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SAND2009-3737C

Effects of organic vapor adsorption on friction and wear of silicon oxide surfaces – from fundamentals to MEMS applications

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Air Force Office of Scientific Research

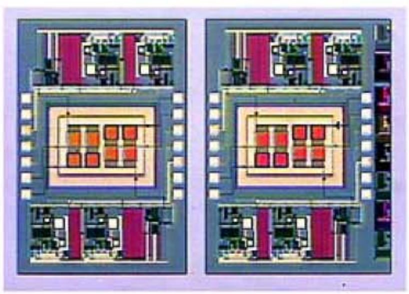
13th IACIS International Conference on Surface and Colloid Science
83rd ACS Colloid and Surface Science Symposium
July 14-19, 2009 (New York)

National Nuclear Security Administration

Sandia National Laboratories

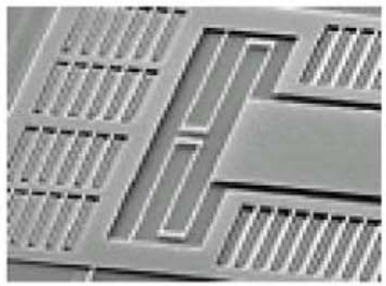
MEMS Reliability Taxonomy

Class I
No Moving parts



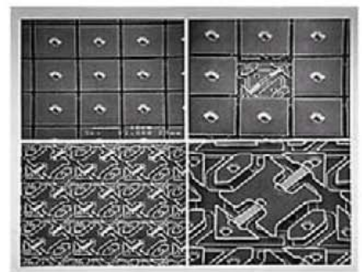
Accelerometers
Pressure Sensors
Ink Jet Print Heads
Strain Gauge

Class II
Moving Parts, No Rubbing or Impacting Surfaces



Gyros
Comb Drives
Resonators
Filters

Class III
Moving Parts, Impacting Surfaces



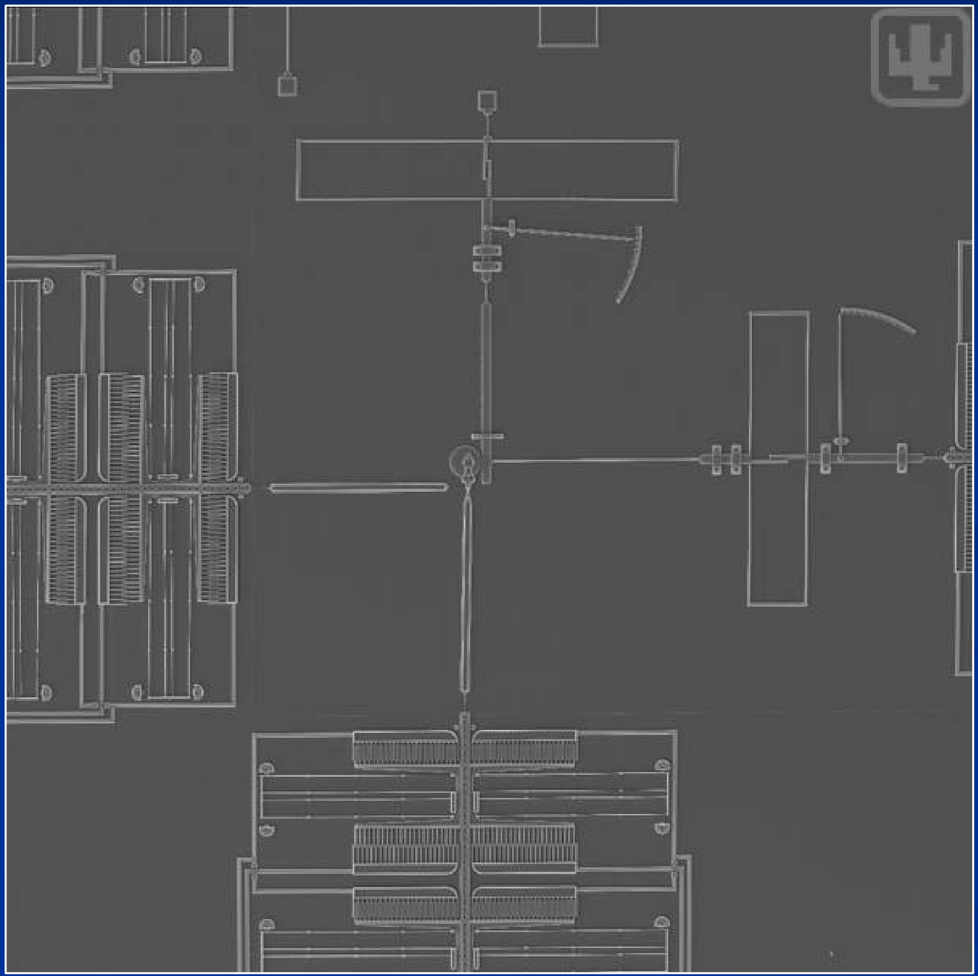
TI DMD
Relays
Valves
Pumps

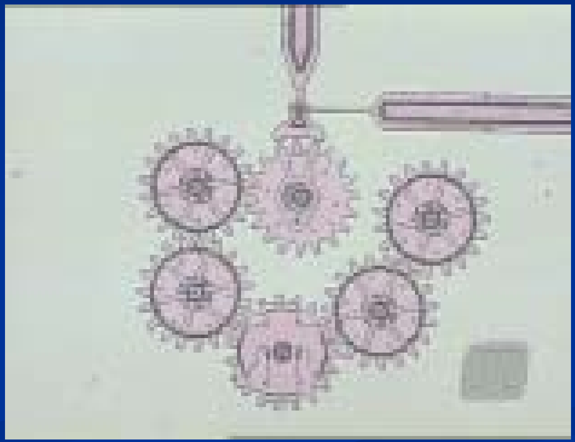
Class IV
Moving Parts, Impacting and Rubbing Surfaces

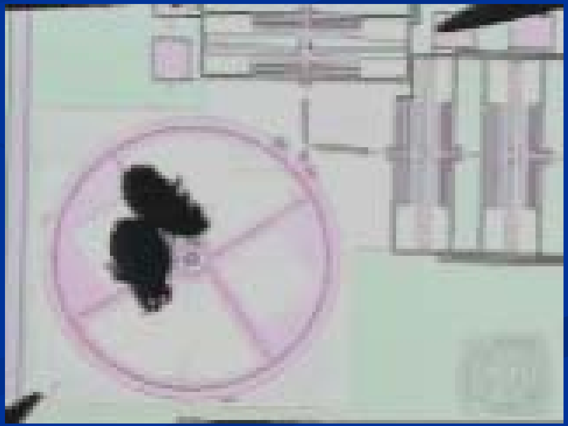
Optical Switches
Corner Cube Refl.
Shutters
Scanners
Locks
Discriminators

Romig, et. al. *Acta Materialia* **51** (2003) 5837

An example of Class-IV MEMS devices



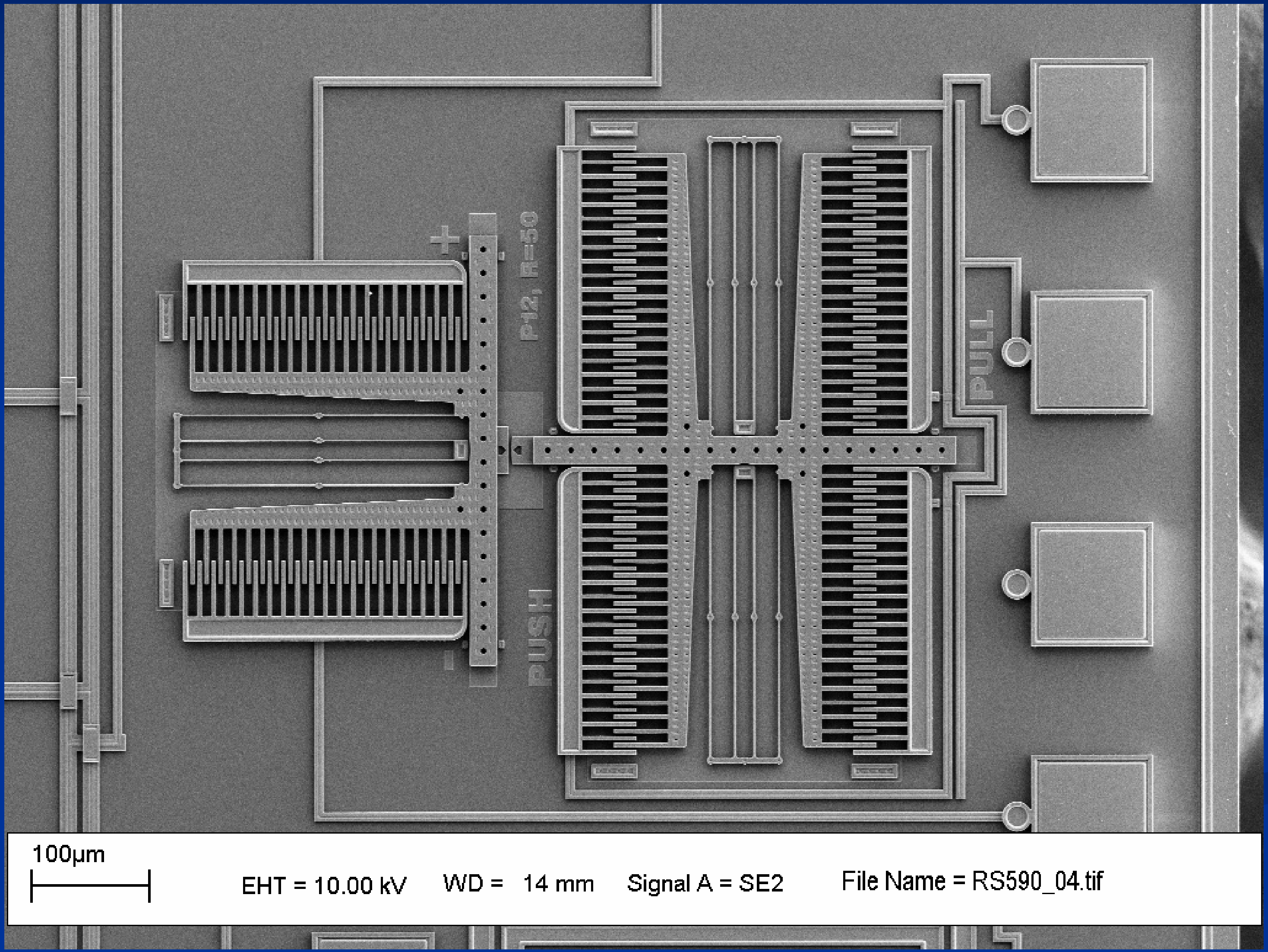




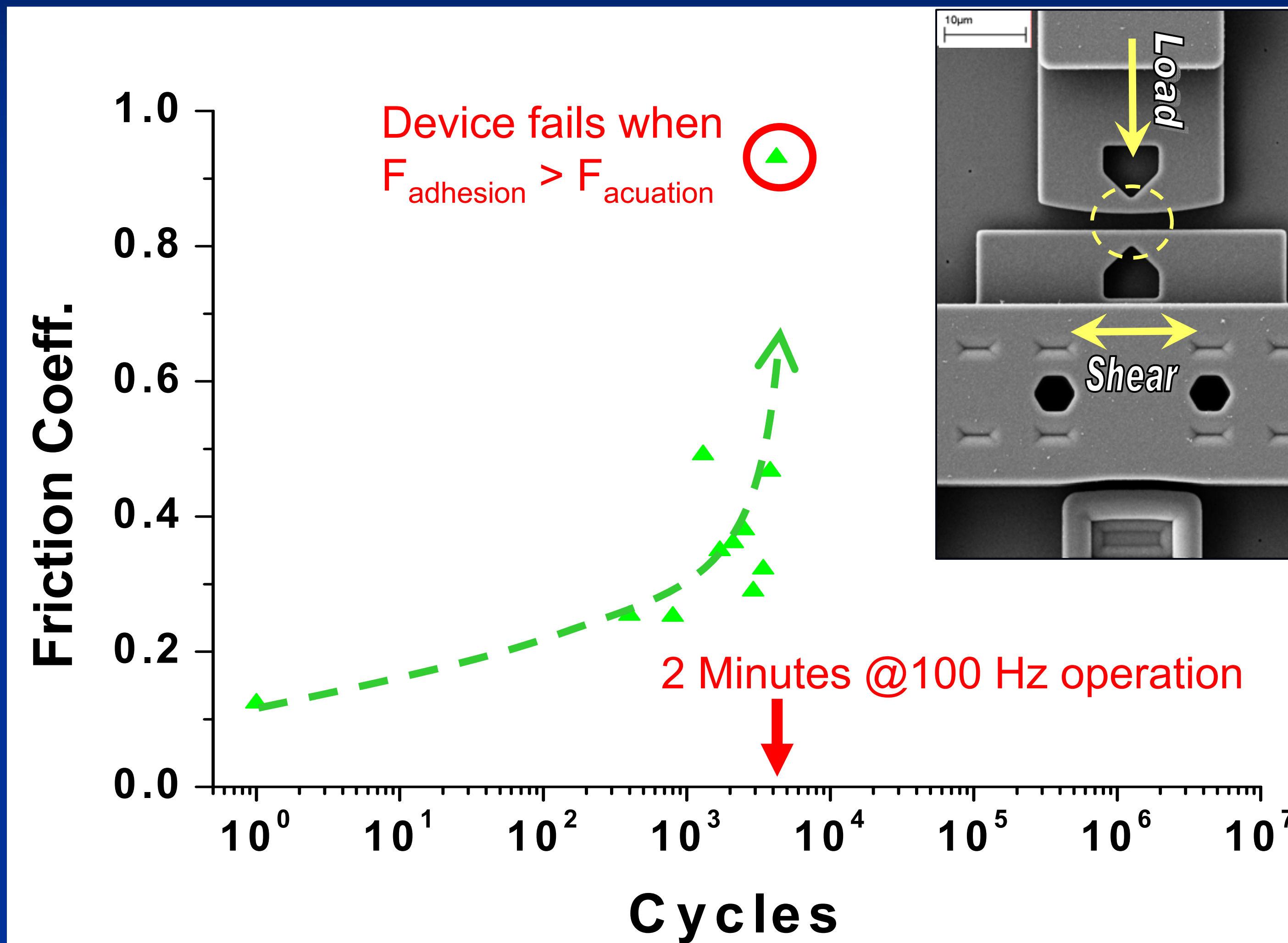
"Courtesy Sandia National Laboratories, SUMMiT™ Technologies, www.sandia.gov/mstc"

MEMS side-wall tribometer

Initially coated with "lubricious" fluorinated self-assembled monolayer



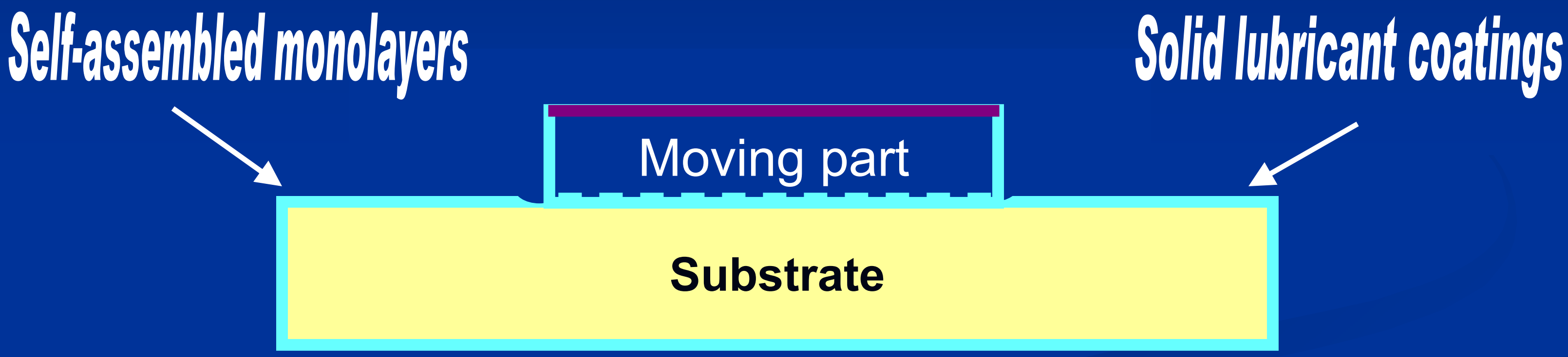
Device fails once the lubricious coating layer is worn off and the adhesion of the newly exposed bare surfaces becomes larger than the actuation force.



D. B. Asay, M. T. Dugger, and S. H. Kim, *Tribol. Lett.* **2008**, 29, 67.

Current "State-of-the Art"

Solid lubricant (thin film coating)



Advantages:

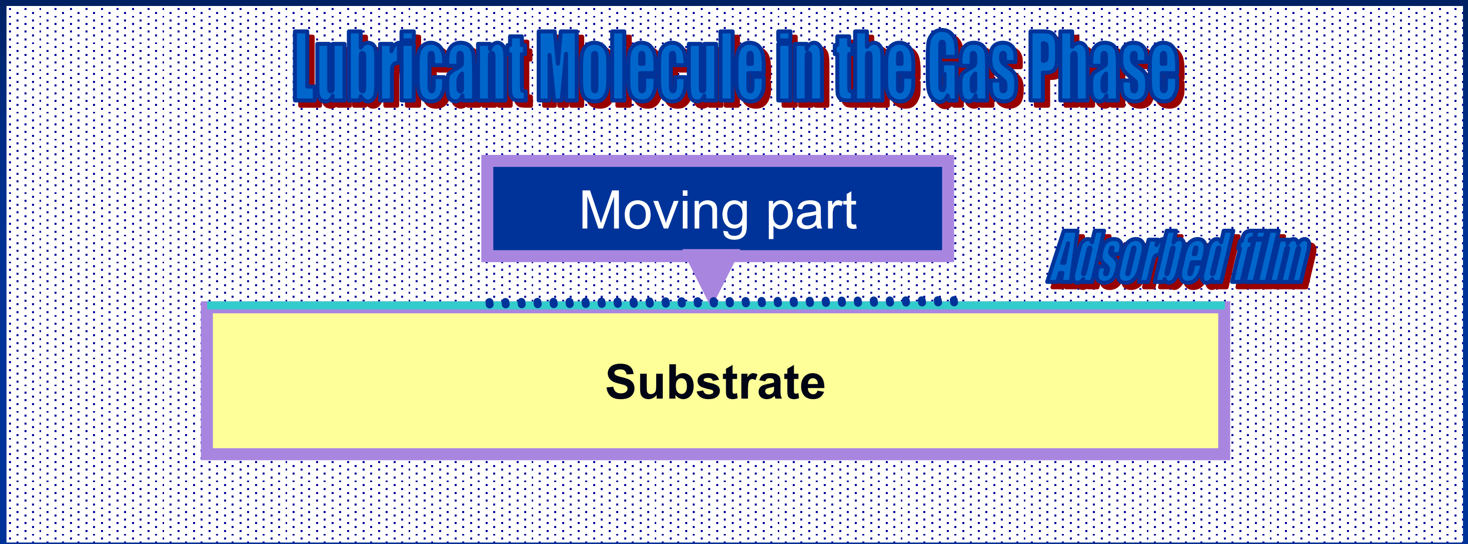
- Easily incorporated into device while being fabricated
- Reduces friction

Disadvantages:

- Not always conformal (difficult to coat buried surfaces)
- Doesn't last forever → lubricant is not replenished

Kim SH, Asay DB, & Dugger MT, "Nanotribology and MEMS" *NanoToday 2* (5): 22-29, **2007**

In-situ Vapor Phase Lubrication



Advantages:

- ***Lubricant is continuously replenished***
- Coats all surfaces exposed (Totally Conformal)
- No Power Dissipation (vs. liquid lubricants)

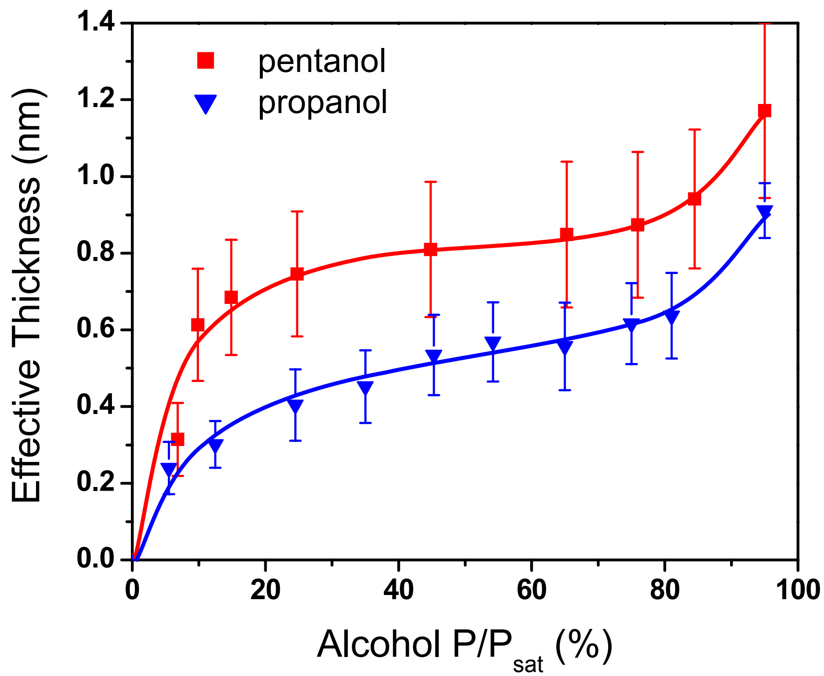
K. Strawhecker, D. B. Asay, J. McKinney, and S. H. Kim, *Tribol. Lett.* **2005**, *19*, 17

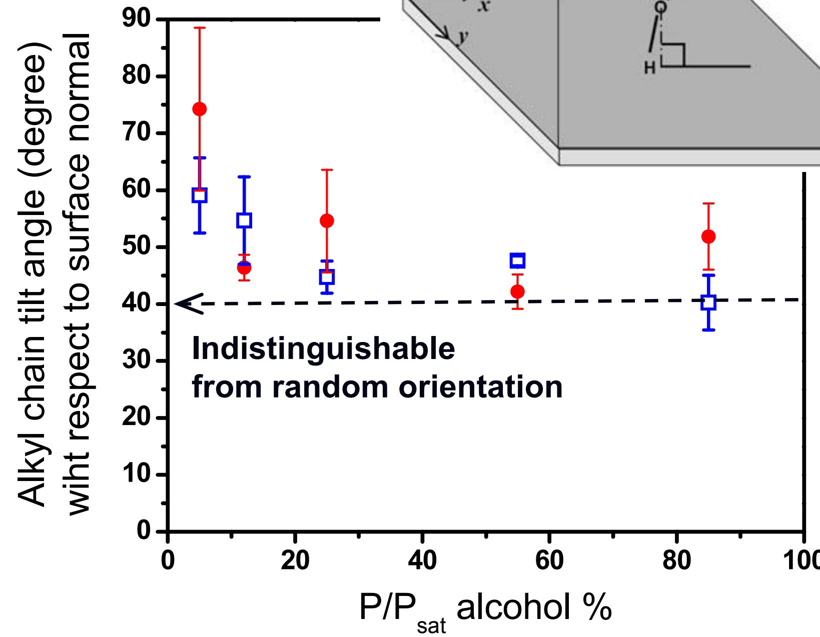
How much lubricant is on the surface?

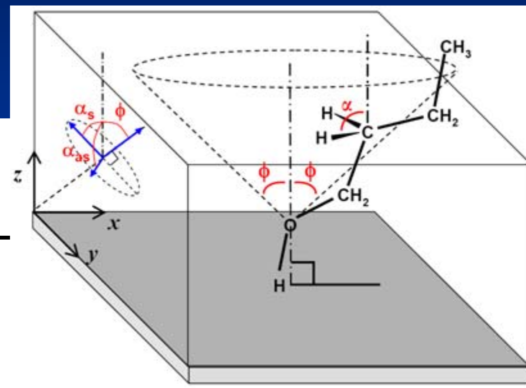
→ Adsorption isotherm study

Adsorption isotherm and molecular orientation of alcohols on SiO_2

Measured with ATR-IR spectroscopy







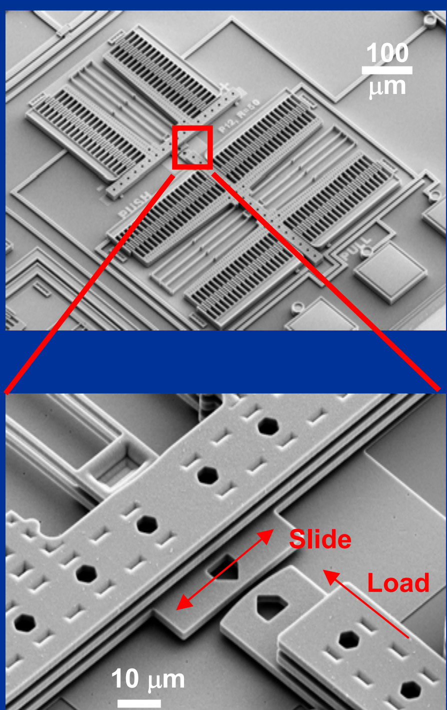
Barnette, Asay, Janik, and Kim, *J. Phys. Chem. C.* **2009** (in press; DOI: 10.1021/jp901064r)

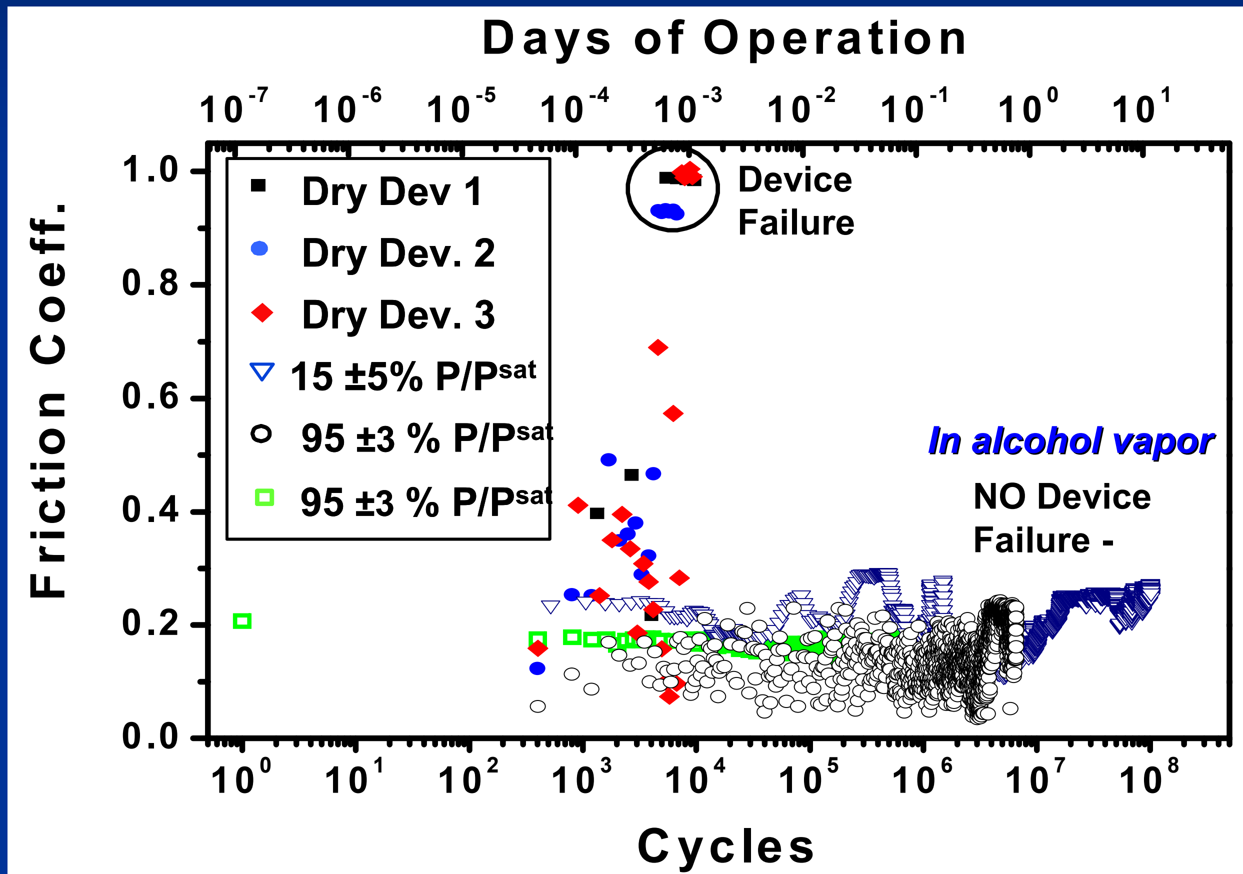
A molecule-thick alcohol layer…

Does it lubricate MEMS effectively?

Unprecedented improvements in MEMS operating life are observed with alcohol vapor lubrication.

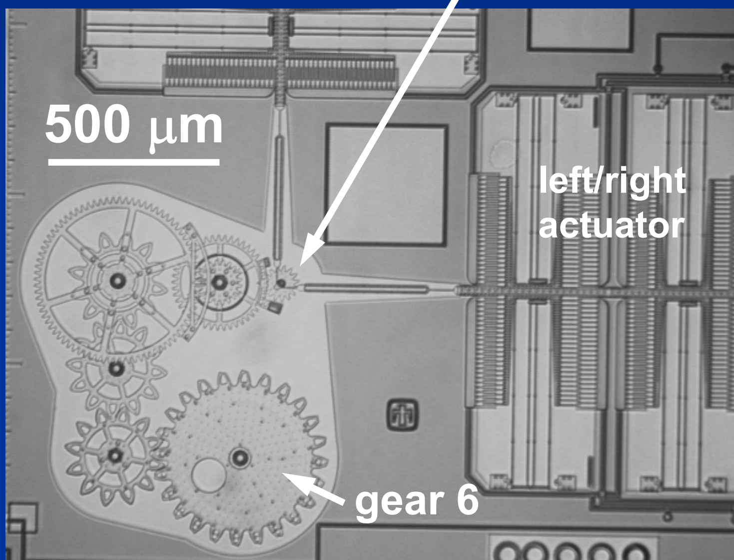
MEMS tribometer



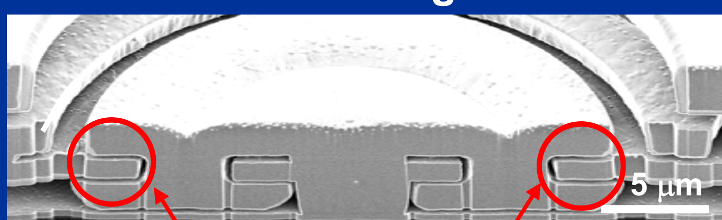


D. B. Asay, M. T. Dugger, and S. H. Kim, *Tribol. Lett.* **2008**, 29, 67.
D. B. Asay, M. T. Dugger, J. A. Ohlhausen, and S. H. Kim, *Langmuir* **2008**, *24*, 155.

Increased operating life of gear train with pentanol vapor phase lubrication



FIB section through hub



With fluorinated SAM alone,

→ device failed at ~5×10^4

With pentanol vapor,

→ device ran >5×10^8 ***without failure***

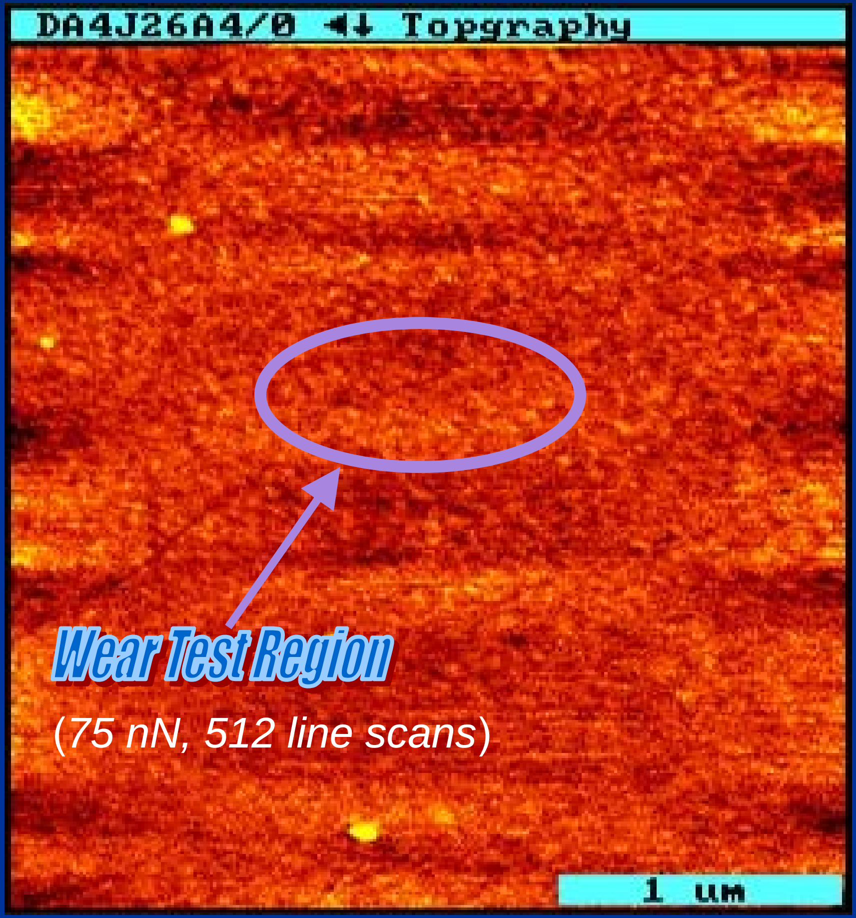
M. T. Dugger (Sandia)

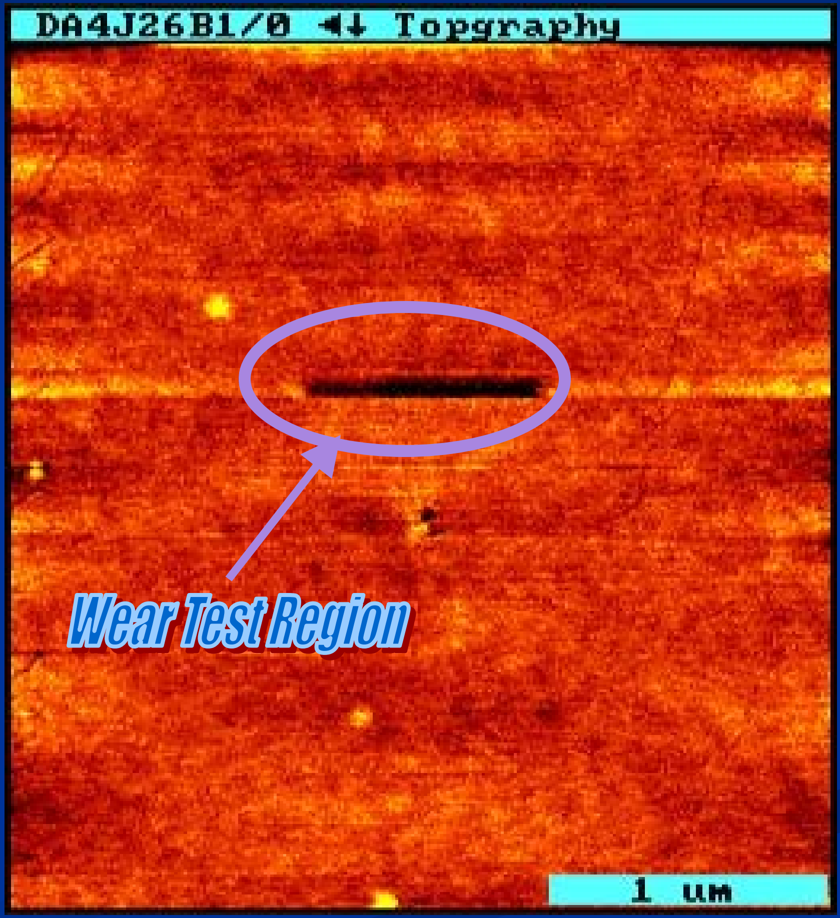
The alcohol vapor-phase lubrication works at the MEMS-scale…

Does it work at the nano-scale?

AFM wear test of silicon oxide

In humid air (RH = 75%)

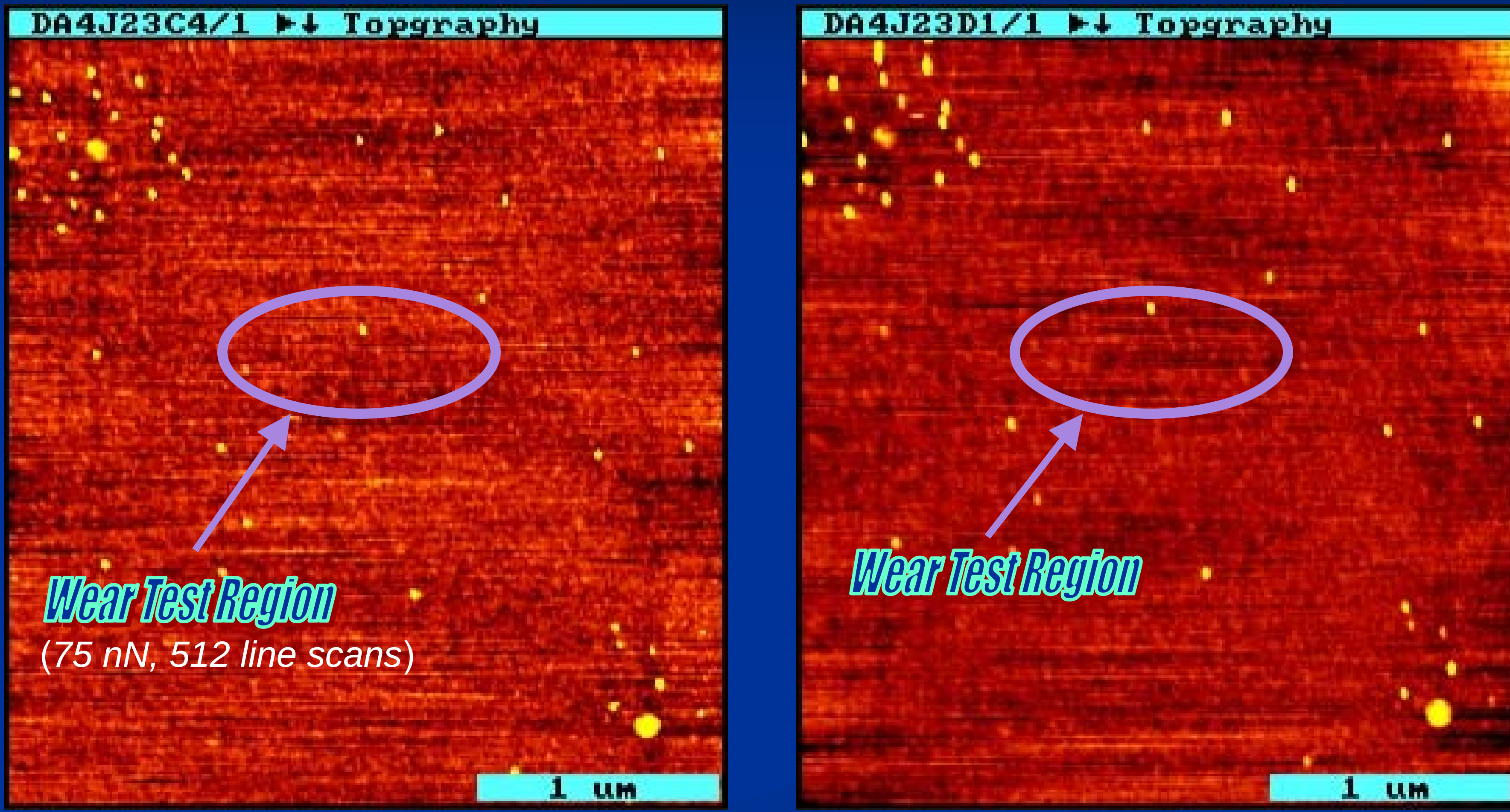




10 Å deep trench

Full Z-scale ~1nm

In 75% P/P_{sat} n-propanol vapor



D. B. Asay, M. T. Dugger, J. A. Ohlhausen, and S. H. Kim, *Langmuir* **2008**, *24*, 155.

It works at the MEMS-scale
& the nano-scale…

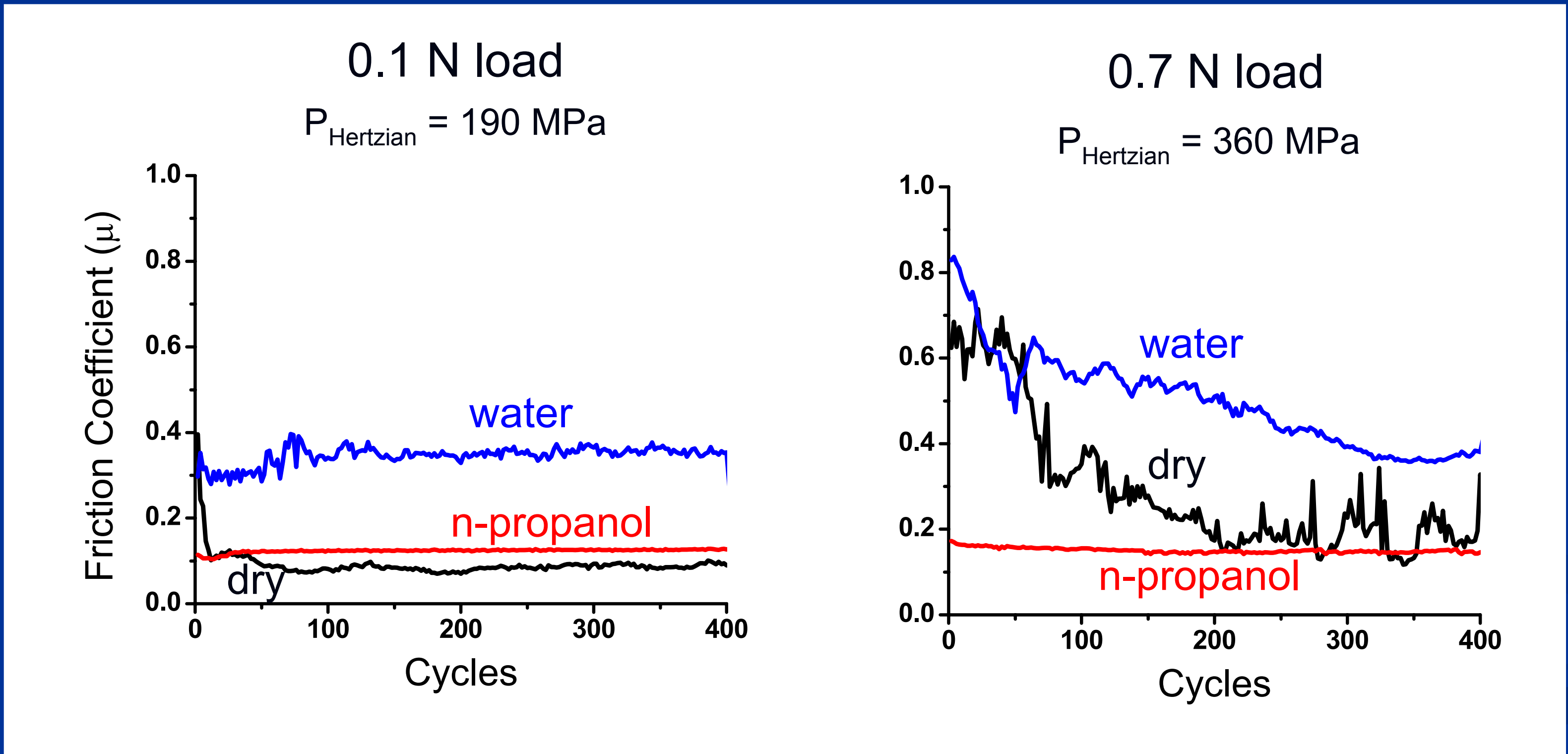
Then, how about at the macro-scale?

Effects of vapor adsorption on friction coefficient

Pin-on-disc tribo-tests

Substrate: Si wafer with amorphous oxide (2nm thick)

Ball : fused silica (3mm diameter)



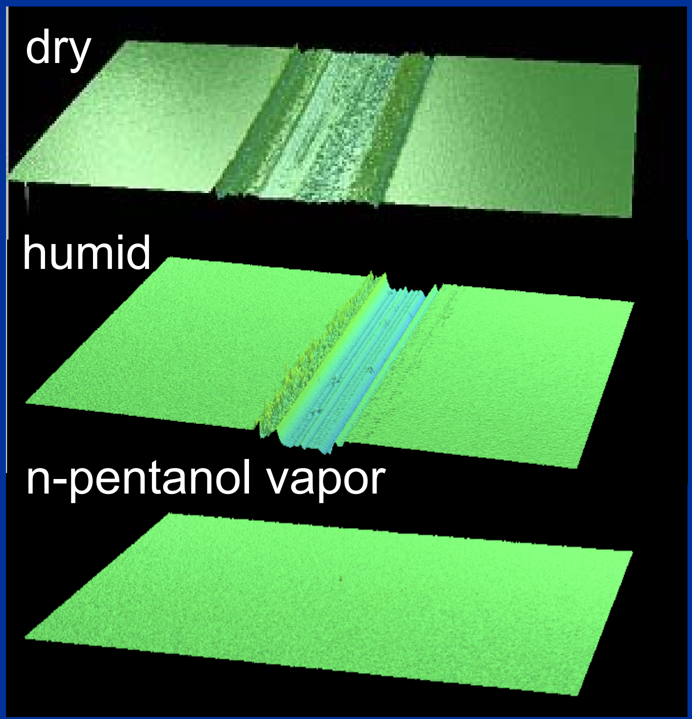
Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* (submitted).

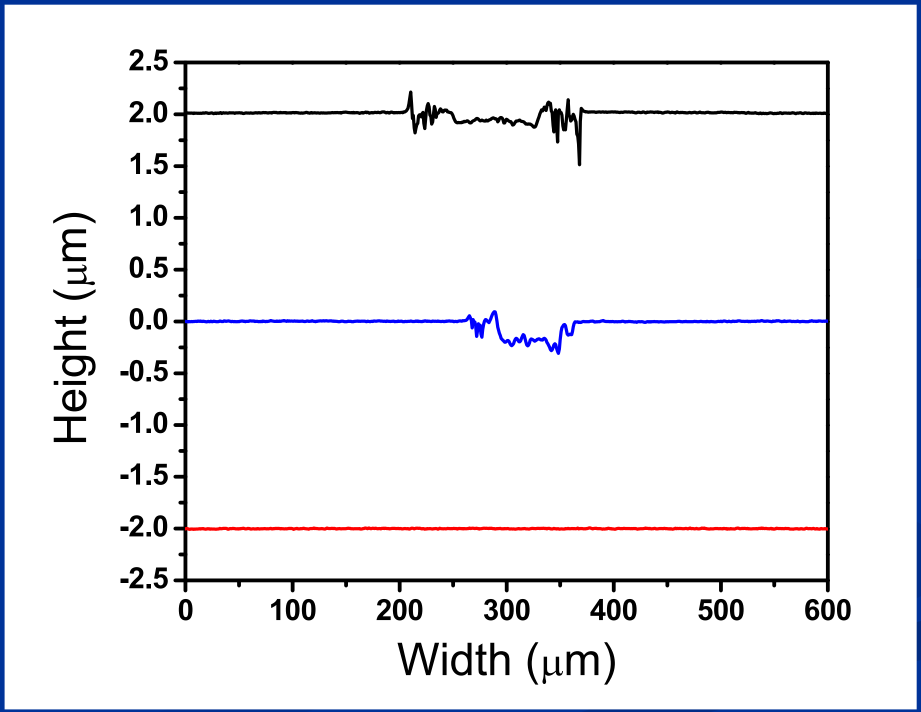
Effects of vapor adsorption on wear of SiO_2/Si

0.1 N load on 3mm dia fused silica ball sliding on SiO_2/Si

(Nominal $P_{Hertzian}$ = 190 MPa)

Optical profilometry





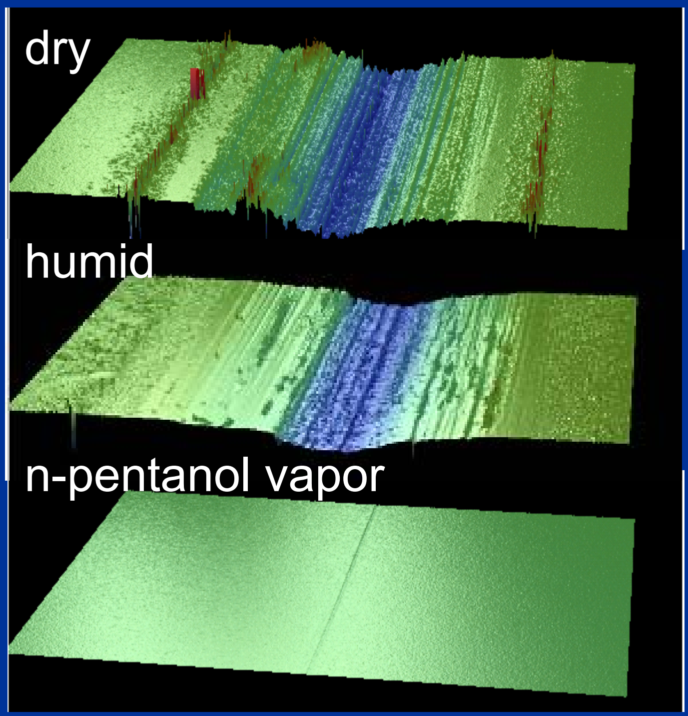
Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* (submitted).

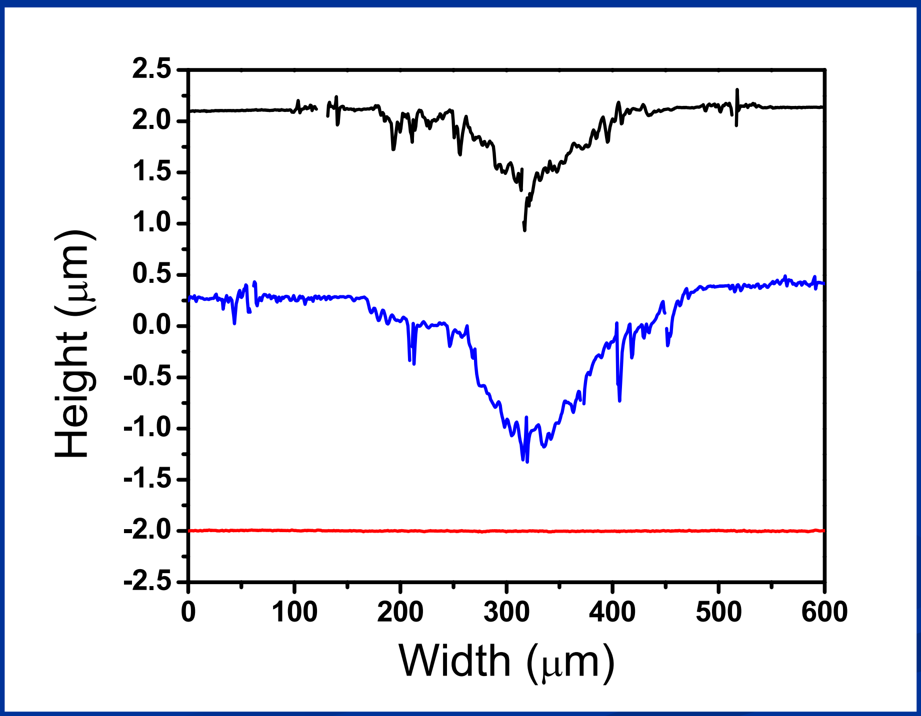
Effects of vapor adsorption on wear of SiO_2/Si

0.7 N load on 3mm dia fused silica ball sliding on SiO_2/Si

(Nominal $P_{Hertzian}$ = 360 MPa)

Optical profilometry





Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* (submitted).

In order to understand vapor phase lubrication mechanisms and improve MEMS reliabilities, — *Nanotribology*

Just knowing what solid materials are exposed at the interface in not enough… — *Materials Science*

One must know what molecules are on the surface (even though they are not visible), how much, and what happens to them when sheared at the molecular level… — *Surface Science*

Understanding the lubrication mechanism ?

→ Tribo-tests + Spectroscopic analysis

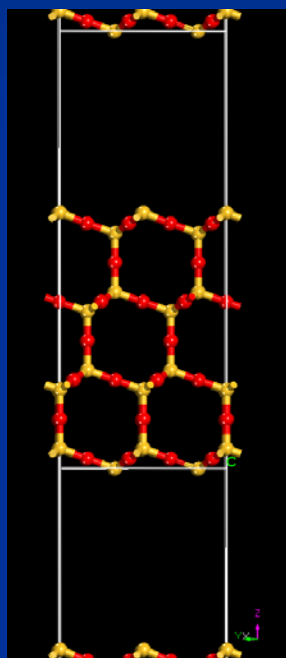
Why is the SiO_2 wear accelerated in humid environments and prevented in alcohol vapor environments?

- All tests were done at the same load (same *nominal* contact pressure) and with the same materials.
- The only difference is the vapor environment.
- So, it must be due to the ***chemistry of adsorbed vapor molecules***, rather than purely mechanical effects.

Density Functional Theory (DFT) calculation of Si-O-Si bond dissociation by rxn with gas molecule

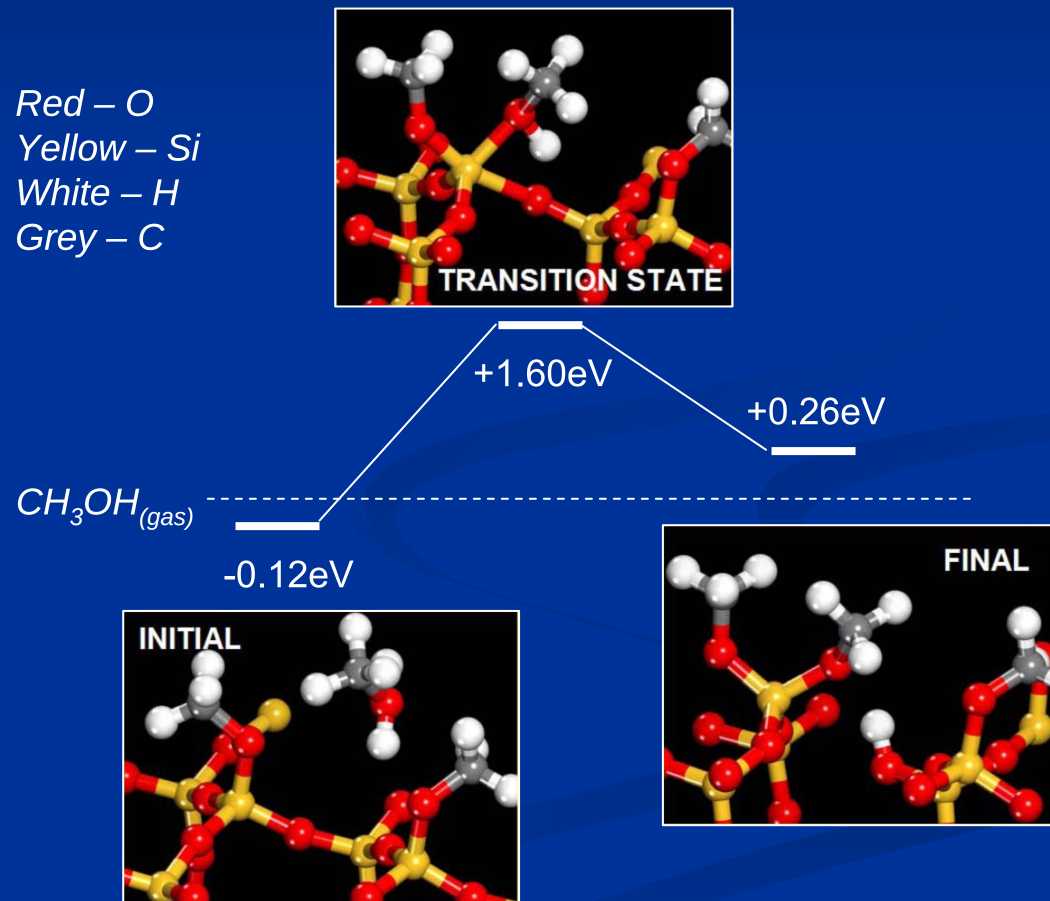
Model System:

β-cristobalite (111)



Stable & low density form of SiO_2

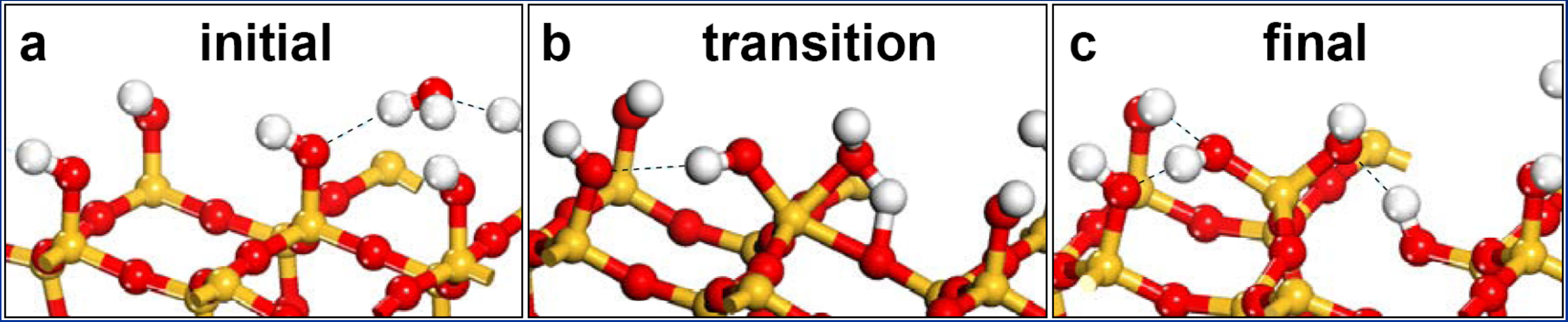
Si-O-Si Rupture via Methanol



Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* (submitted).

Si-O-Si bond dissociation by reaction with water

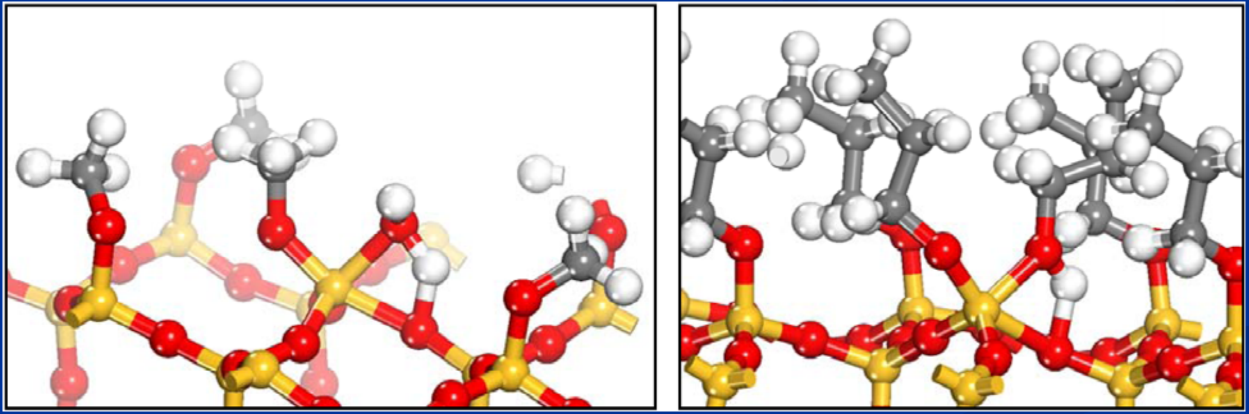
SiO_2 surface terminated with hydroxyl group



Transition states for

CH_3O terminated surface

$CH_3CH_2CH_2O$ terminated surface

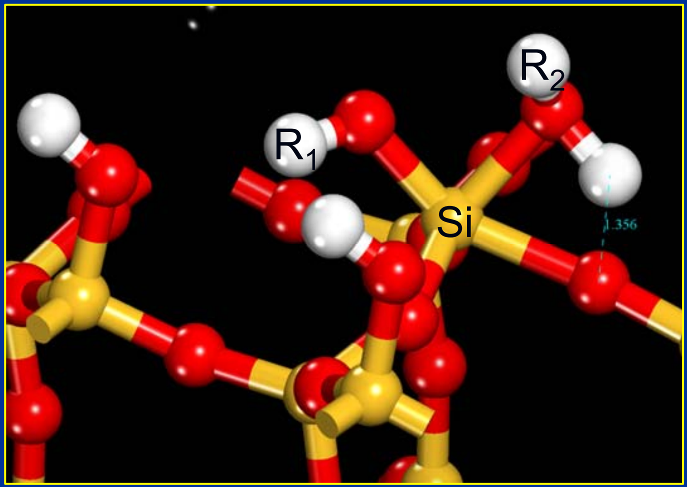


Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* (submitted).

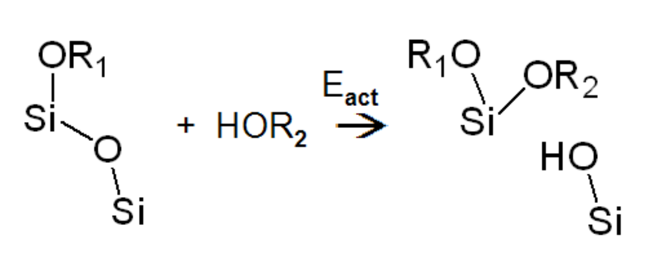
DFT calculation of activation energy for different surface terminations

Alcohol termination (OR) increases the activation barrier necessary to break Si-O-Si linkages…

Transition State for Si-O-Si break



$$Rxn\ rate \propto \exp\left(-\frac{E_a}{RT}\right)$$



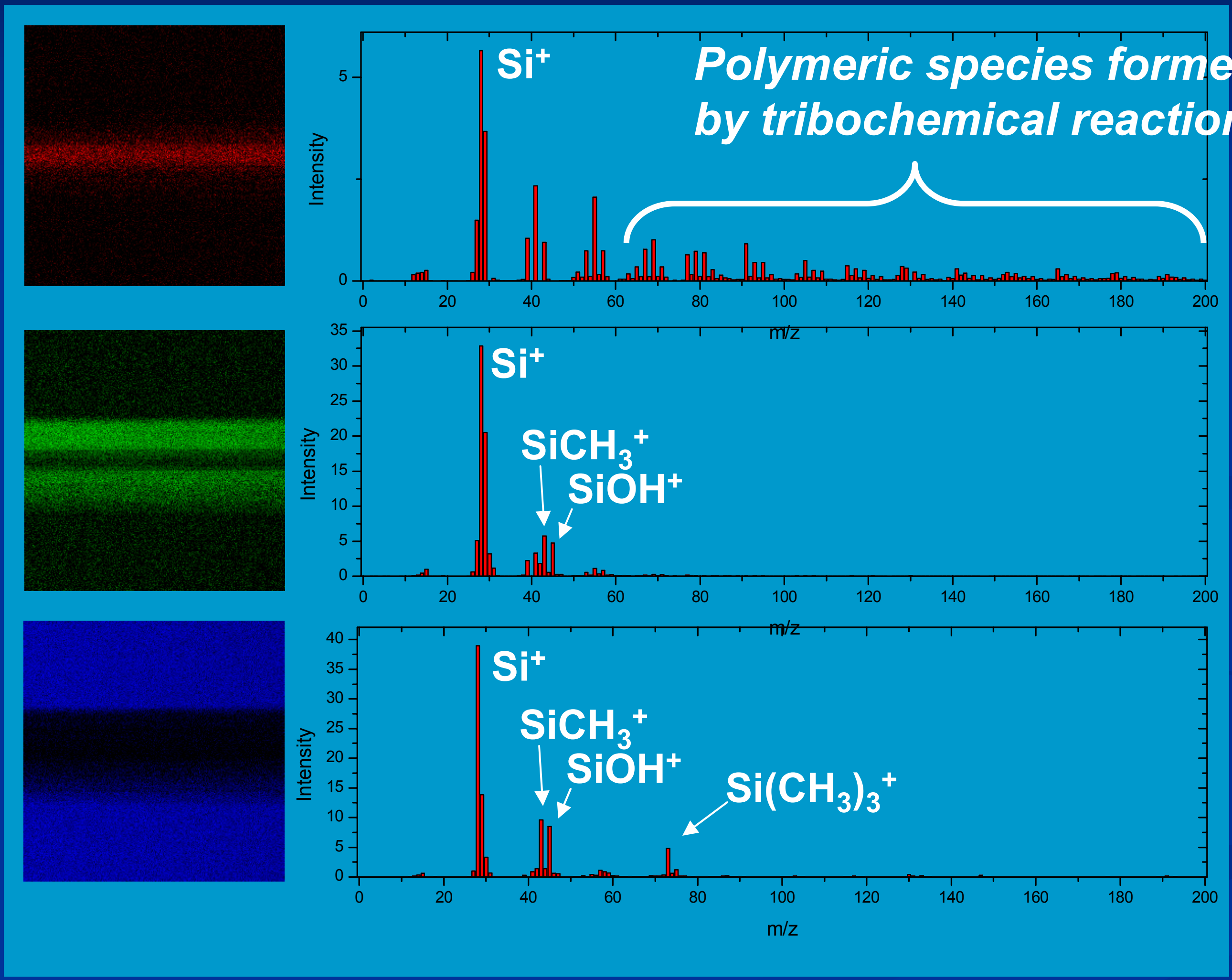
R_1	R_2	E_a (eV)
H	H	1.18
CH_3	H	1.56
H	CH_3	1.16
CH_3	CH_3	1.60
propyl	propyl	2.32

Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* (submitted).

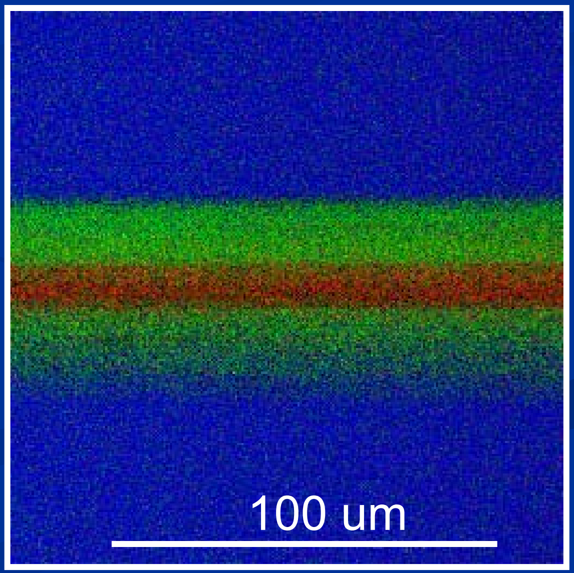
The continuous passivation of the silicon oxide surface via alkoxide formation might be enough to prevent wear of silicon oxide surface...

What happens if the vapor pressure is not sufficiently high or the contact pressure is too high ?

ToF-SIMS multivariate image analysis after sliding in 20% P/P_{sat} n-Pentanol



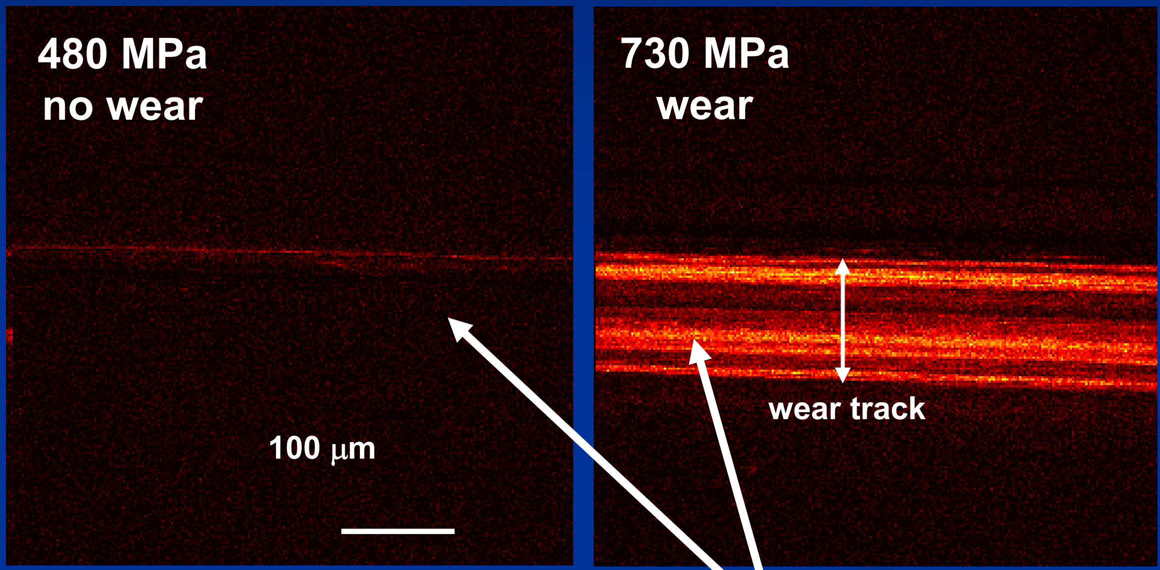
Load = 0.1 N



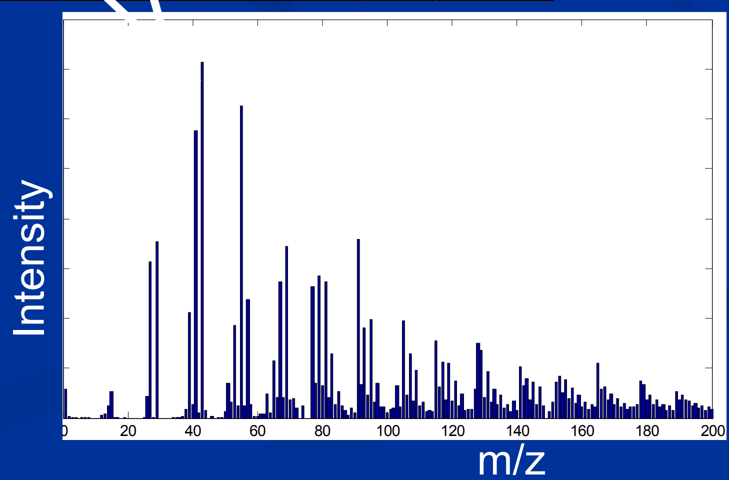
D. B. Asay, M. T. Dugger, J. A. Ohlhausen, and S. H. Kim, *Langmuir* **2008**, *24*, 155.

When load is increased, wear can be observed even at 50% p/p_{sat} n-pentanol

ToF-SIMS reaction product spatial maps



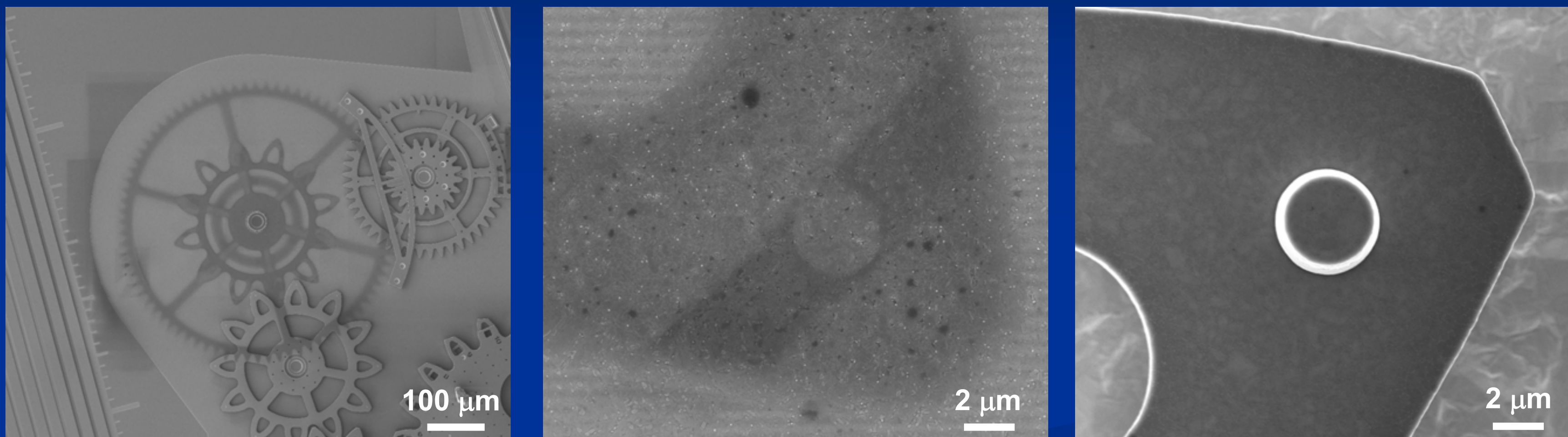
Tribochemical reaction products are observed when wear occurs…

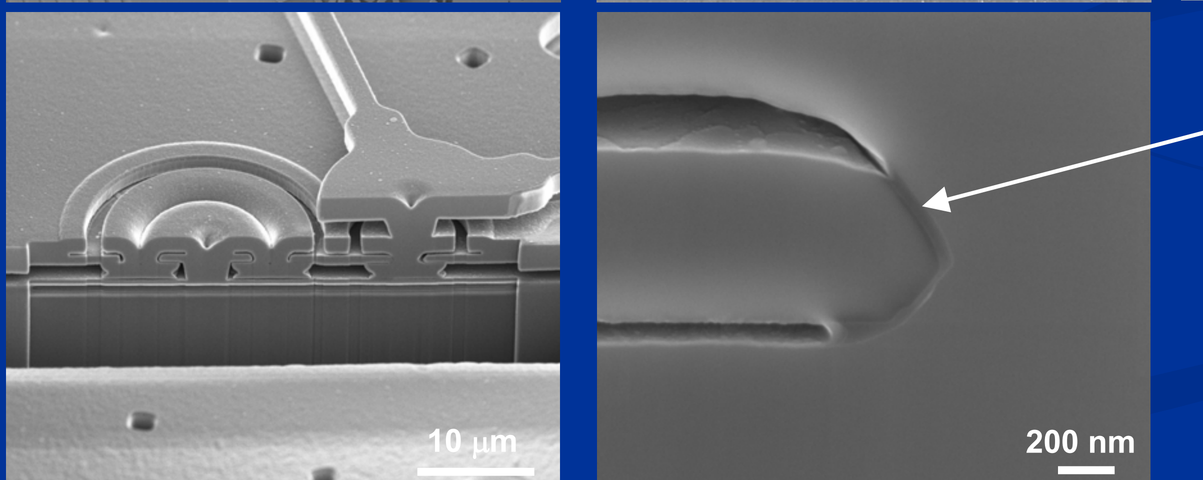


Wear test with a pin-on-disc instr.
Ball: quartz
Substrate : Si wafer covered with amorphous SiO_2
Vapor condition : n-pentanol P/P_{sat} = 50%

Tribochemical reaction product formed in MEMS gear train

After 7×10^8 cycles operation in n-pentanol vapor





These tribochemical reaction products may help preventing further wear from occuring.

If too much is formed, they may cause a power dissipation problem.

Conclusions

Alcohol (lubricant) adsorption isotherm

P/P_{sat} < 20 % → submonolayer, tilted alkyl chains

P/P_{sat} > 20% → monolayer, randomly oriented

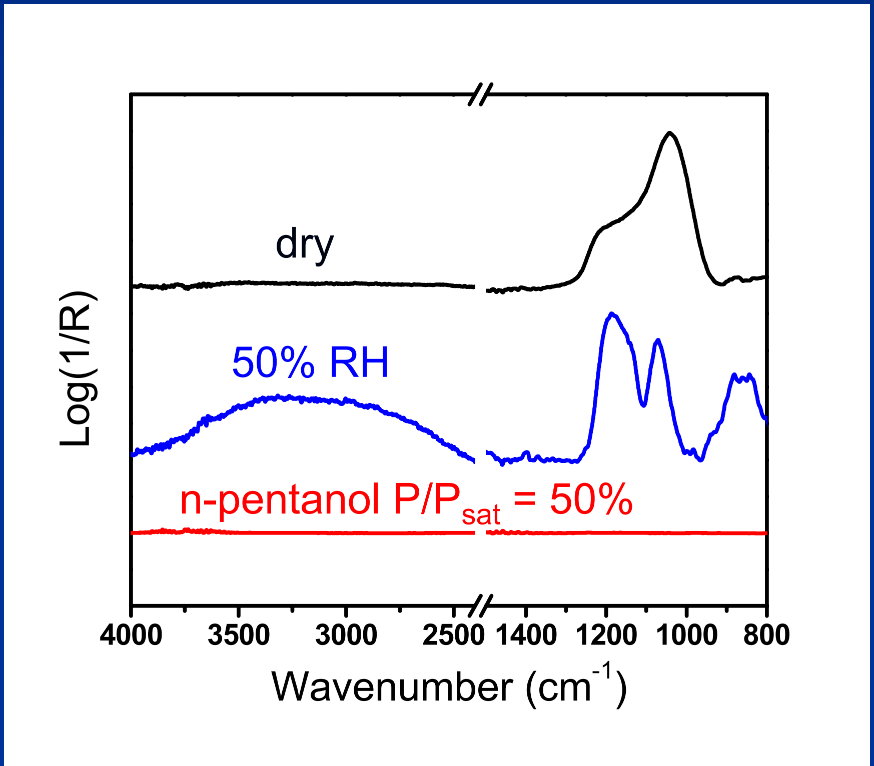
The adsorption of 1 ML of alcohols seems to be enough to lubricate SiO_2/Si surfaces at nano-, MEMS-, and macro-scales.

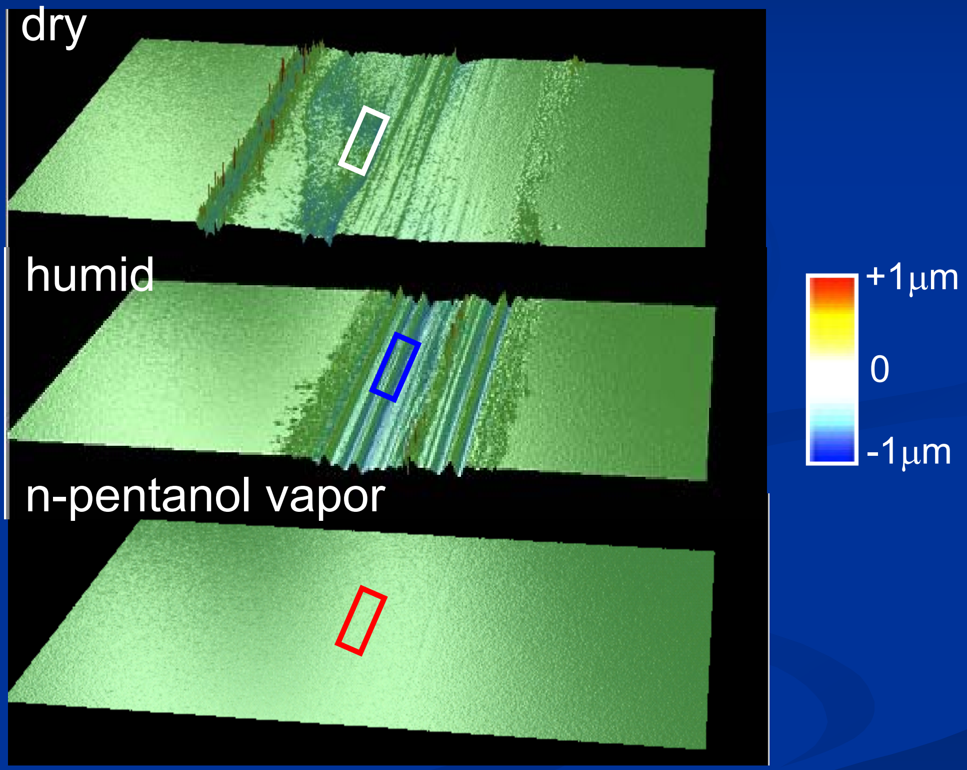
Alkoxide formation on the SiO_2 surface can increase the activation energy for the Si-O-Si bond dissociation occuring via reactions with the vapor molecule impinging from the gas phase.

If the alcohol partial pressure is not high enough or the applied load is too high, then wear of the solid surfaces and tribochemical reactions forming polymeric species take place under the alcohol vapor phase lubrication condition.

Effects of vapor adsorption on wear of SiO_2/Si

Micro-IR detection of wear debris





Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* (submitted).