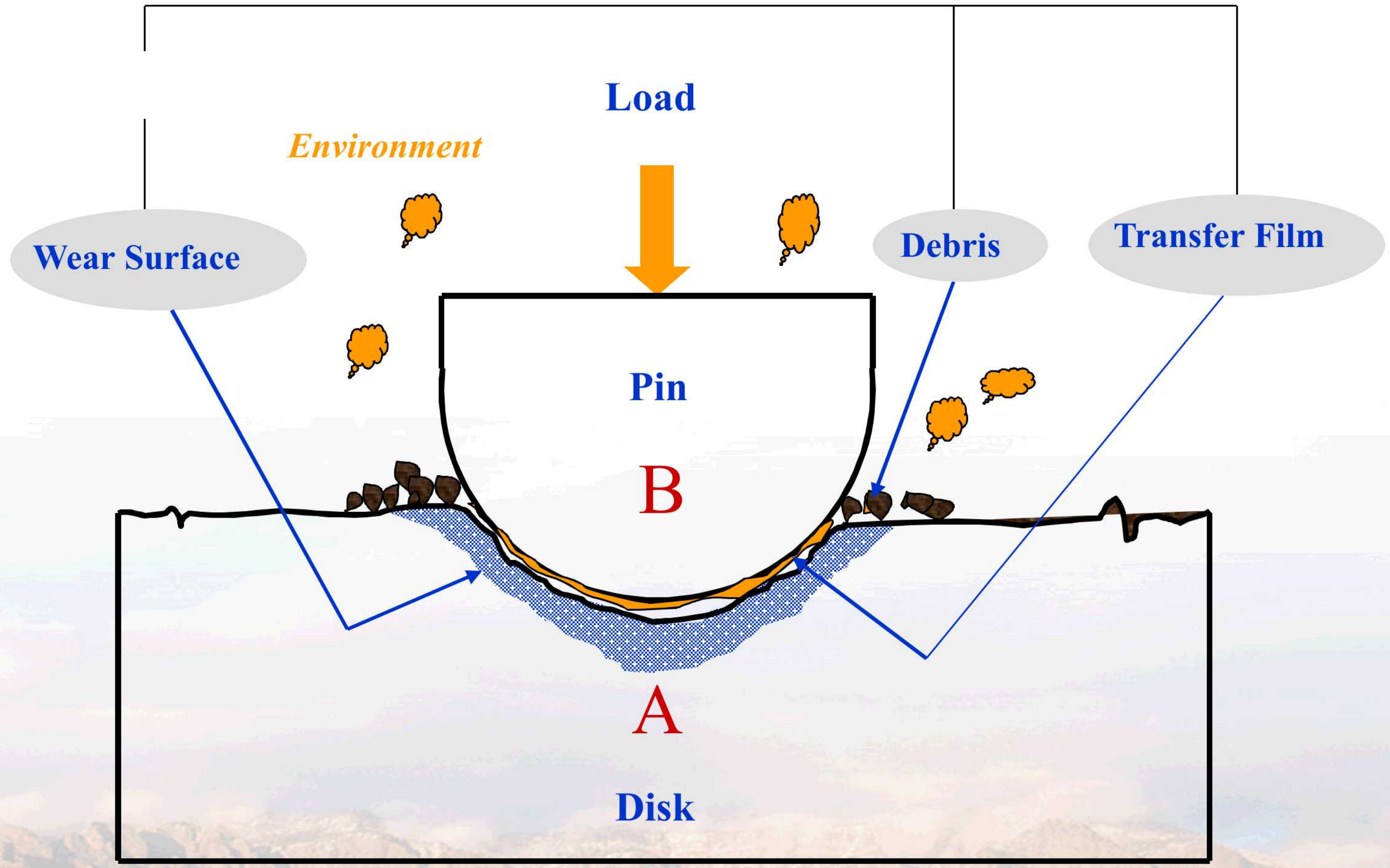
- Burnishing
- Resin Bonding
- Physical Vapor Deposition
- Chemical Vapor Deposition

- Plasma Enhanced Chemical Vapor Deposition (PECVD)
- Atomic layer Deposition (ALD)

Wear (Tribology) is a systems property

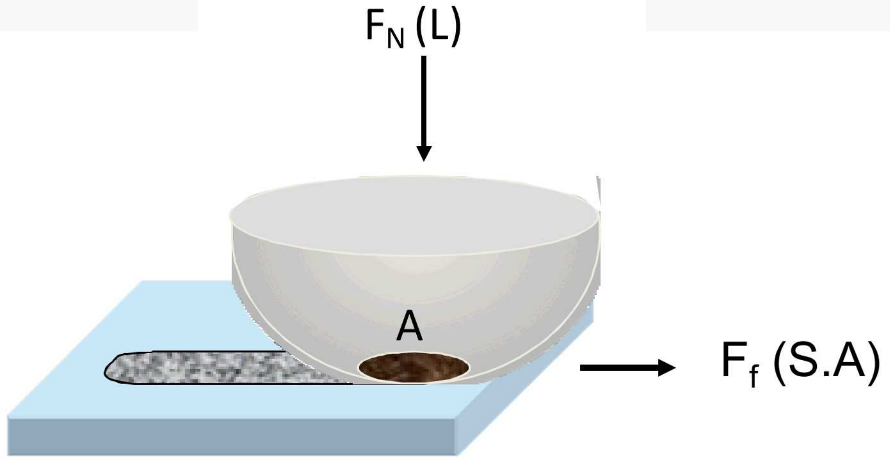
- *Engineering surfaces are never perfectly flat*
- *The real area of contact is a small fraction of the apparent area of contact*

- Plastic deformation
- Diffusion
- Tribochemistry
- Transfer Films
- Environmental Reactions



S. V. Prasad and K. R. Mecklenburg,, *Tribology Transactions* **39** (1996) 296-305.
T. W. Scharf and S. V. Prasad, J Mater. Sci. 48 (2013) 511–531
D. A. Rigney and J. P. Hirth, Wear 53 (1979) 345-70

Many Solid Lubricant Coatings Exhibit Load Dependence on Friction



Elastic Contact (Sphere-on-Flat)

$$P = F_N / A$$

$$F_f = S\,A$$

$$S = S_o + \alpha\, P$$

$$\mu = S_o \pi \left(3R/4E\right)^{2/3} L^{-1/3} + \alpha$$

$$\mu = F_f/F_N = S.A/P.A$$

- S_o is the interfacial shear strength (a 'velocity accommodation parameter'), a property of the interface.
- α is a fit constant (the pressure-dependence of 'S')

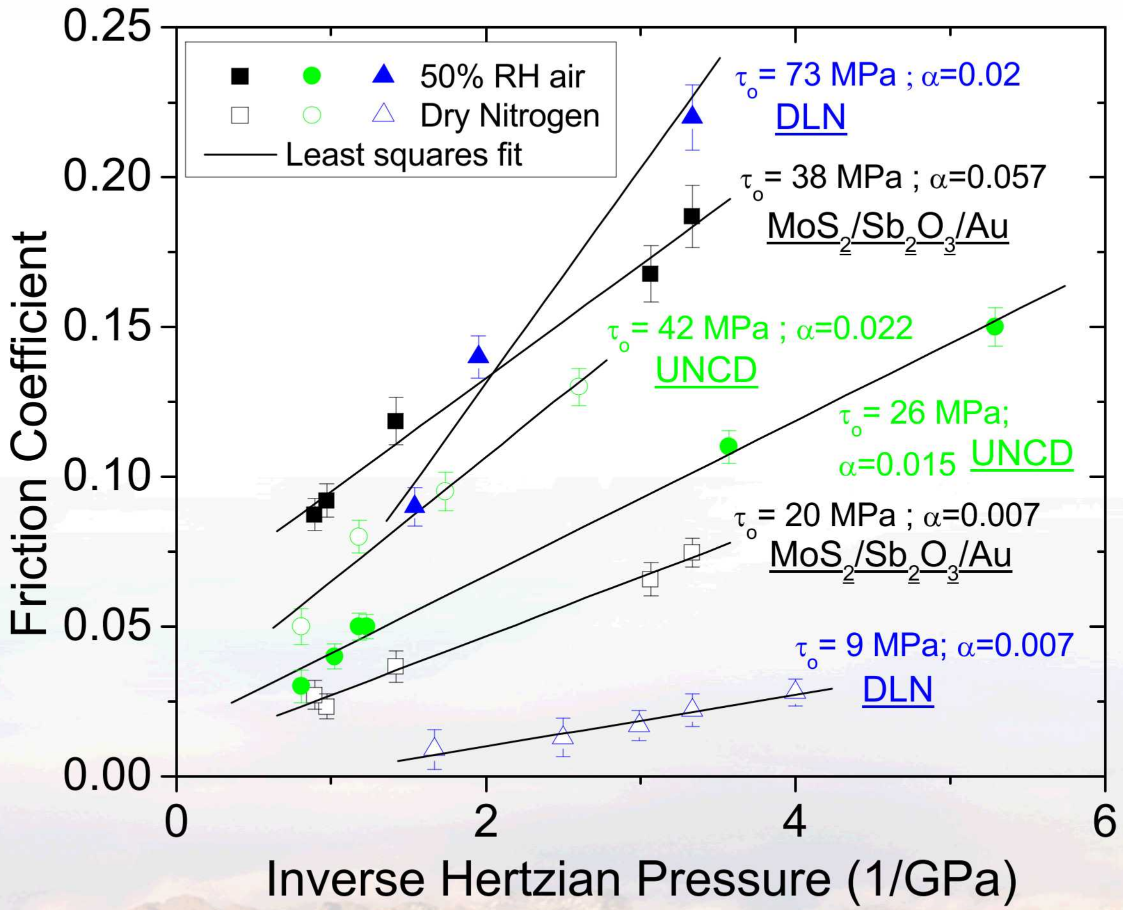
Friction is NOT independent of Load

F. P. Bowden and D. Tabor, "The Friction and Lubrication of Solids", Oxford Science Publications, 1986

I.L. Singer, et al. *Applied Physics Letters* 57, 995 (1990).

B.J. Briscoe and D.C.B. Evans, *Proc. R. Soc. Lond. A* 380, 398 (1982).

Inverse Hertzian Behavior— Non-Amontonian



T. W. Scharf and S. V. Prasad, Solid Lubricants: A Review, J. Maters. Science (2013) 48:511-531

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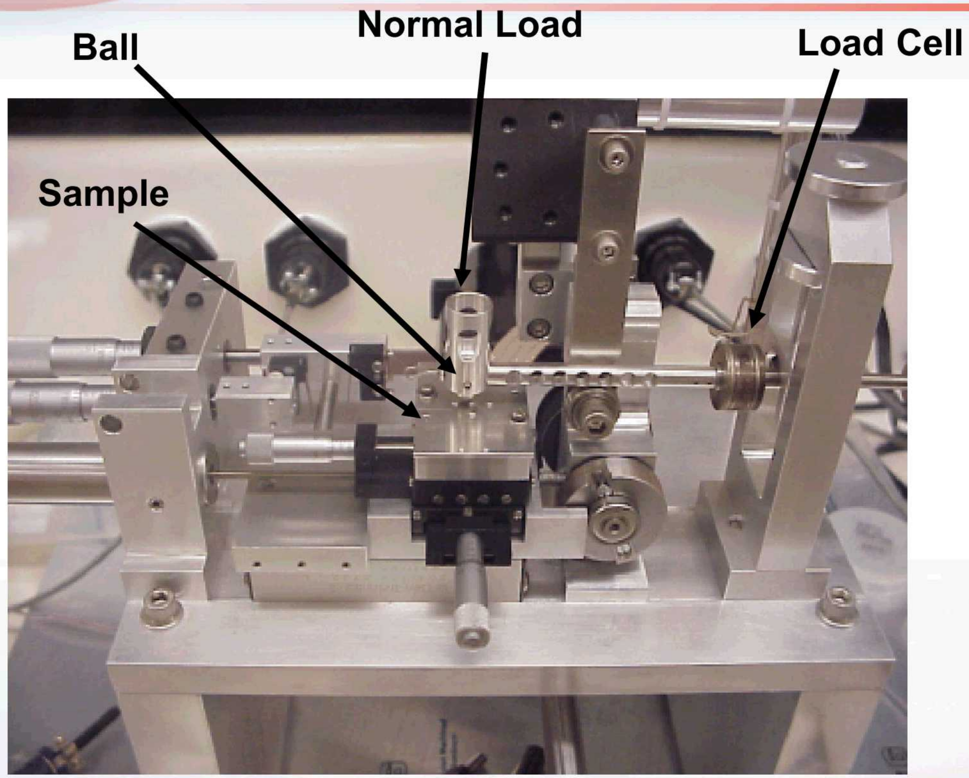
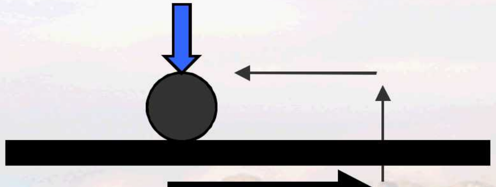
Friction and Wear Measurements





Linear Wear Tester
(Ball-on-Flat configuration)

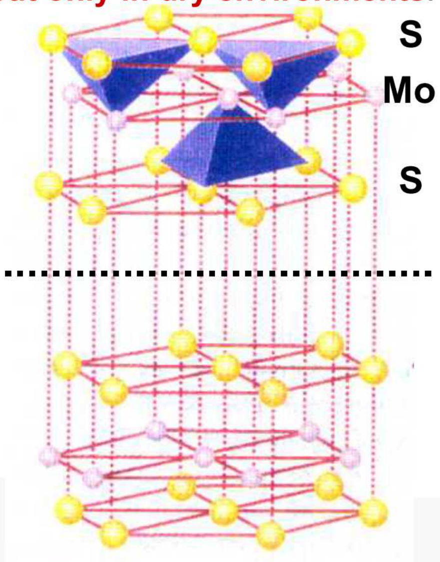
- Contact Pressures: 0.44 GPa to 1.7 GPa
- Environment: Dry Nitrogen; Air (50% RH)

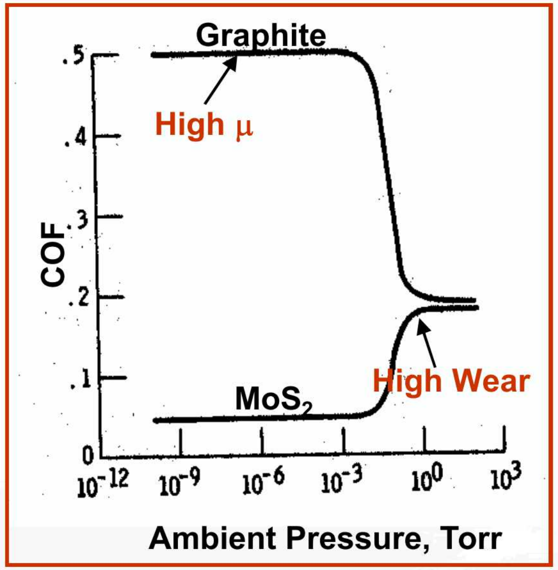
Oxygen Analyzer
Dew Point Measurement

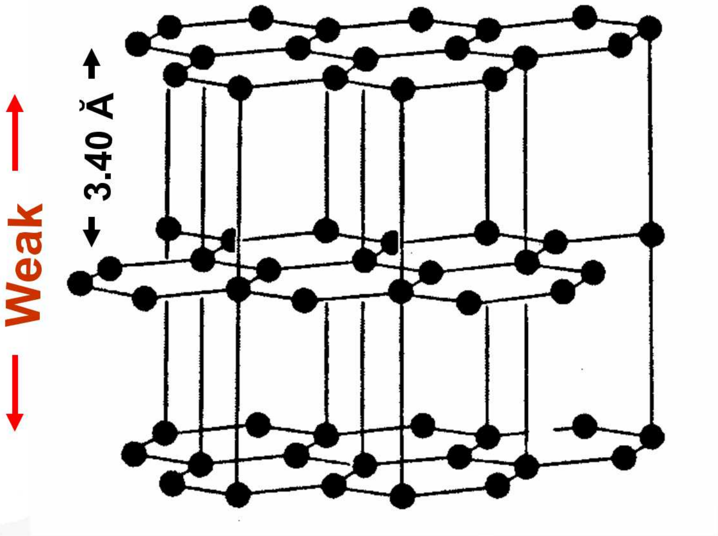
Environmental Control

Classic Examples of Environmental Effects on Transfer Films & Friction

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



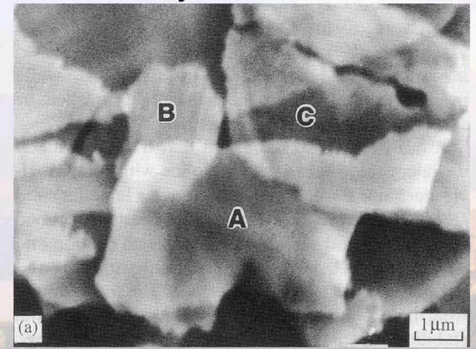


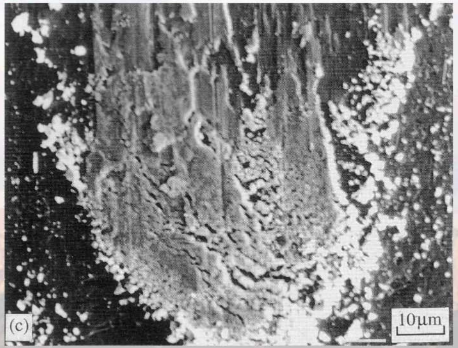


Mo/W Disulfide

Graphite

They form thin transfer films on the counterface



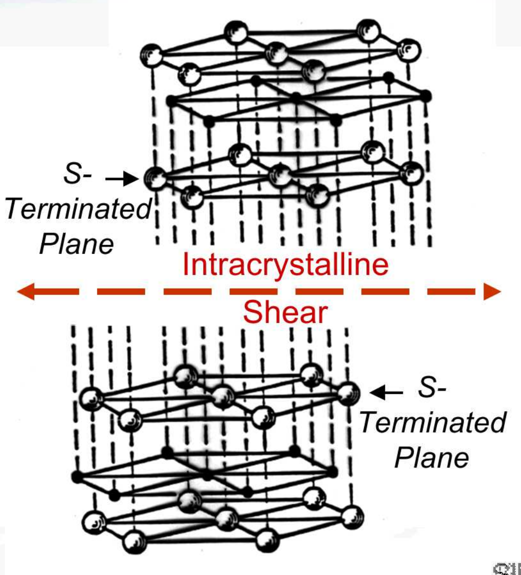


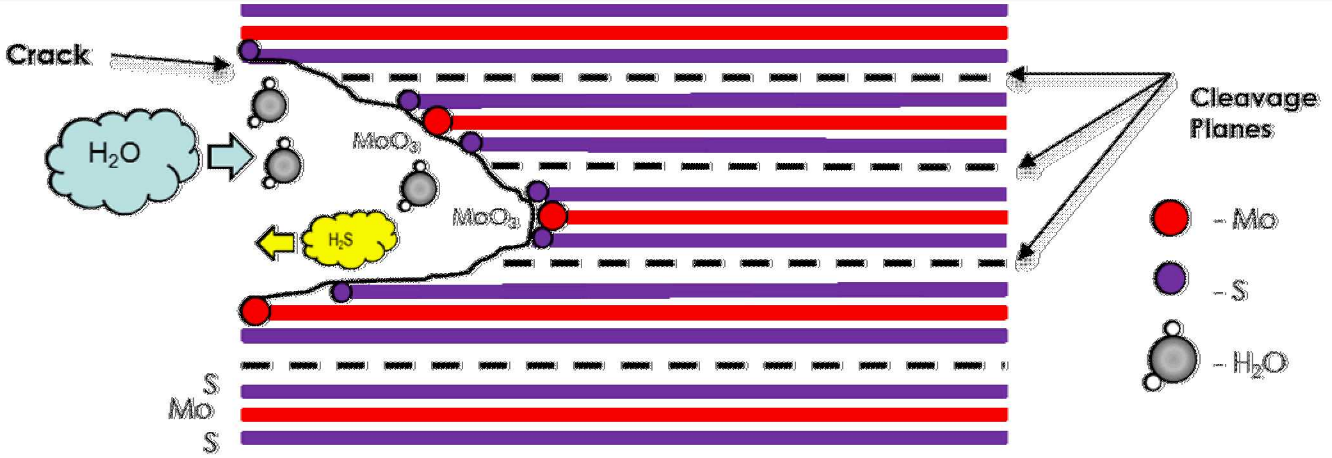
- Graphite needs moisture or adsorbed gases in the environment (>100 ppm) (they either act as intercalants, or passivate the dangling covalent bonds) to lubricate.
- In vacuum, graphite exhibits high friction and wear—a phenomenon known as "dusting", first observed in the late 1930's on graphite brushes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

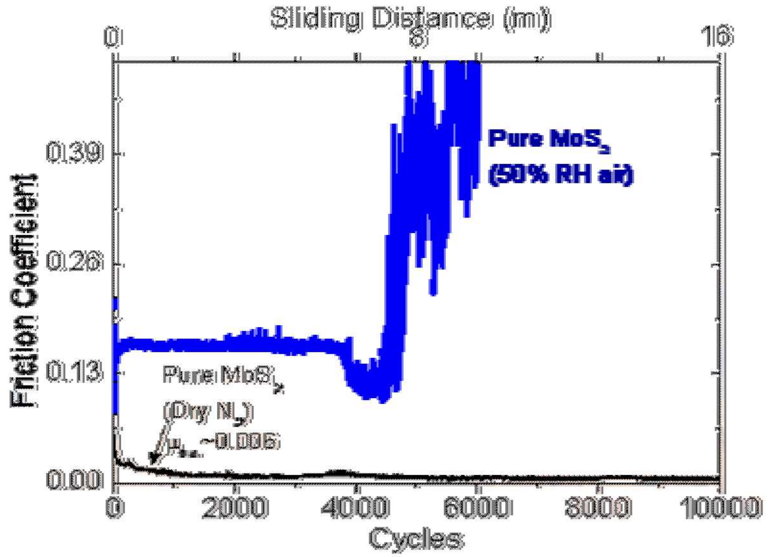
S. V. Prasad and J. S. Zabinski, J. Mater. Sci. Lett. 12 (1993) 1413-1415

Transition Metal Dichalcogenides: MoS_2, WS_2

Effect of humidity and water vapor on the friction behavior of MoS_2







Reactions with water
Tribo-oxidation (MoO_3 formation)
Increase in the COF
Reduced Wear Life

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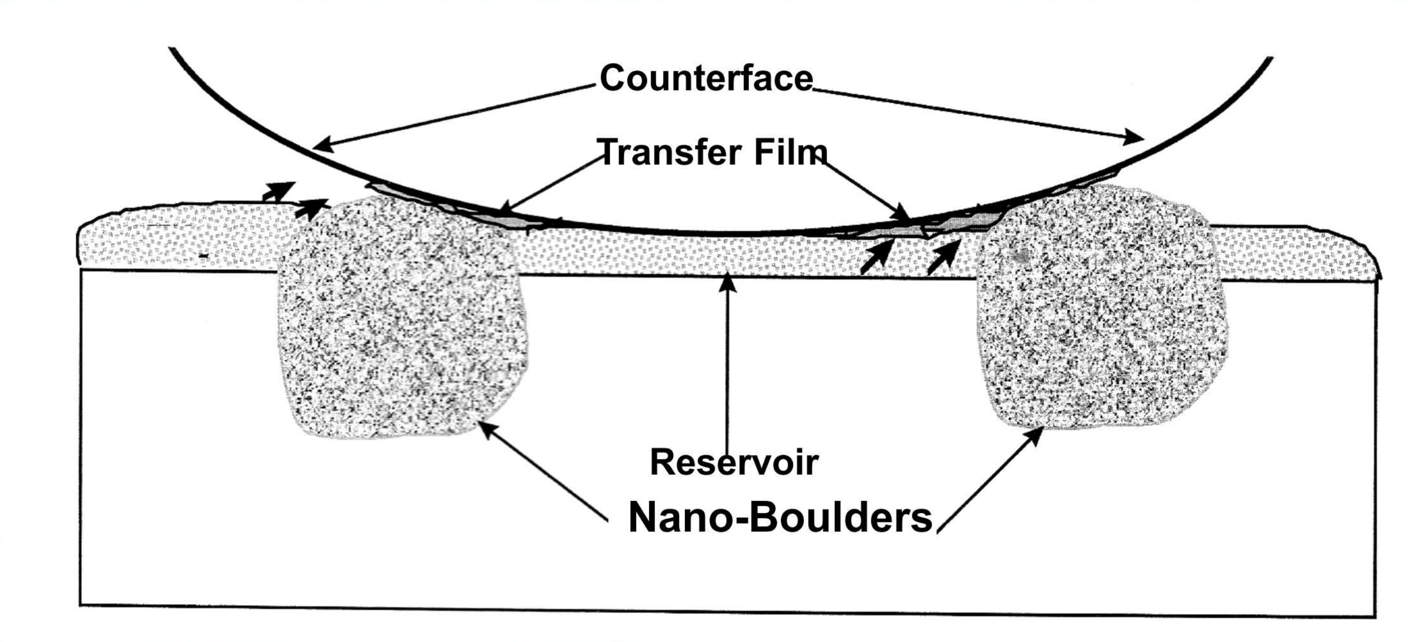
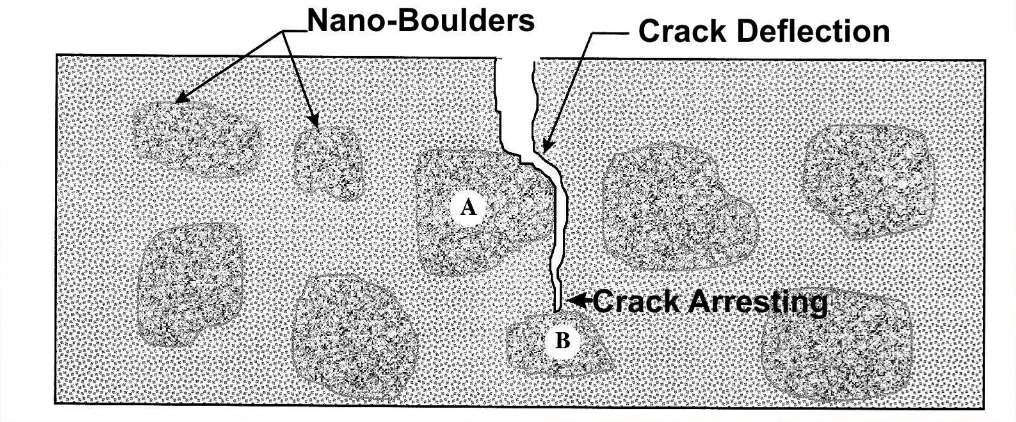
Novel Concepts for Materials Synthesis





S. V. Prasad, N. T. McDevitt and J. S. Zabinski, Wear 230 (1999) 24-34

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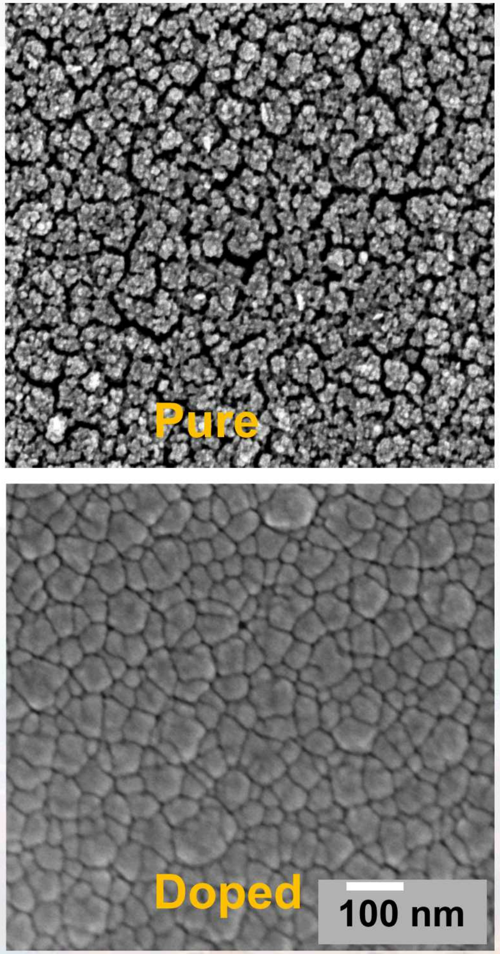
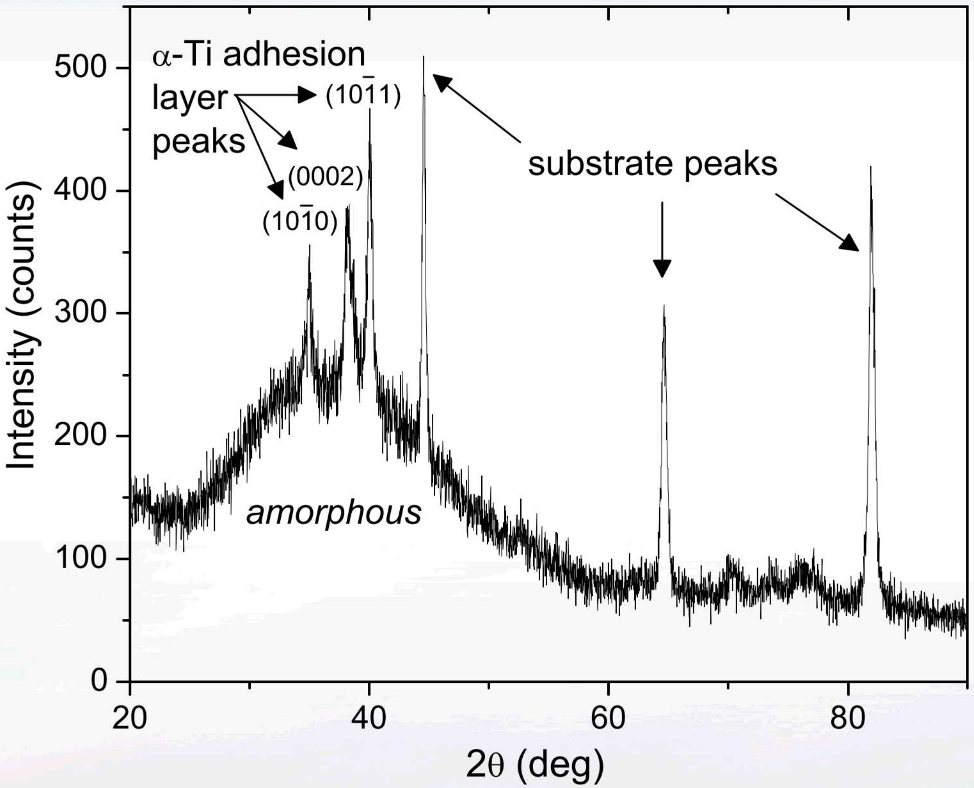
Doped MoS_2 (Sb_2O_3 and Au) from Tribologix

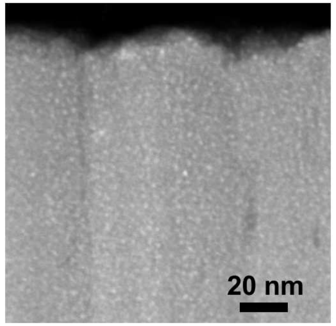


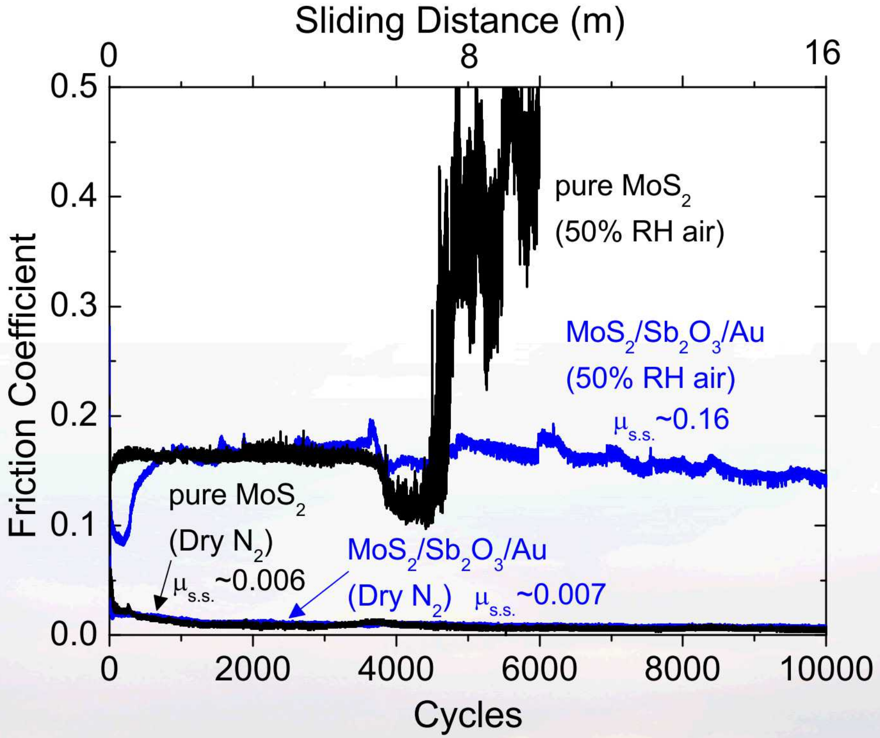


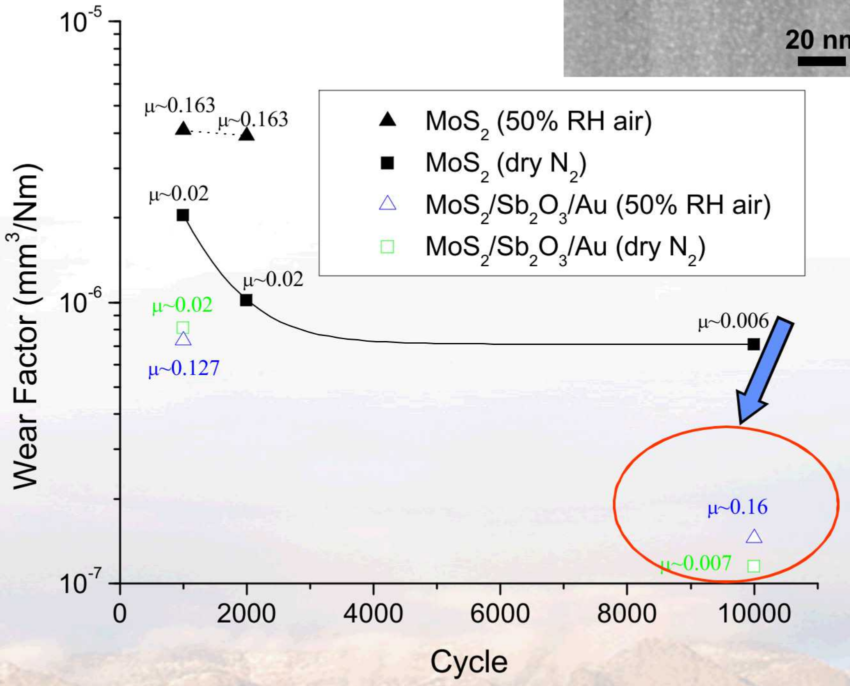
- Note the absence of peaks characteristic of any of the three constituent phases
- Instead there is a broad indicating the presence of an amorphous phase
- Doped films are much denser

Friction and Wear of Doped and Undoped MoS_2

Whether the MoS_2 is in nanocrystalline form or amorphous, friction induces crystallization with basal planes aligning parallel to the surface







T. W. Scharf, P. G. Kotula and S. V. Prasad, Acta Materialia 58 (2010) 4100-4109

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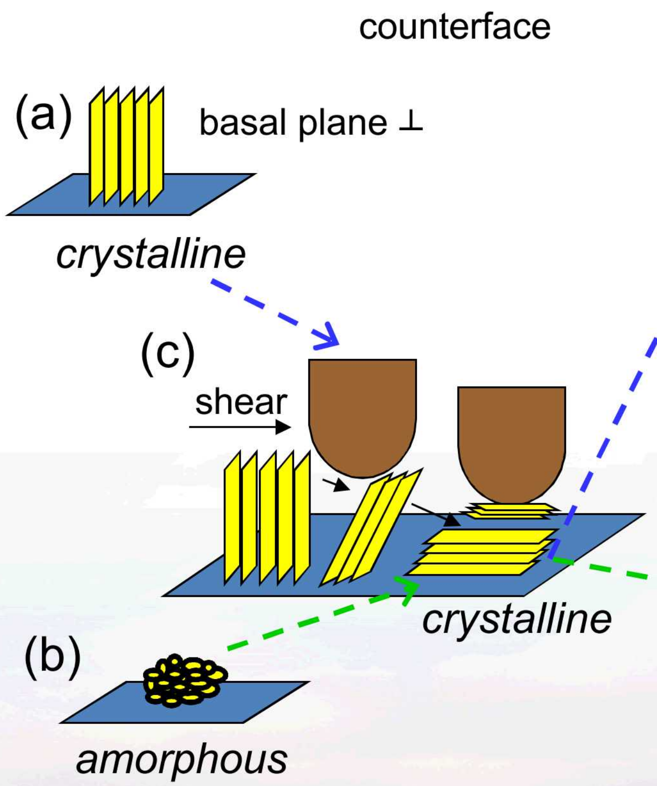
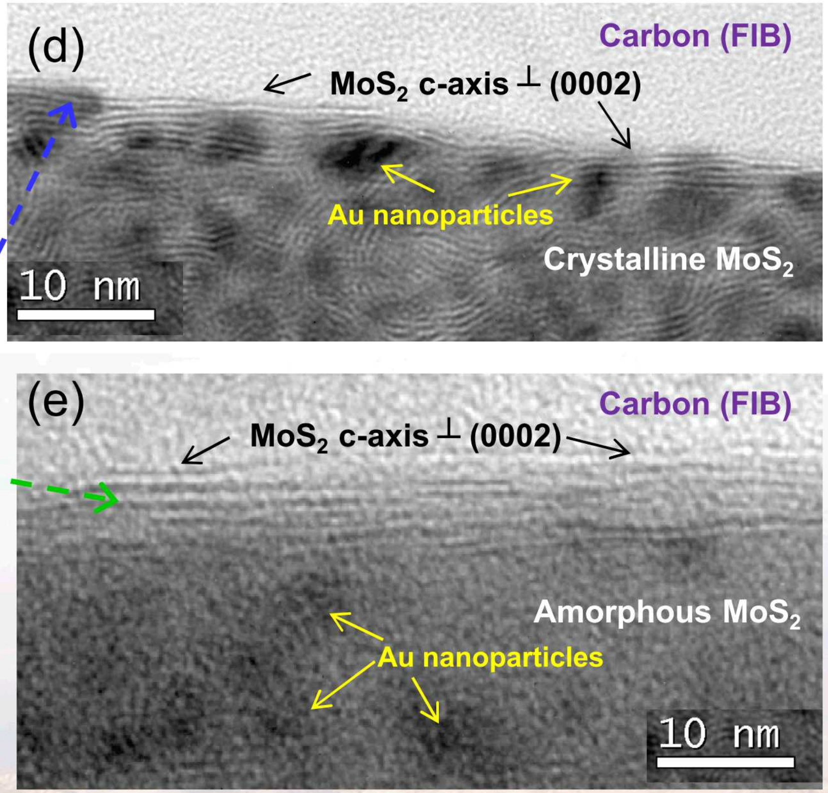
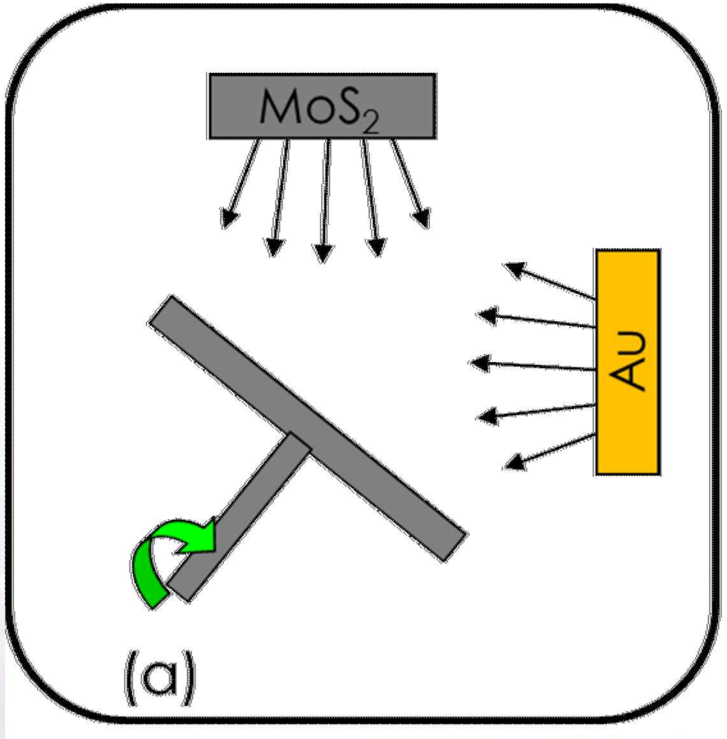
Friction-induced crystallization and reorientation of basal planes



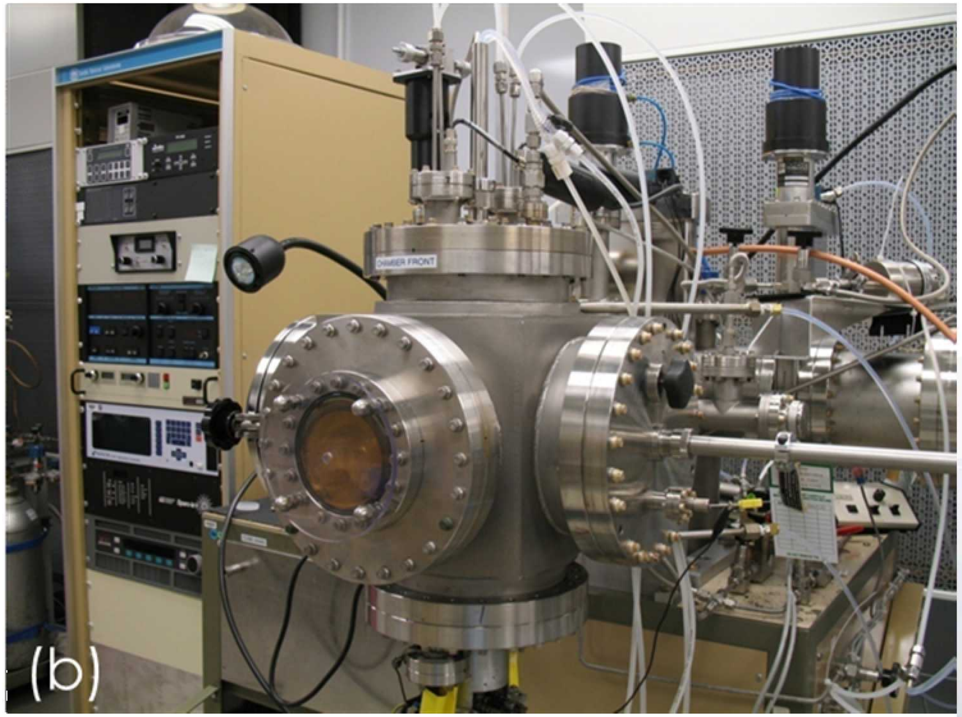


PVD-Co-Deposition for the Synthesis of MoS_2-Au Nanocomposites

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



Experimental sputter co-deposition system used in this study



Independent rate control with stage rotation for uniformity

Independent QCM for rate monitor and control
Hot stage
DC Bias

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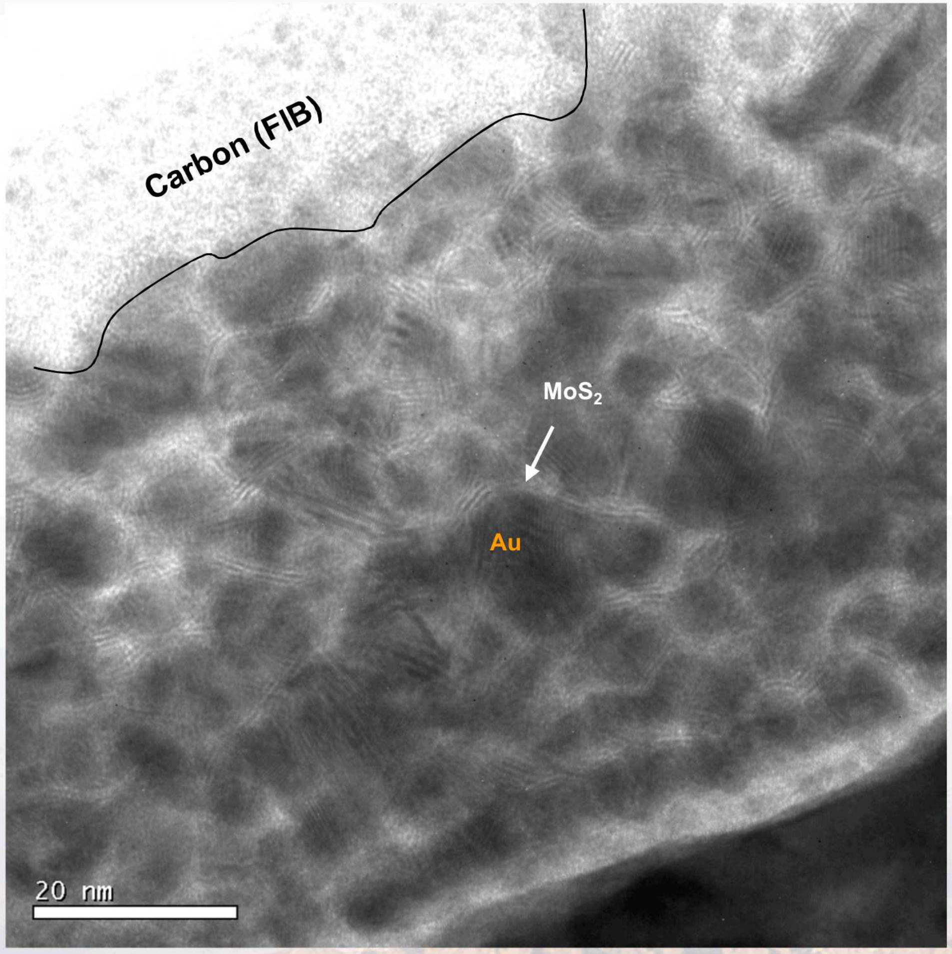
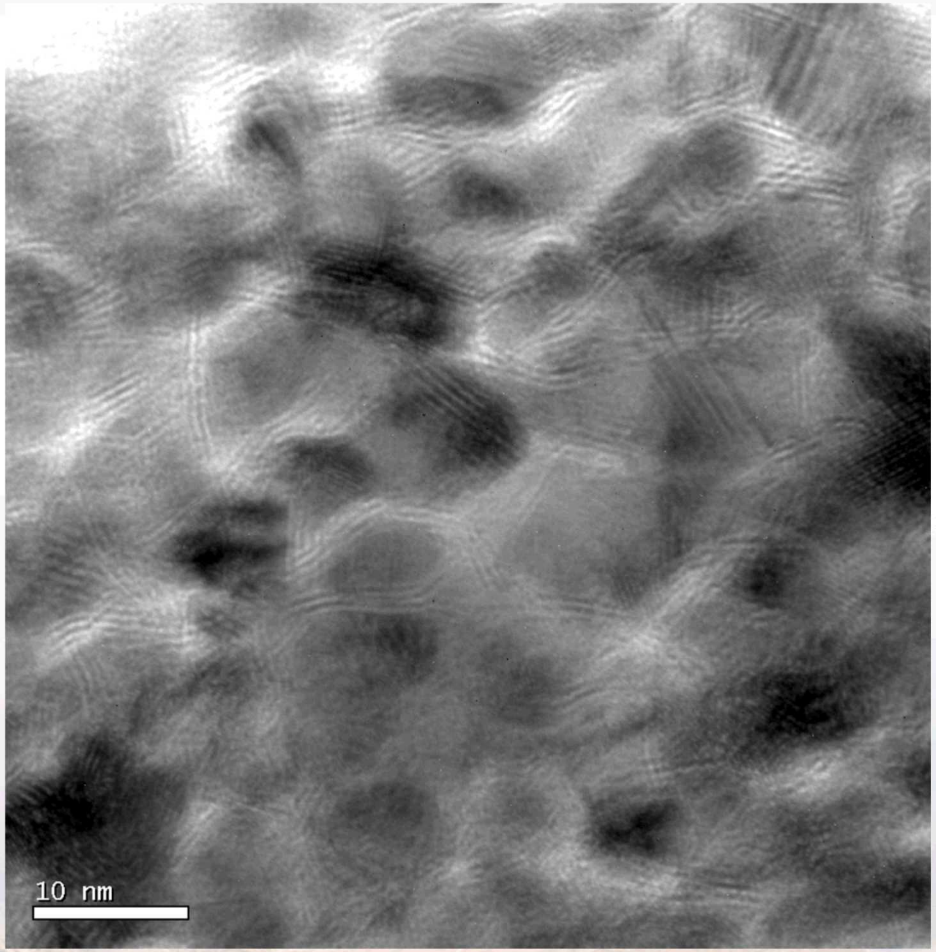
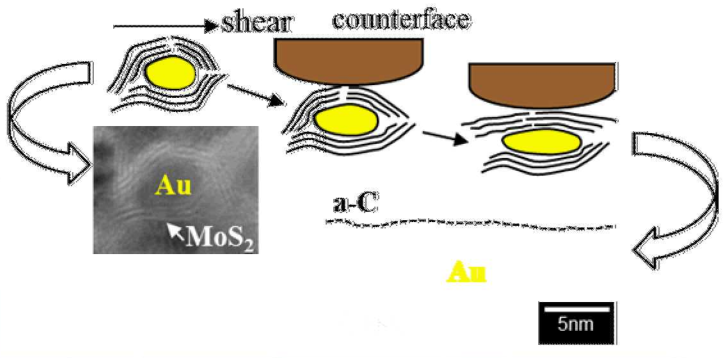
XTEM of MoS_2-Au nanocomposite grown at 200°C

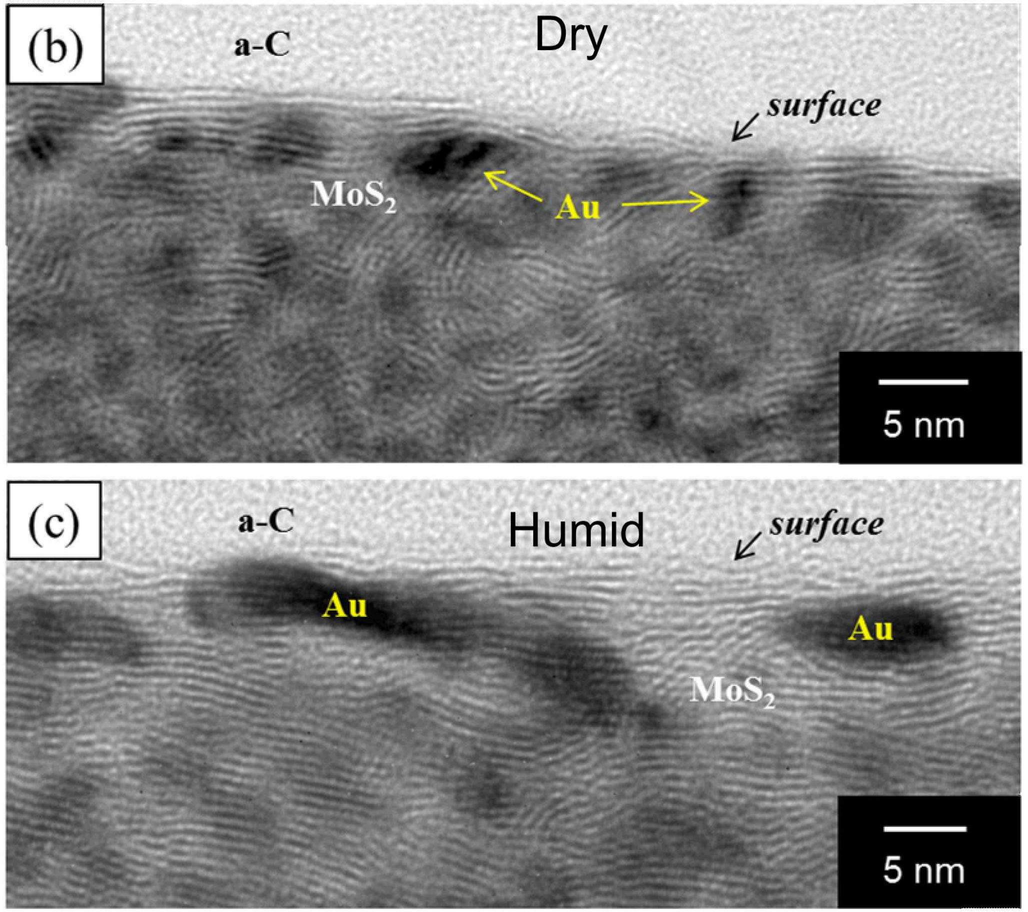




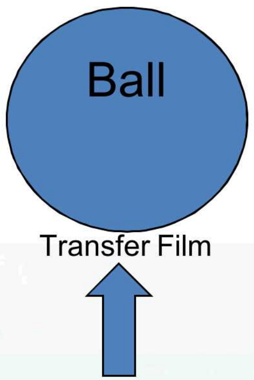
Nanocrystalline Au (~10 nm) core with MoS_2 basal planes encircling

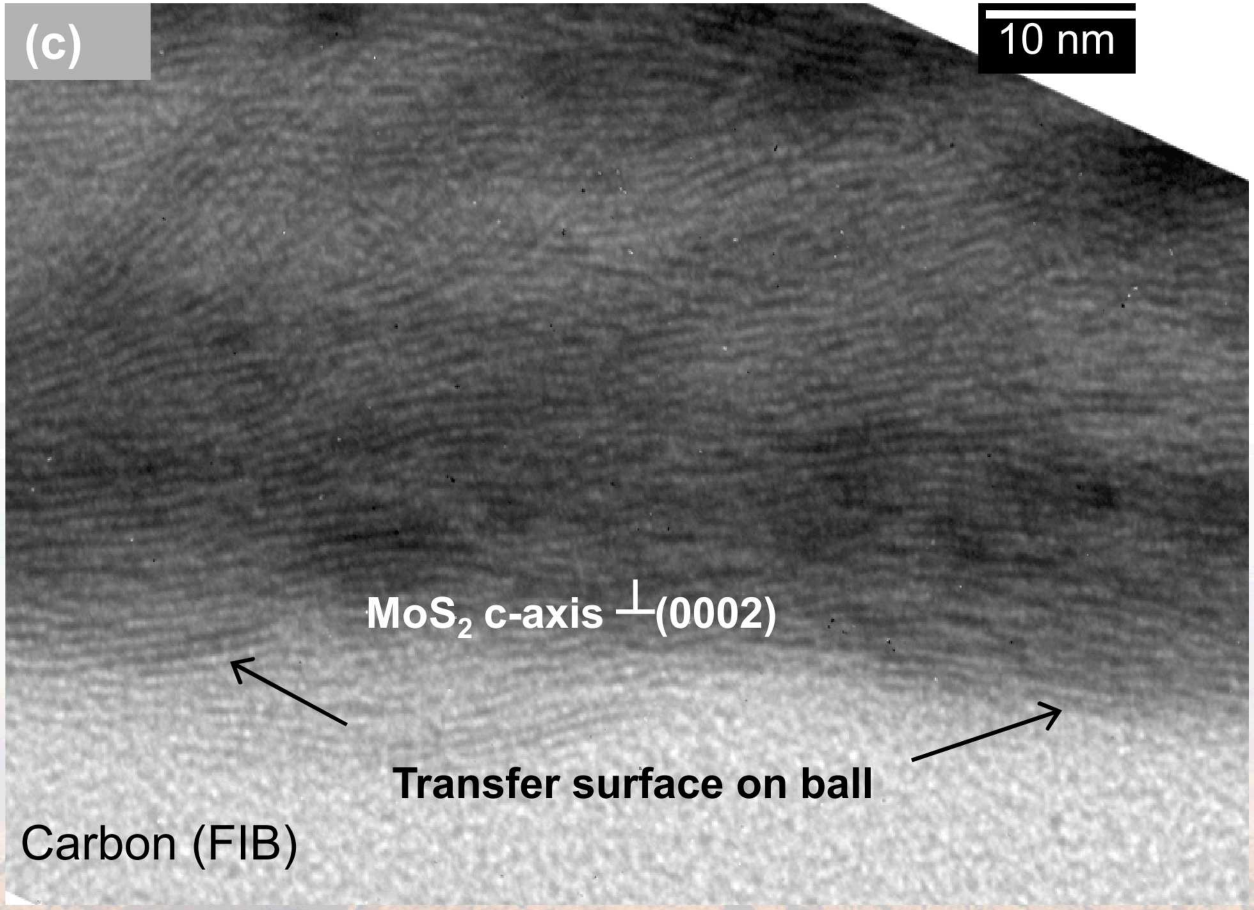
Shear-induced exfoliation of MoS_2 (0002) with basal planes parallel to the sliding direction





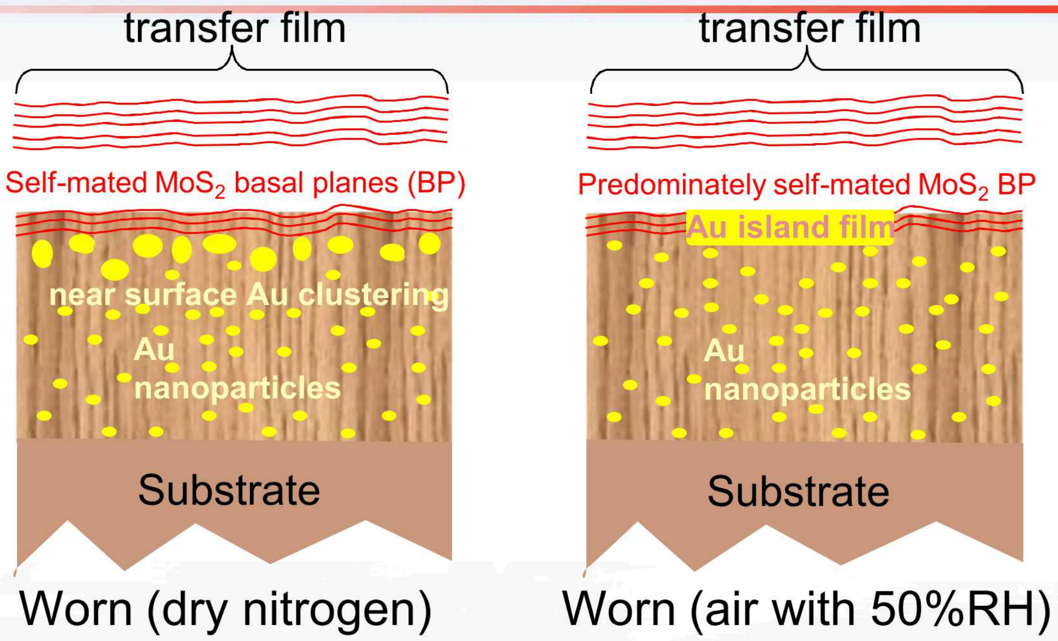
Cross-section of a Transfer Film Air (50% RH)





HRTEM

Mechanisms of Friction



- Whether the MoS_2 is in nanocrystalline form or amorphous, friction induces crystallization with basal planes aligning parallel to the surface
- COF in air is higher but the wear rate is almost identical, indicating the environmental robustness of wear for the nanocomposite (MoS2/Sb2O3/Au) coating
- Sb_2O_3 makes the coating brittle

Atomic Layer Deposition (ALD)

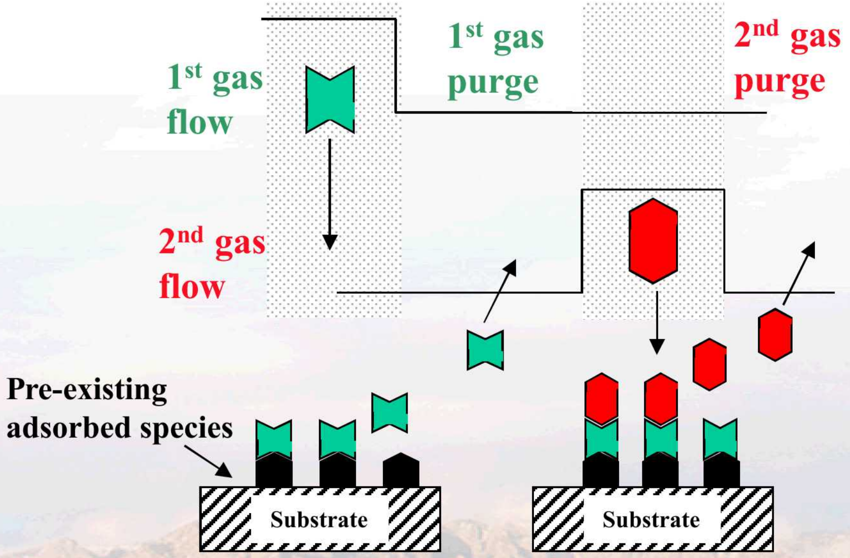
Sequential introduction of gaseous precursors and selective chemistry

•Thin Film Electroluminescent (TFEL) flat panel displays

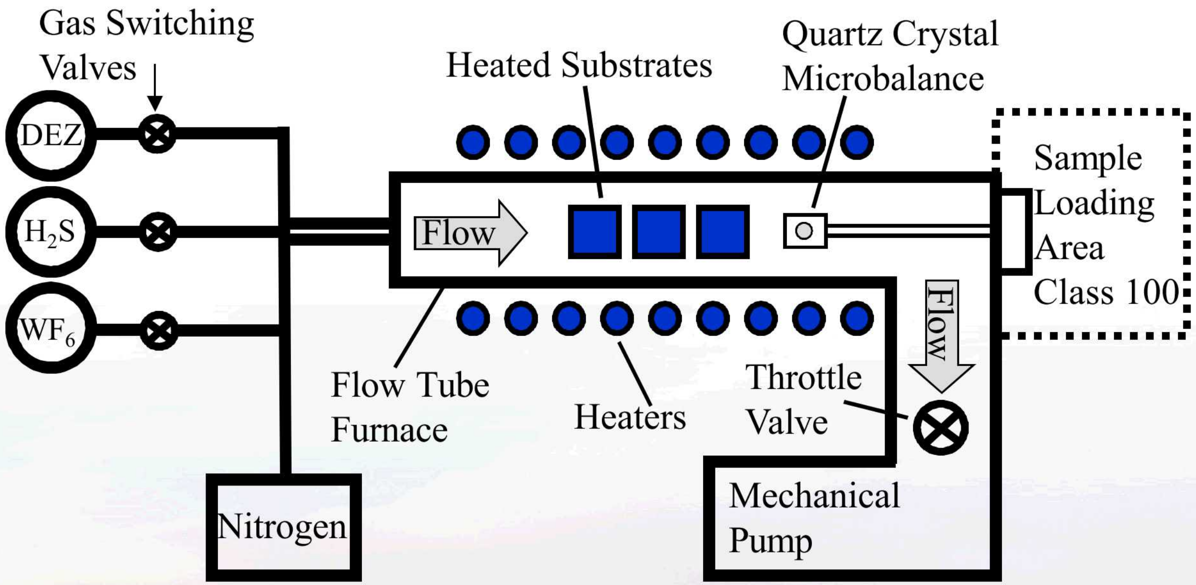
- •Luminescent ZnS:Mn
- •Insulating Al_2O_3
- ➢M. Ritala and M. Leskela, Handbook of Thin Film Materials, ed H. S. Nalwa, Academic Press,(2002)

•Transparent Conducting Oxides, ZnO

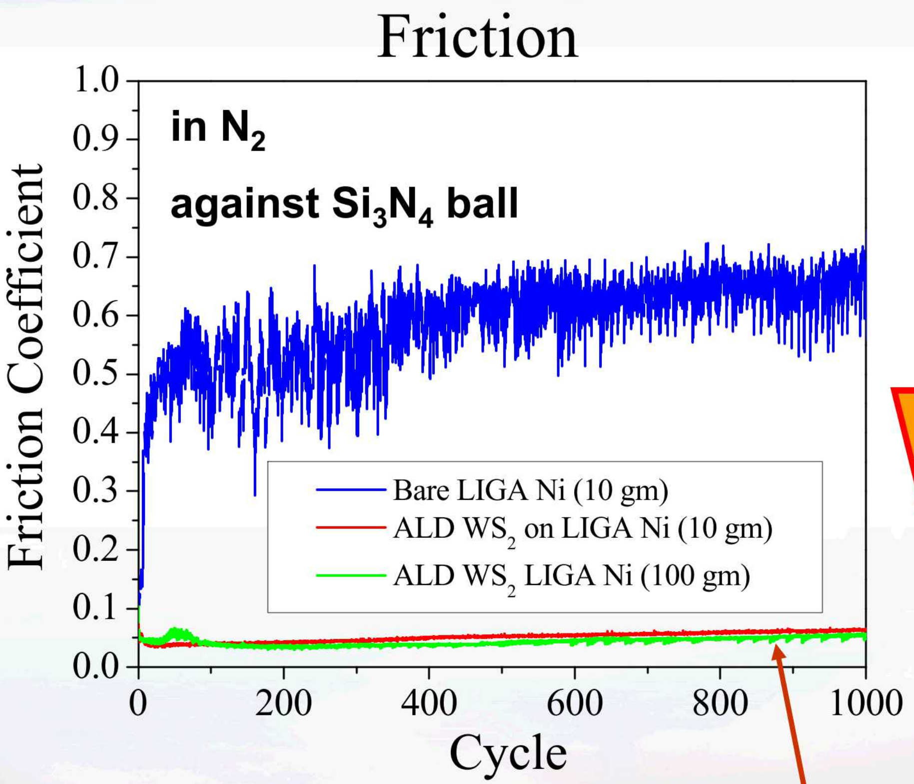
- ➢S. George et al. J. Vac, Sci. Technol. A23 (2005) 118.



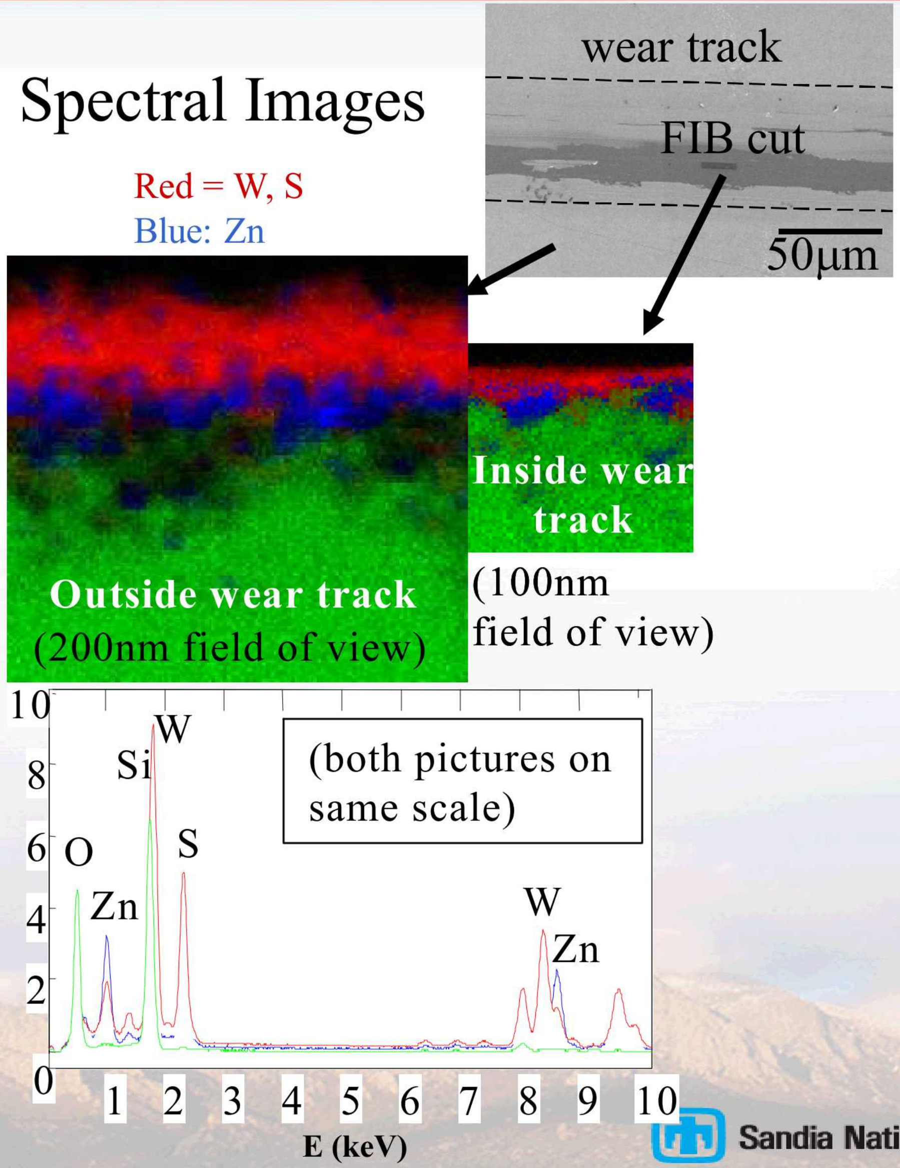
ALD reactor for the synthesis of WS_2 films



Tribology of ALD WS_2 Films



μ = 0.05 - 0.06



- **ALD WS_2 films have been grown on: Si, SiO_2, Au, stainless steel, LIGA Ni**
- **Some of the wear is a result of film material being transferred to the counterface (Si_3N_4)**

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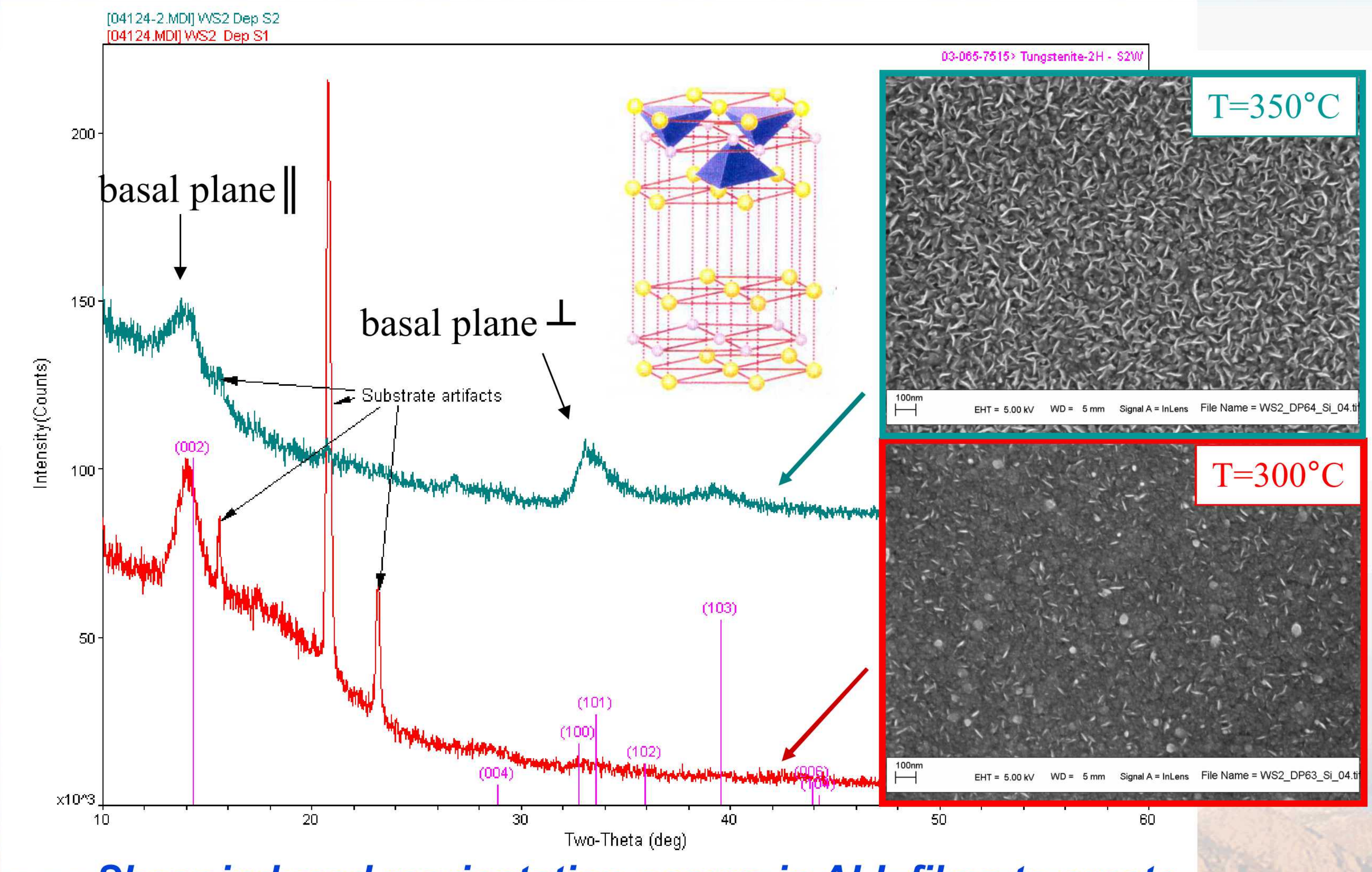
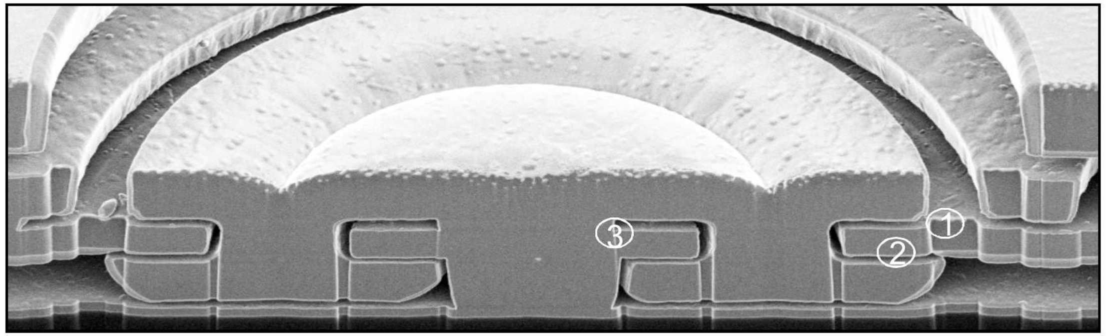
Crystallographic texture of ALD WS_2 is growth temperature dependent

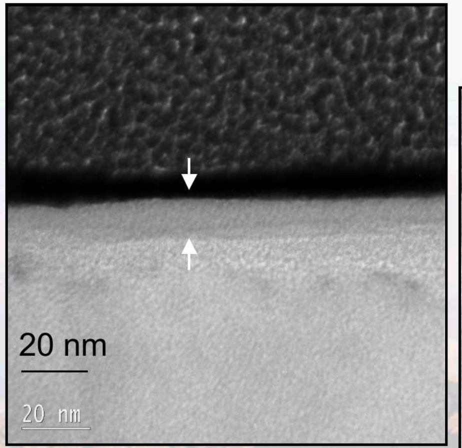


Shear-induced reorientation occurs in ALL films to create basal planes parallel to the sliding direction

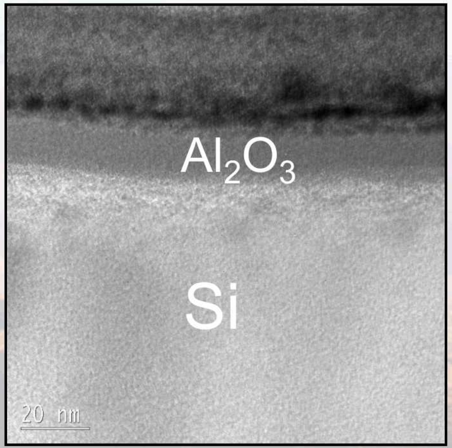
ALD conformally coats very high aspect ratio structures and buried interfaces



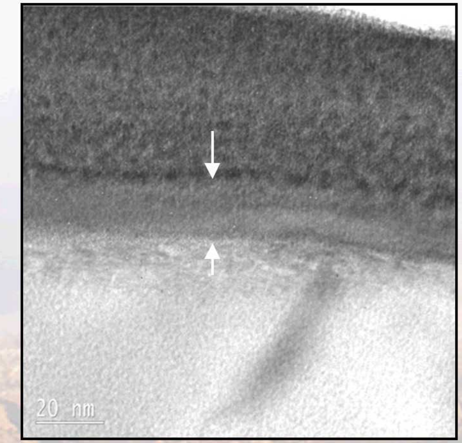
1. Gear top exposed



2. Gear bottom shadowed



3. Hub interior aspect ratio ~100



Diamond-Like Carbon (DLC)

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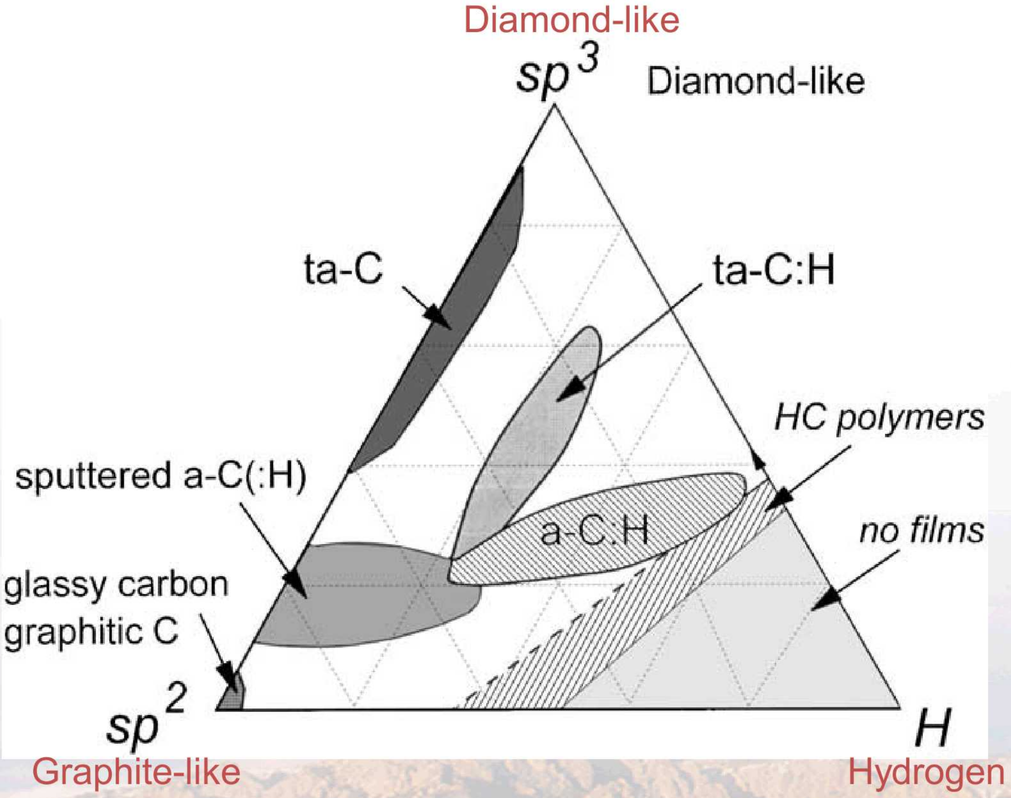
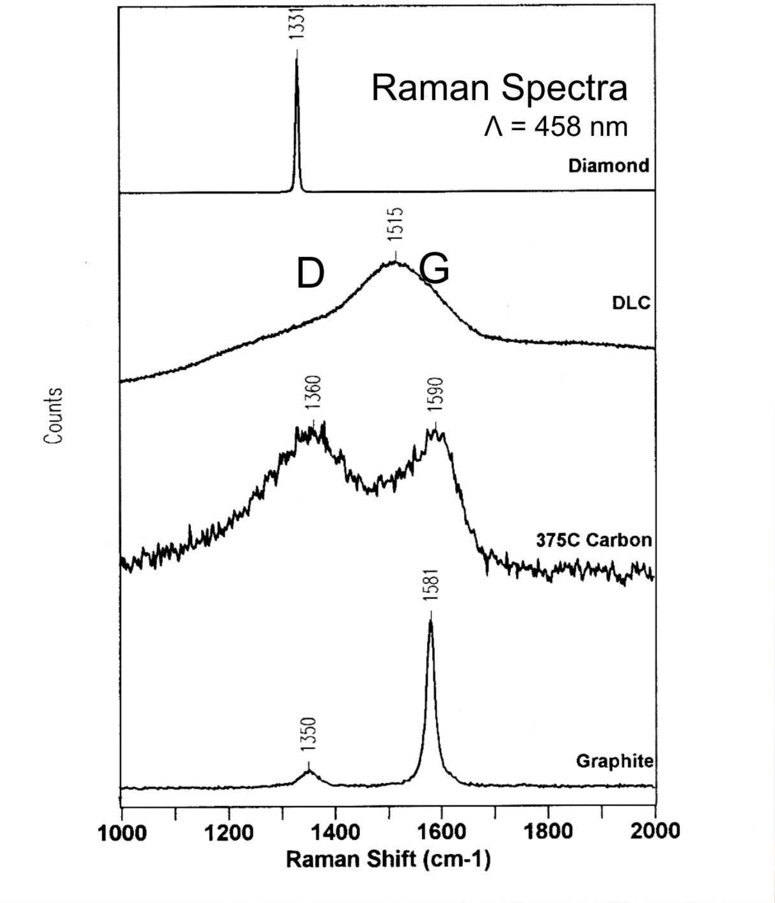
Ternary phase diagram of bonding in amorphous carbon-hydrogen materials

- Diamond-like Carbon has mixed sp^2/sp^3 bonding with majority being metastable sp^3, unless it is stabilized with C-H bonds.
- DLC cab be amorphous (a-C) or hydrogenated amorphous carbon (a-C:H) (typically 10-50 atomic % H).



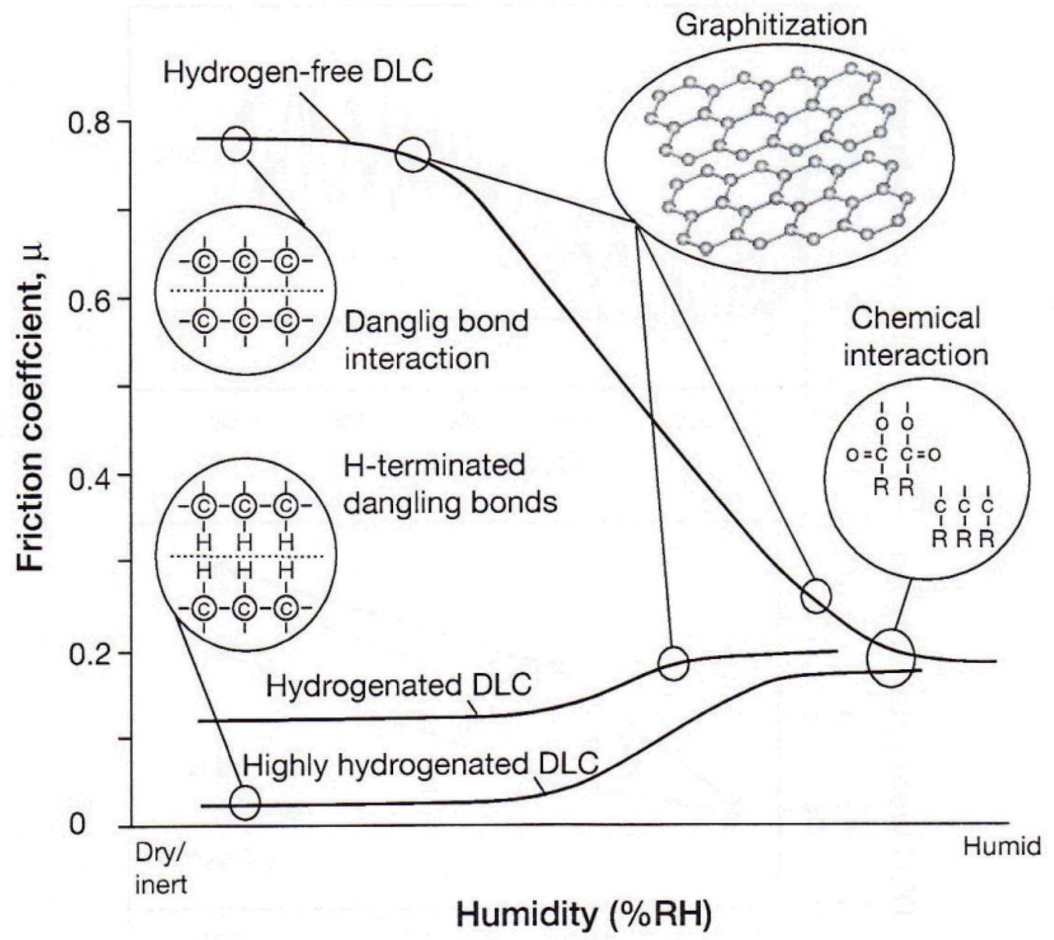


From J. Robertson (2002) Mater Sci Eng R 37: 129.

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

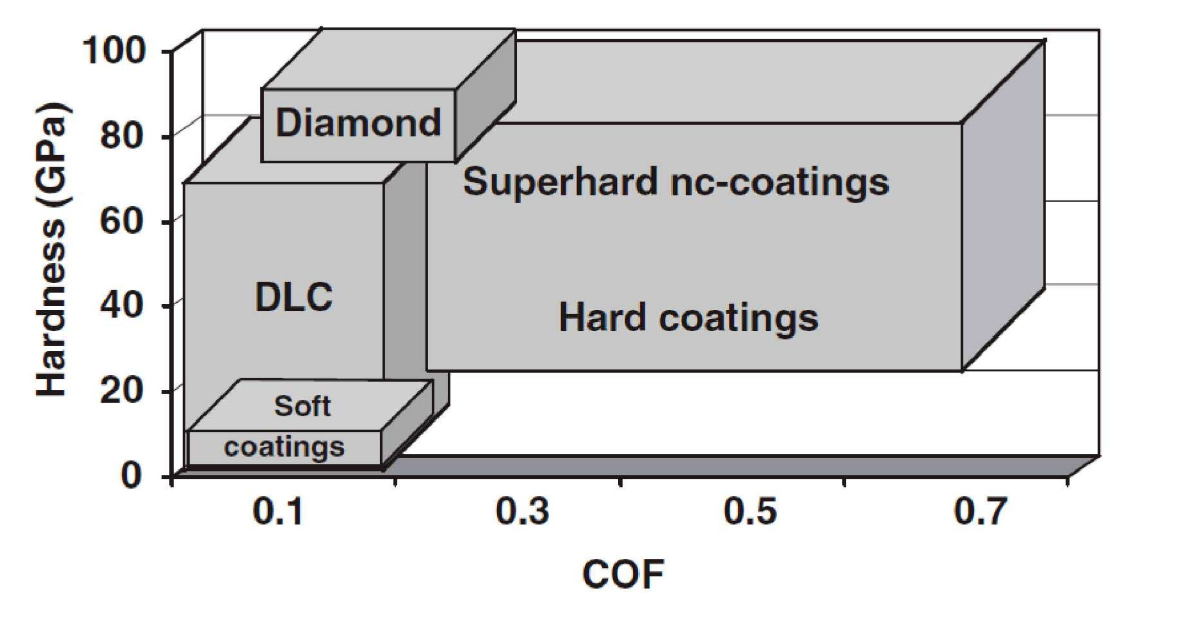
Synthesizing an Environmentally Robust DLC is Still a Challenge!

- Hydrogenated DLCs give low friction in dry environments.
- Hydrogen free DLCs require moisture to terminate dangling bonds.



H. Ronkainen and K. Holmberg, “Environmental and Thermal Effects on the Tribological performance of Coatings”, In: C. Donnet and A. Erdemir (eds.), *Tribology of Diamond-Like Carbon Films: Fundamentals and Applications*. Springer 2008

DLC can provide both high hardness and low friction



- DLCs exhibit the unusual combination of high hardness and elastic modulus in conjunction with low friction.

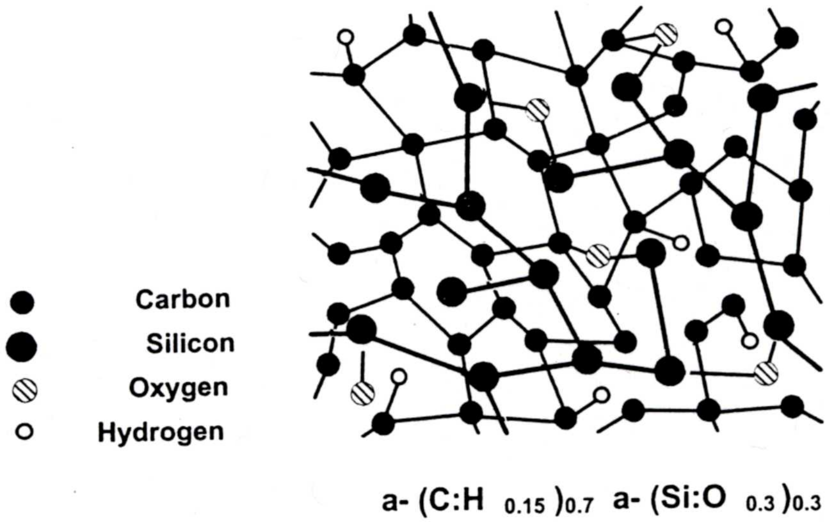
- This appears like an exception to the Bowden and Tabor Model which requires a low hardness for shear accommodation to achieve low friction.

C. Donnet and A. Erdemir "Diamond-like Carbon Films: A Historical Overview," from C. Donnet and A. Erdemir (eds.), *Tribology of Diamond-Like Carbon Films: Fundamentals and Applications*. Springer 2008

Diamond-Like Carbon Nanocomposites

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

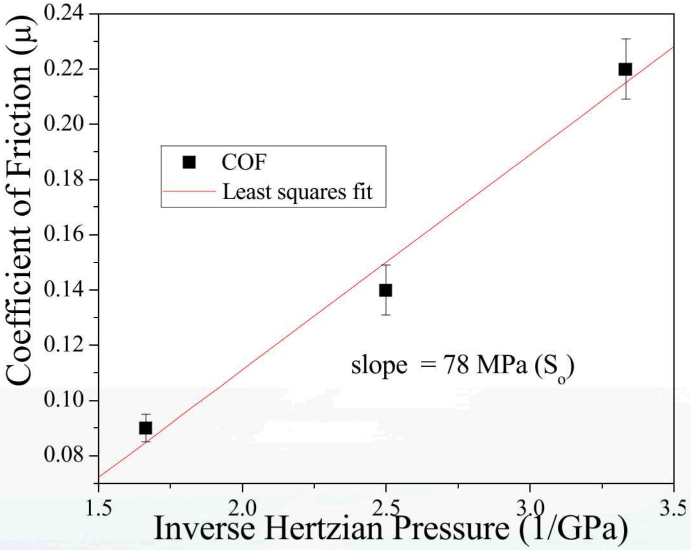
V. F. Dorfman, *Thin Solid Films*, 212 (1992) 267-273

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

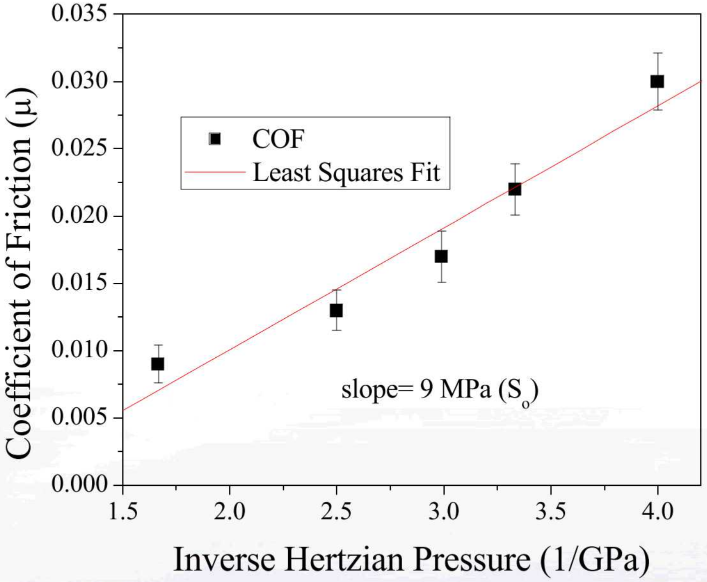
C. Venkatraman, C. Brodbeck and R. Lei, *Surface and Coatings Tech*. 115 (1999) 215-221.

The Friction Behavior is non-Amontonian

Air (50% RH)



Dry Nitrogen



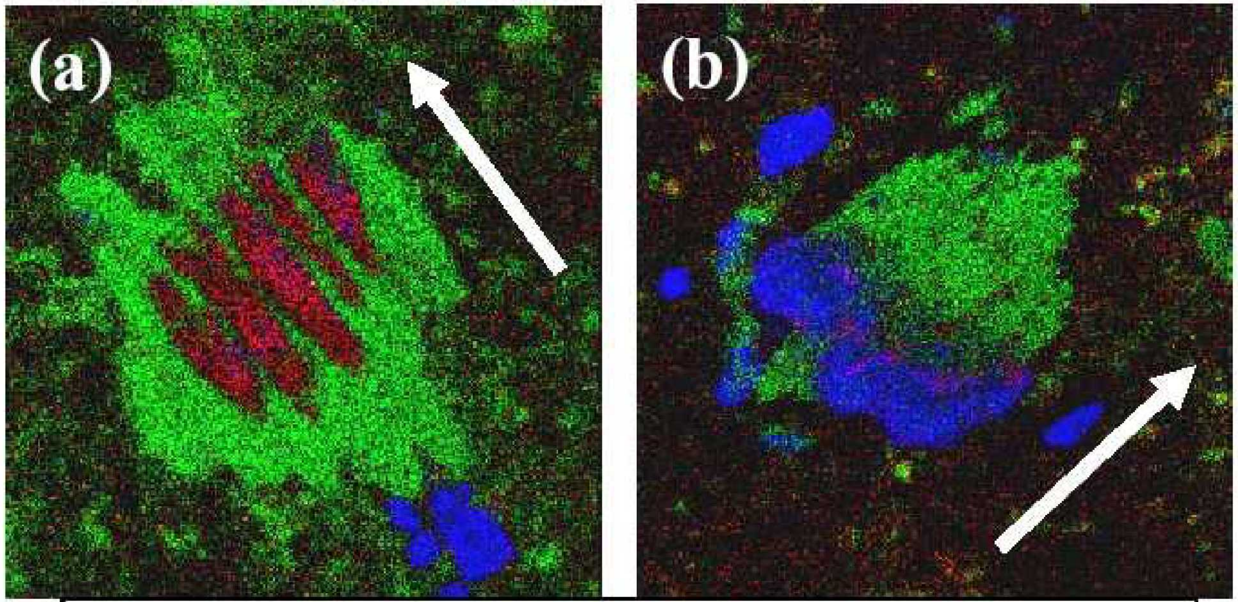
- Load Dependence
- Environmental Effects
- (Note the difference in the slopes)

T. W. Scharf, J. A. Ohlausen, D. R. Tallant, S. V. Prasad, J. Appl. Phys. 101 (2007)

ToF-SIMS of Transfer Films illustrating the Chameleon Nature

Humid Air (μ~.2)

Dry Nitrogen (μ~.02)



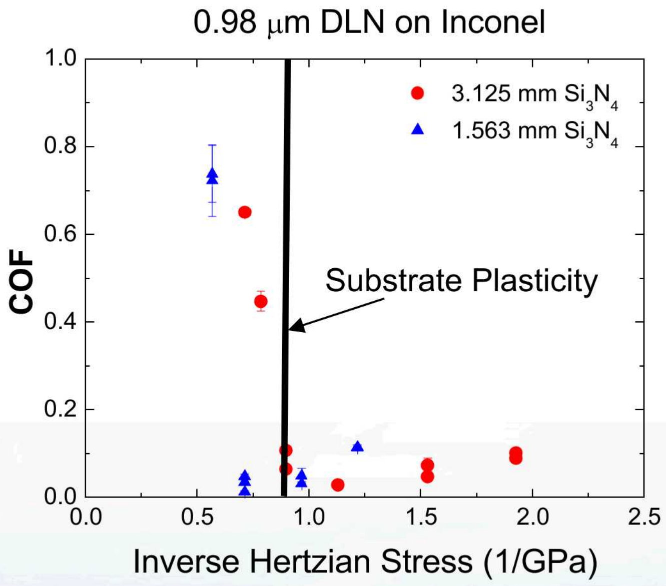
Red: SiO_2 ($O + Si + SiO_2 + SiO_3$)
Green: Long Range Carbon (C_1 to C_4 fragments)
Blue: Hydrogenated Carbon ($CH + CH_2 + C_2H$)

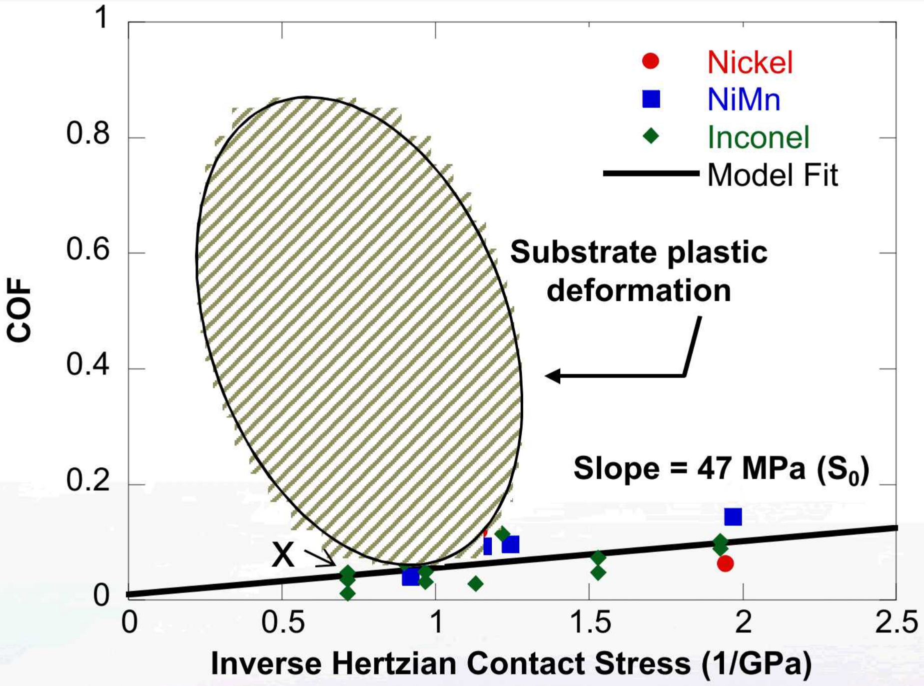
78 MPa

9 MPa

ToF-SIMS

Deviations from Predicted Behavior



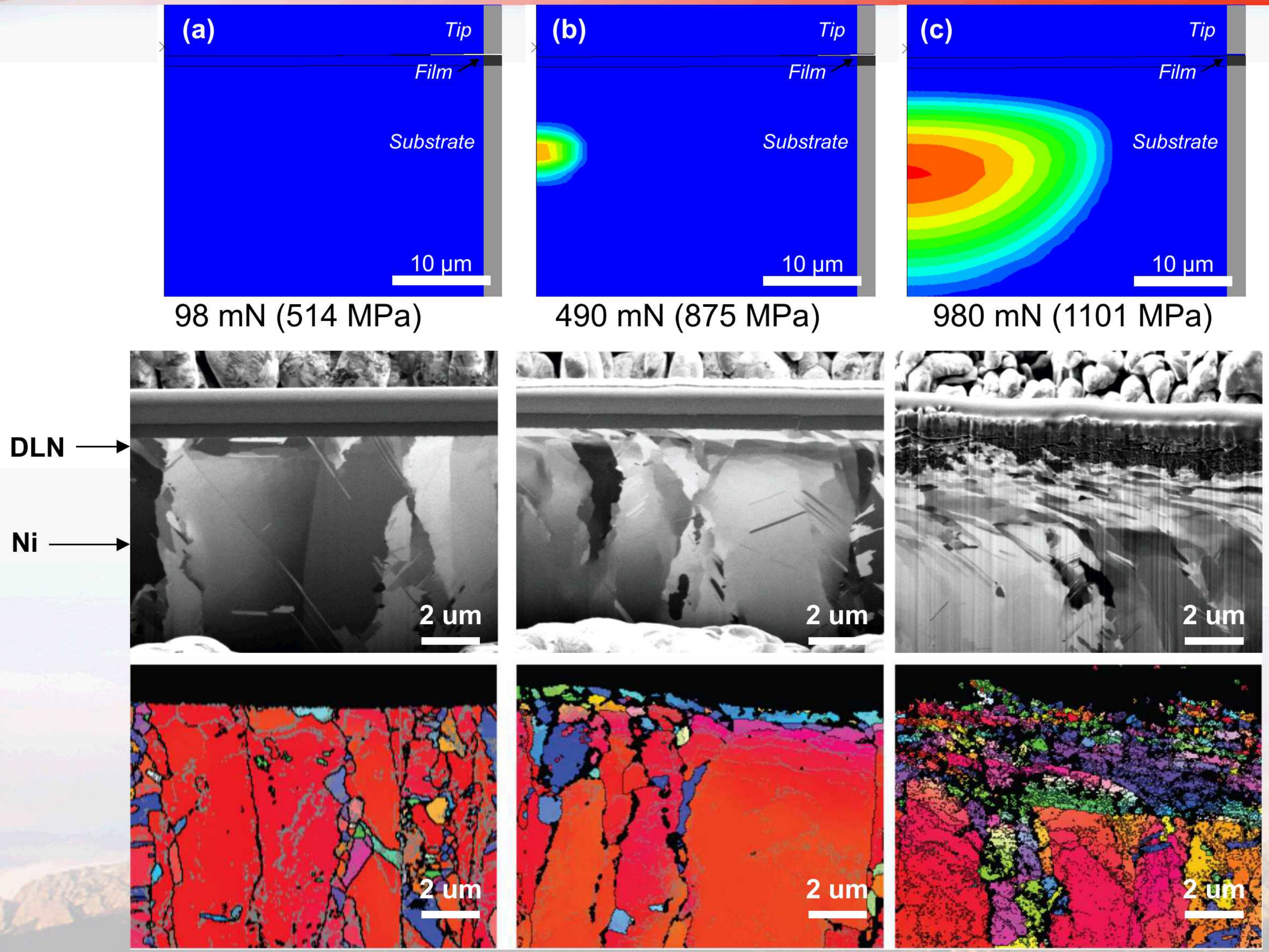


FEM predictions of substrate plastic deformation are in general agreement with observed deviations in Hertzian contact model

Multi-Layer Architectures may be necessary to mitigate substrate plastic deformation

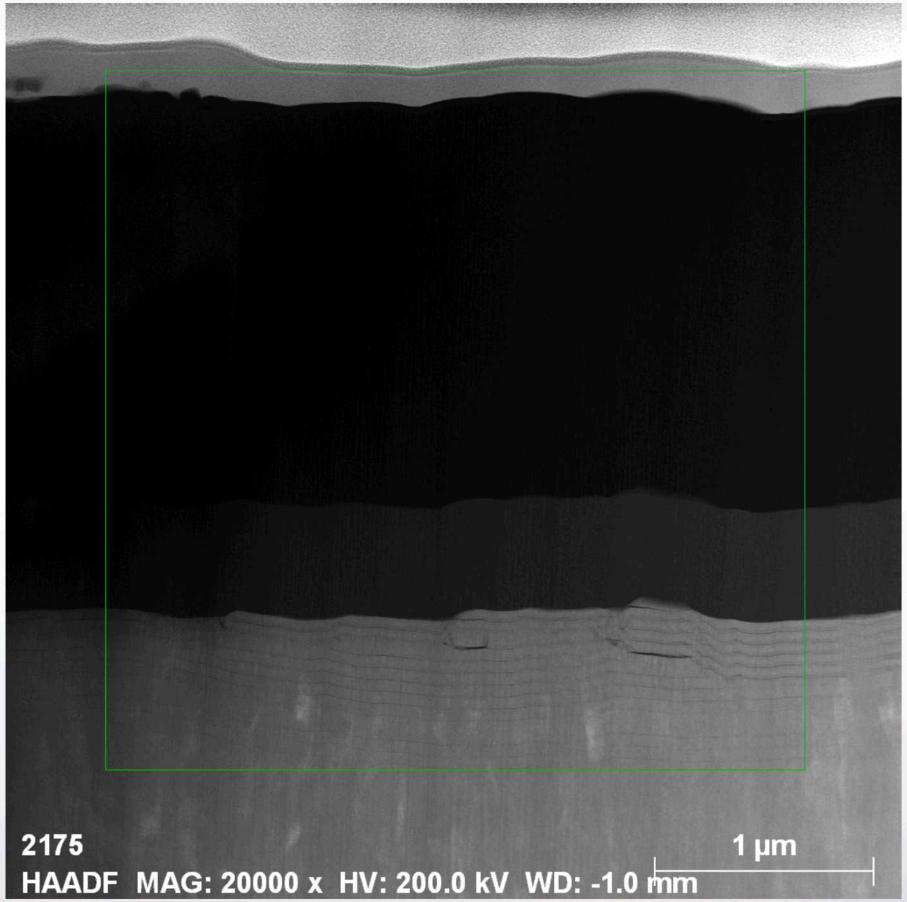
J.M. Jungk, J.R. Michael and S.V. Prasad, Acta Materialia, (2008) 56: 1956-1966.

Friction Induced Plastic Deformation in the Substrate

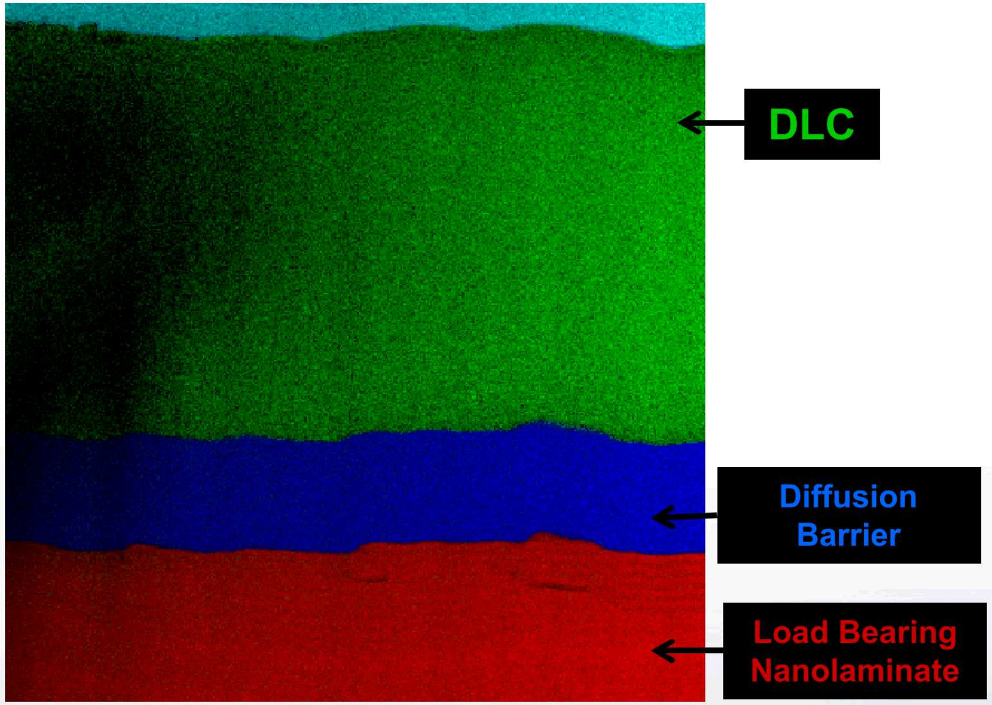


S.V. Prasad, J.R. Michael T. R. Christenson, Scripta Materialia, 48 (2003) 48

Designing Multilayer Coatings Architextures: Adhesion, Load Bearing, Diffusion Barrier



Micro-cracks between nanolaminate layers

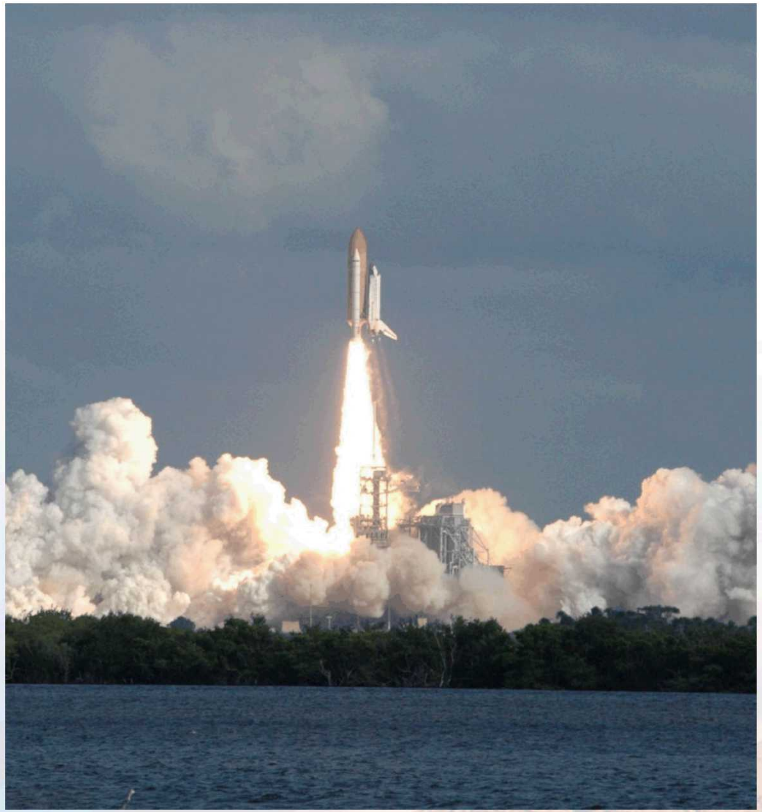


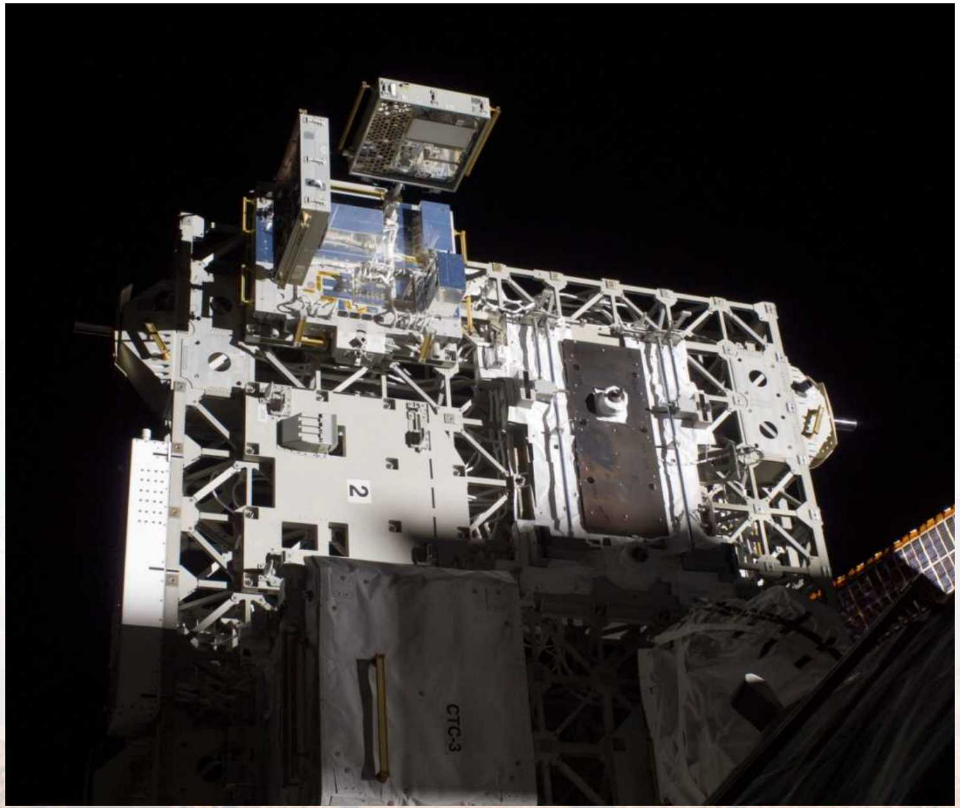
Robust Barrier

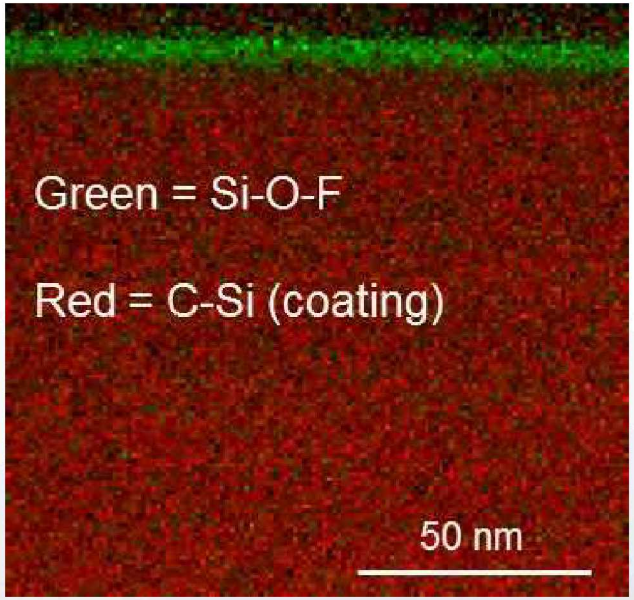
Space: The final Frontier

MISSE-7

Materials on the International Space Station Experiment







DLC post-MISSE (FIB)

Advanced analytical techniques are essential for assessing the materials aging and reliability

M. T. Dugger, T. W. Scharf and S. V. Prasad, “Materials in Space: Exploring the Effect of Low Earth Orbit on Thin Film Solid Lubricants” ADVANCED MATERIALS & PROCESSES 32 • MAY 2014

Concluding Thoughts

- Think beyond the traditional approach identifying ‘a lubrication strategy’ after final decisions on materials selection and fabrication routes have already been made.
- **Materials designed for friction and wear mitigation, commonly referred to as tribological materials, must also meet mechanical and physical property requirements. This balance makes it very challenging from a practical design perspective.**
- **No single phase material can give low friction and wear in all environments and under all operating conditions**
  - Many Solid Lubricant Coatings Exhibit Load Dependence on Friction
  - Environment plays a very significant role in determining the tribological behavior
- **The DLC and MoS_2-bsed composites are two examples of Nanostructured materials that provide some degree of environmentally robustness.**
- **Introduce multilayer coatings if subsurface plastic deformation cannot be avoided.**

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