SAND2007-5646C

Aging Effects on the Surface Chemistry and Resulting Performance of Microsystems

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Microreliability and Nanoreliability in Key Technology Applications

Berlin, Germany
2-5 September, 2007

Collaborators

G. Sawyer and Dan Dickrell, U. Florida

- microscale electrical contacts

S. Kim and David Asay, Pennsylvania State U.

- vapor phase lubrication

J. Krim and Adam Hook, North Carolina State U.

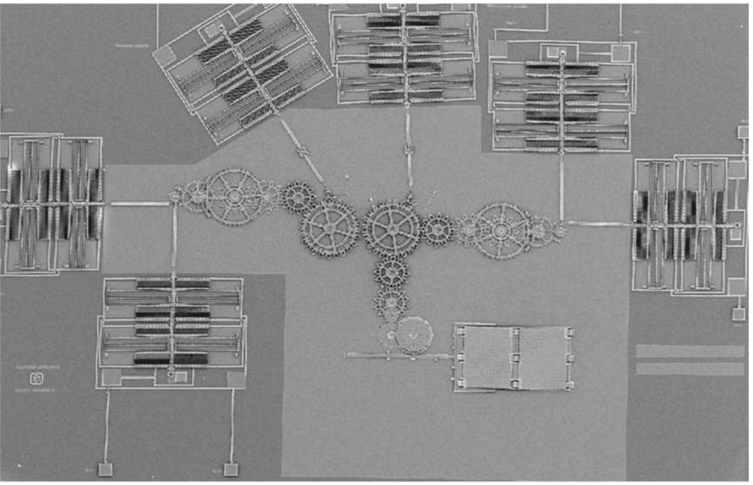
- MEMS surface treatment, tribology in extreme environments

K. Komvopoulos and Shannon Timpe, U. of California, Berkeley

- MEMS adhesion and friction

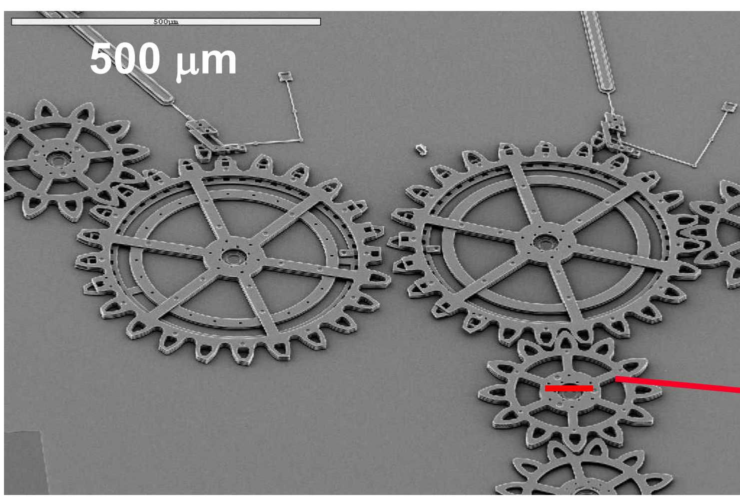
Tony Ohlhausen, Sandia National Laboratories: ToF-SIMS

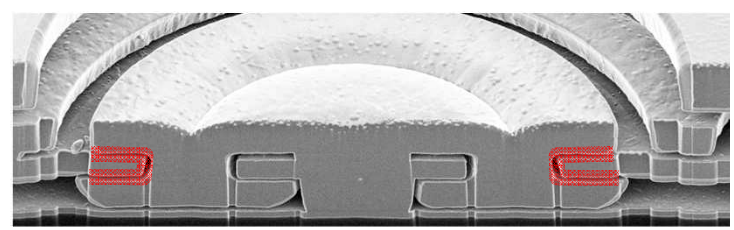
Fully-Assembled MEMS Limit Surface Treatment Options



"no assembly required"

- fabricated using deposition, pattern, and etch techniques borrowed from microelectronics
- contain on-chip actuators (electrostatic or thermal)
  - limited actuation and restoring forces
- take advantage of complexity afforded by multiple layer process
  - deeply buried sliding surfaces





What Factors Limit the Reliability of Microsystems?

process

Silicon most popular due to mature fabrication infrastructure

- **processes well known to grow, pattern, and etch**
- **can control residual stress**

Particles (more sensitive than microelectronics)

Fracture (handling or overshock)

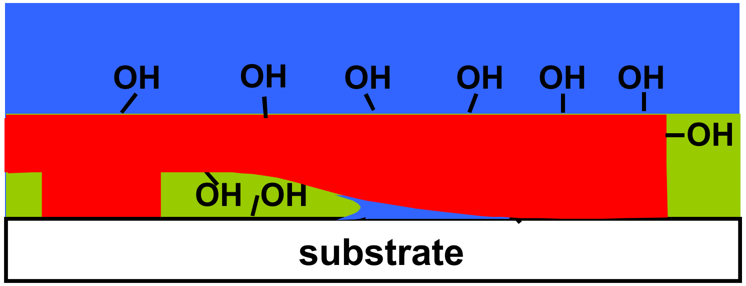
tribology

Adhere after fabrication

- **“in-process adhesion”**

Adhere during use

- **“in-use adhesion”**



initial adhesion no longer an issue with monolayer surface treatments

Friction exceeds available actuation force (monolayer wear)

Wear (solid wear and debris formation)

Aging changes surface interaction forces

SiC Has Been Explored As A Structural MEMS Material For Harsh Environments

Sensors for measurement of temperature, pressure, and combustion gases in high-temperature environments

- M. Mehregany et. al, (Case Western) Proc. IEEE vol. 86 (1998) p. 1594.
- high temperature CVD required to avoid excess Si; delaminated from SiO_2 with higher growth temperature
- etch in KOH > 600°C, or O_2/CHF_3 plasmas; selectivity compared to mask only ~5:1

Multi-User Silicon Carbide (MUSiC)

- fabricated by FLX Micro
- process for SiC device fabrication similar to MUMPS
- no longer available

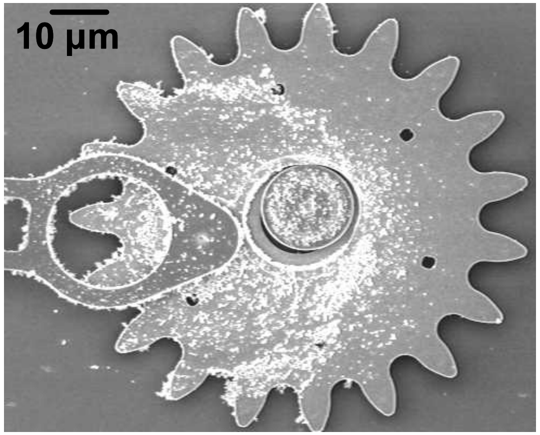
Processing challenges precluded the development of complex, multilayer devices

Wear and Aging are the Main Impediments to MEMS with Sliding Surfaces

Wear

- abrasion of oxidized silicon leads to debris generation in air
- adhesion and grain pull-out in vacuum (Patton et. al)
- *removal of surface treatment due to mechanical contact*

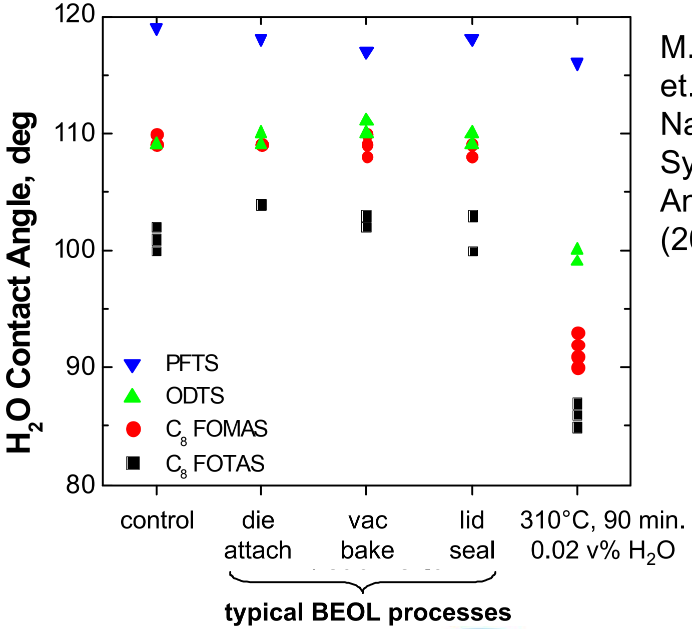
600,000 rev, 1.8% RH



D. Tanner et. al IRPS 1998

Aging

- changes in surface forces in the absence of mechanical contact
- desorption or decomposition of surface treatment
- contaminant adsorption from within package
- reaction with environmental species



M.T. Dugger et.al, ACS Nanotribology Symposium, Anaheim, CA (2004)

Numerous Monolayer Chemistries Have Been Explored for Si MEMS Surface Treatment

Film Type	Contact Angle		Work of Adhesion	Coefficient of	Particles	Ref.
	Water	Hexadecane	$\mu J/m^2$	Static Friction		
LDDMS	103°	38°	45	0.28	intermediate	[32]
VDDMS	102°	38°	62	0.35	low/none	[33]
LFDTS	111°	72°	<10	~0.10	very high	[34], [35]
VFDTS	111°	72°	3	0.12	low/none	[36]
VFOTS	≥110°	—	≤20	~0.3	low/none	[37], [38]
LOTS	110°	38°	12	0.07	very high	[32]
Oxide	~0–30°	~0–20°	~20,000	1.1	n/a	[32], [39]

W.R. Ashurst et. al, IEEE Trans Devices and Mat. Rel. vol 3 (2003) p. 173

Challenges

- **Reproducibility**
  - **reduced steps with vapor phase processing; still exhibit variability**
- **Scale Up**
  - **treat at wafer level as opposed to individual device; dice after release**
- **Wear**
  - **coatings few nm thick – easily worn off**

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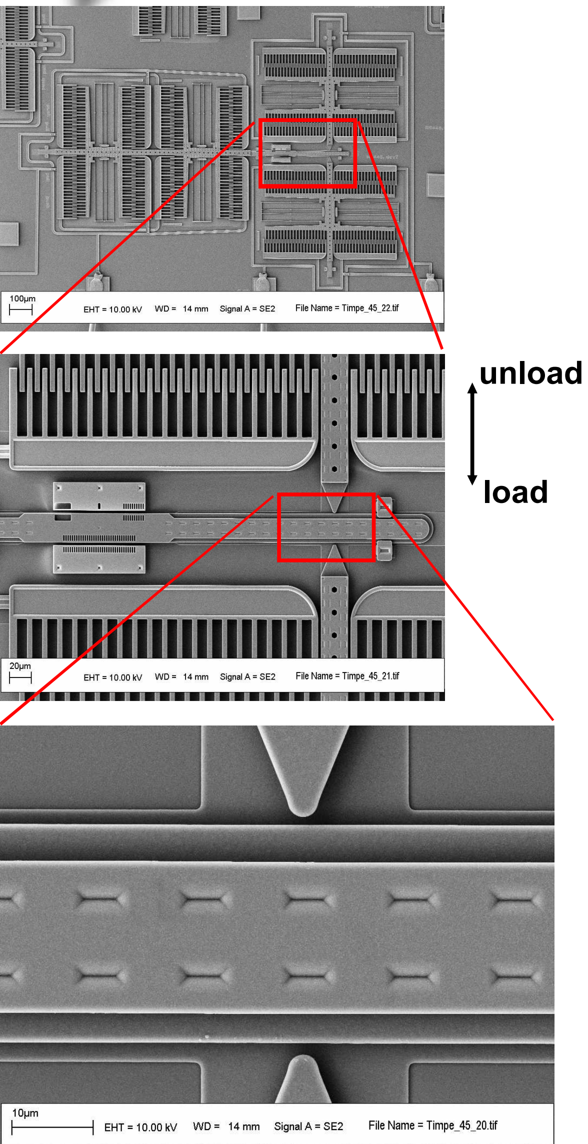
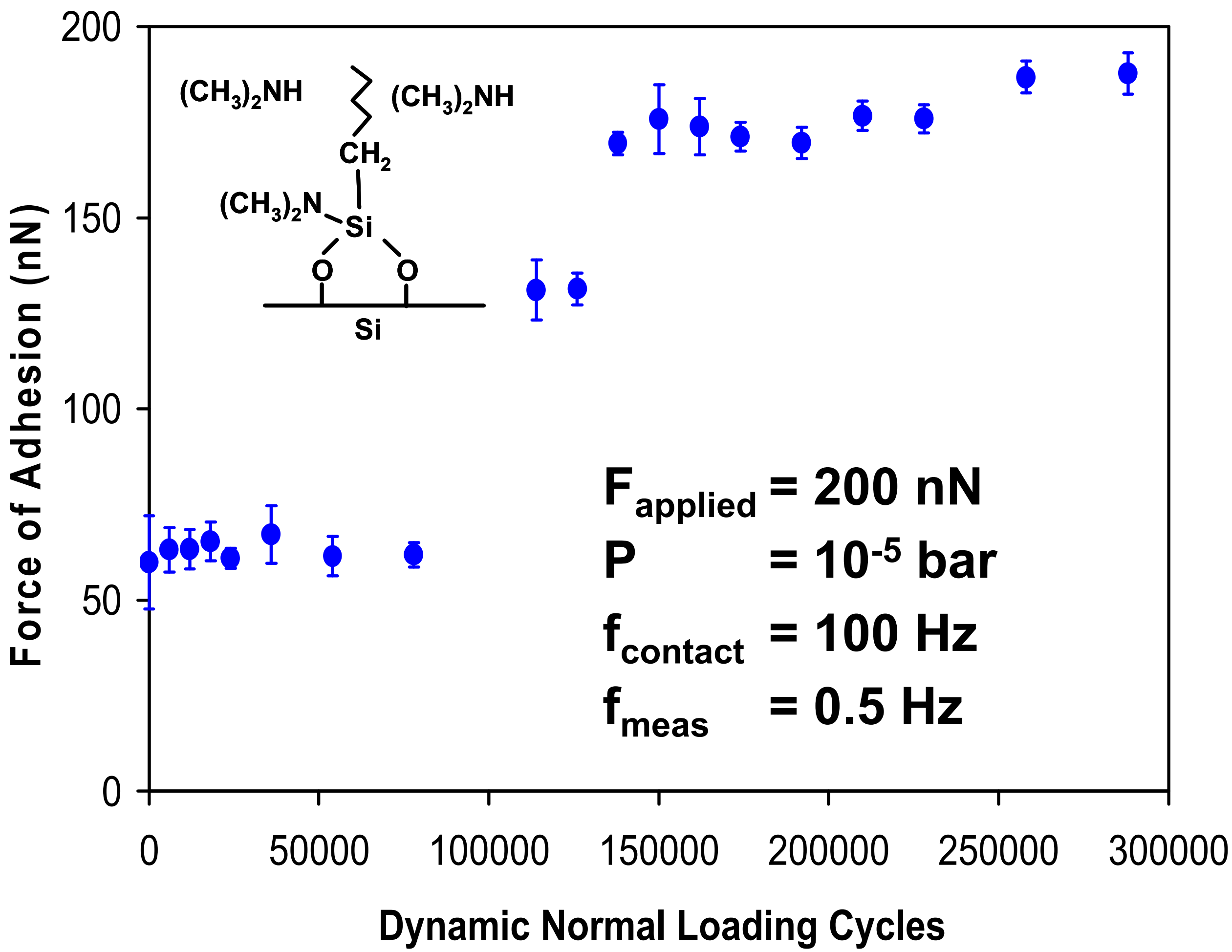
Chemisorbed monolayers do not survive repeated normal contact





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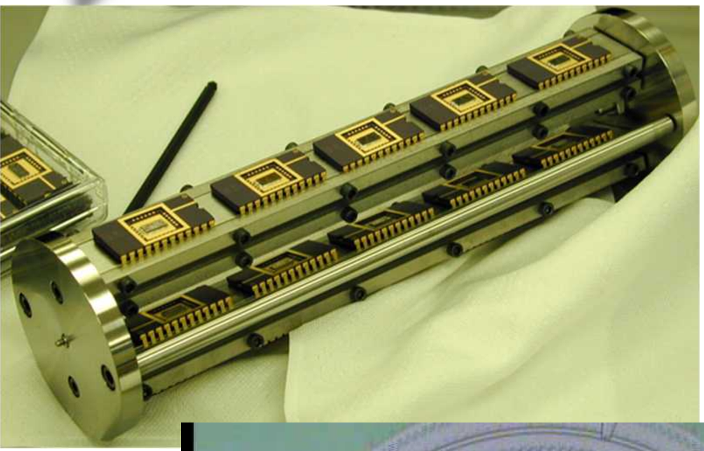
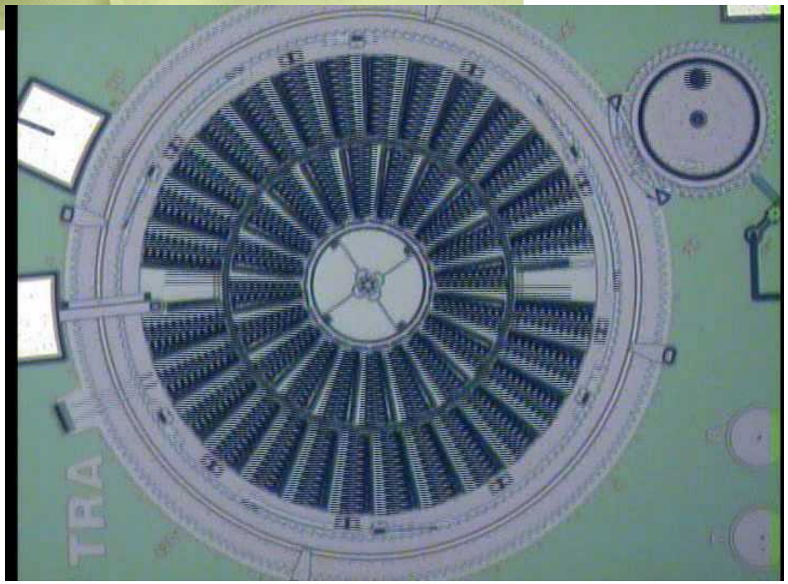
Device failure is associated with the presence of water in the exposure environment

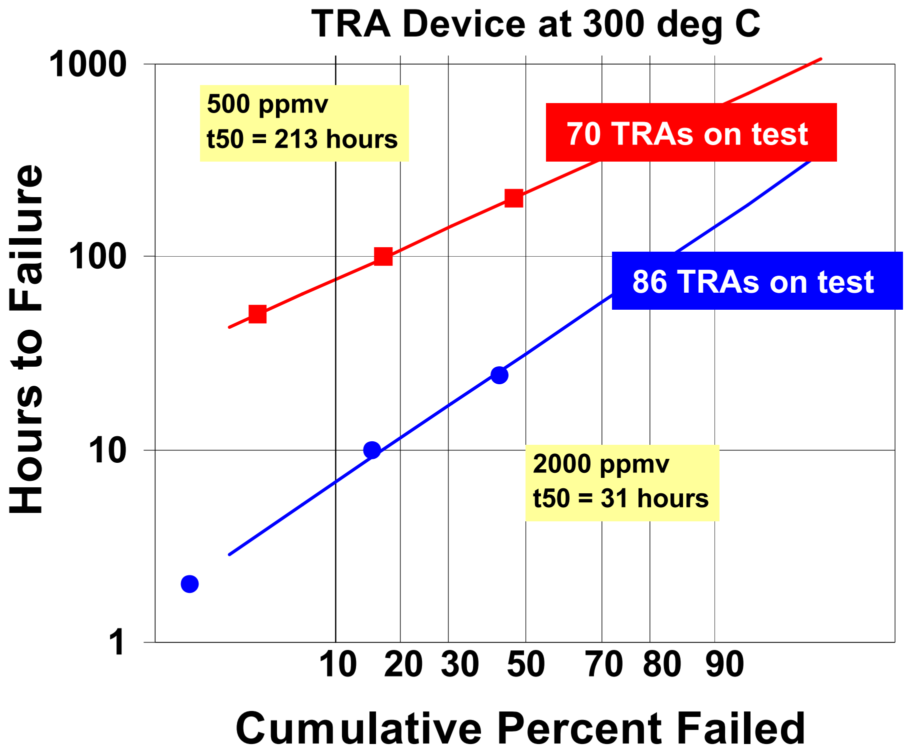


fixture for controlled environment aging of packaged MEMS



Torsional Rotary Actuator (TRA) for functional tests

Device experiments
Danelle Tanner, SNL



- MIL spec for microelectronic packaging 5000 ppm H_2O
- low levels of water may impact monolayer behavior over long term storage

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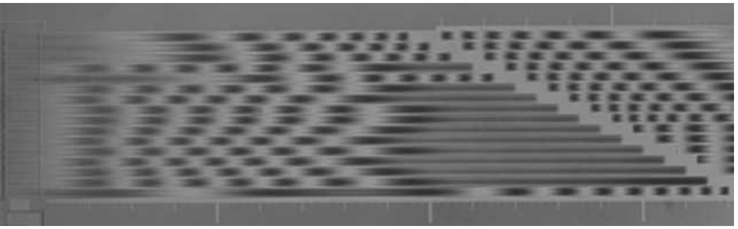
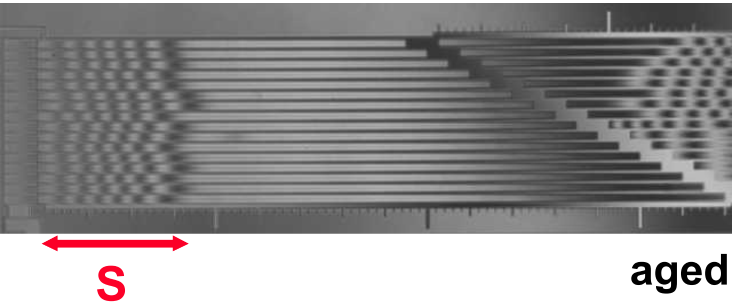
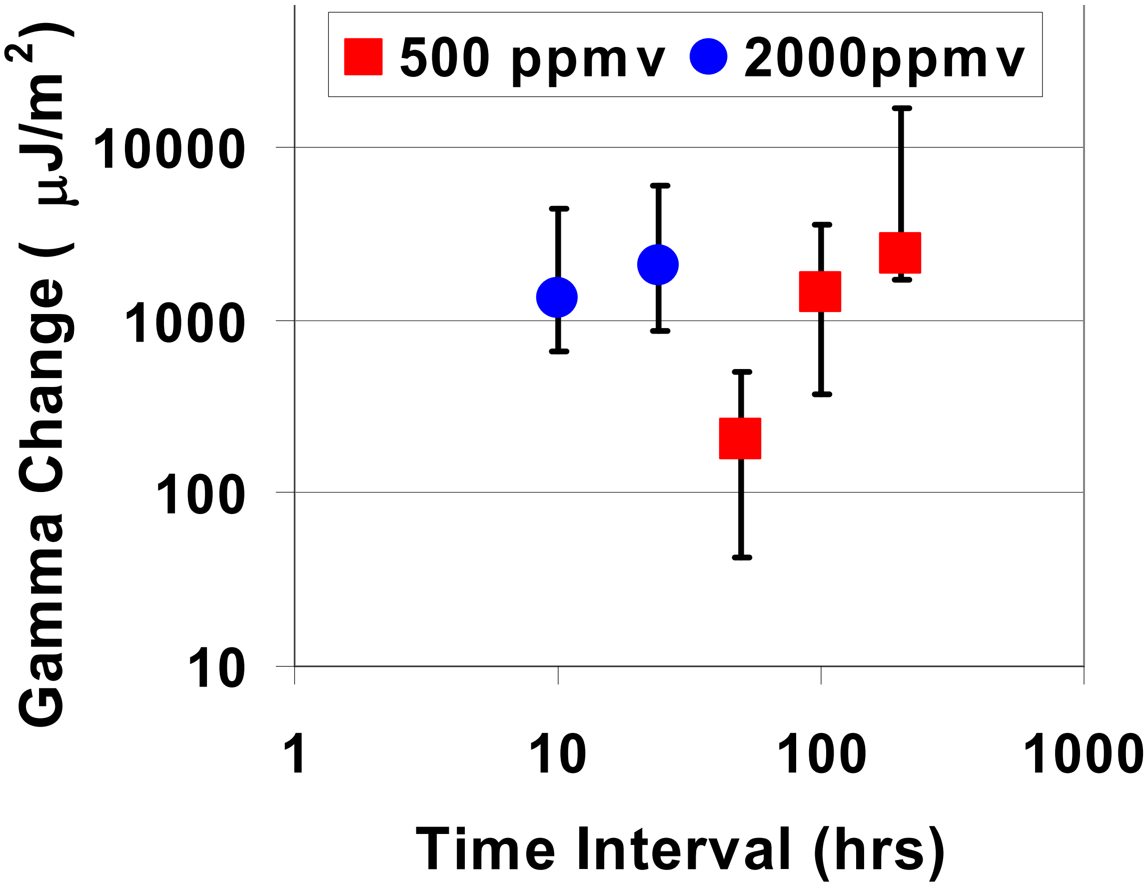
Crack length changes yield apparent surface energy changes due to environment

interferometry of cantilever beam arrays





aged at 300ºC, in N_2 + H_2O

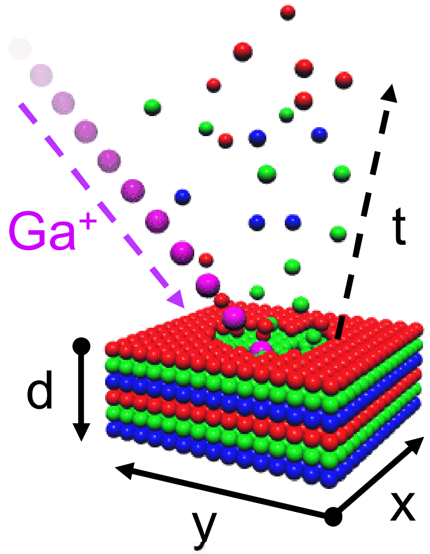


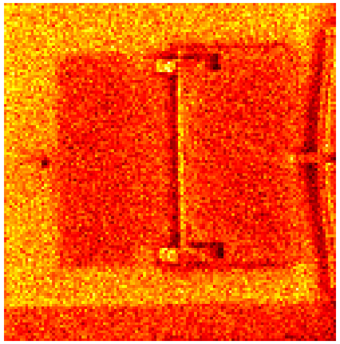
$$\Gamma = \frac{3Et^3h^2}{2s^4}$$

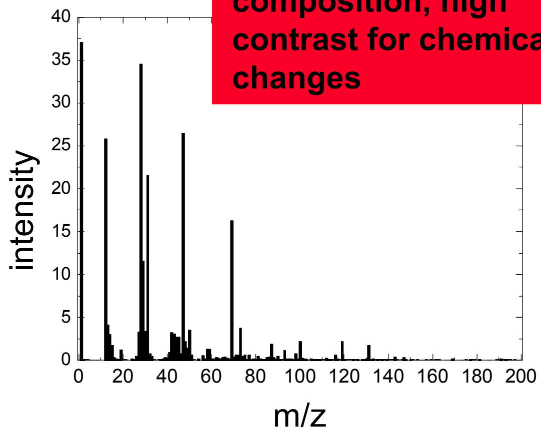
Multivariate statistical analysis of SIMS data can identify subtle changes in chemistry

Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS)

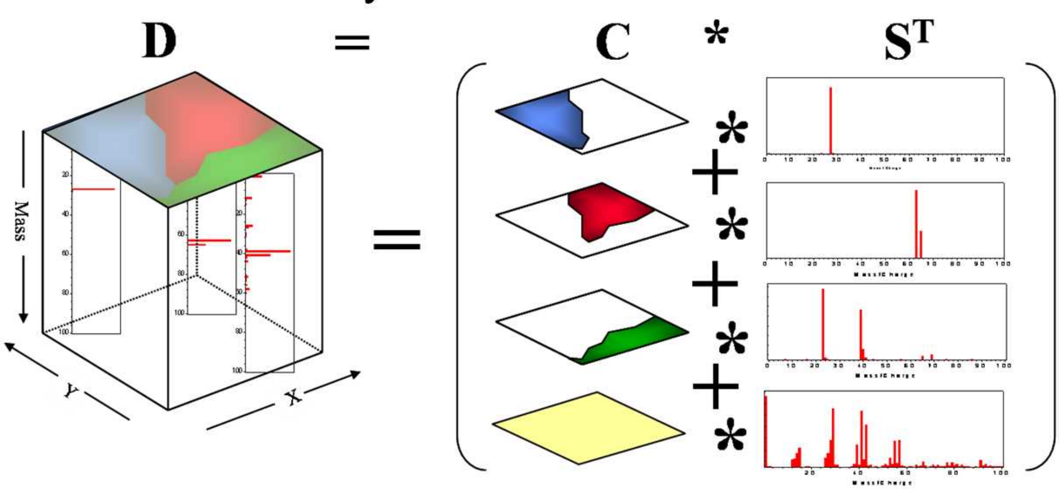
+ Automated eXpert Spectral Image Analysis (AXSIA)







Unbiased analysis of composition, high contrast for chemical changes



- **solve $D=C*S^T$ using constrained alternating least squares**
- **constrain to physically realistic solutions**
- **number of components C is the minimum needed to reconstruct the original data, minus noise**
- **no bias or assumptions; rapidly identifies subtle changes**

M. Keenan and P. Kotula, *Surf. Interface Anal.* ***36*** (2004) 2433.

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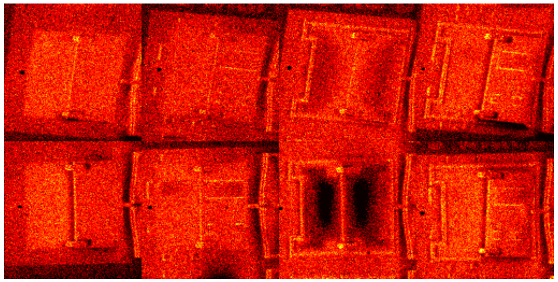
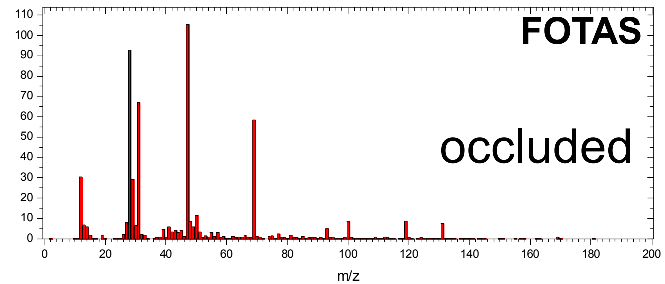
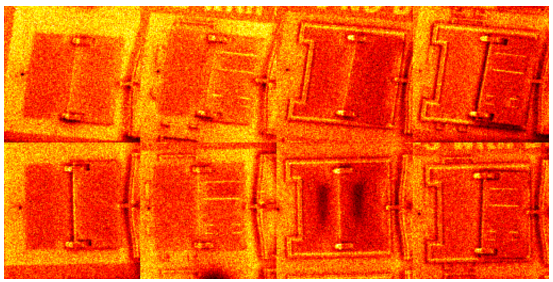
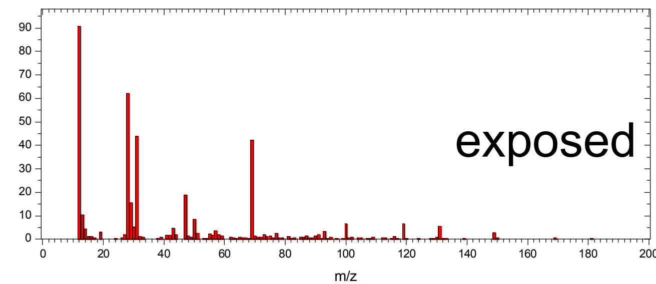
TOF-SIMS+AXIA reveals different composition on exposed vs hidden surfaces

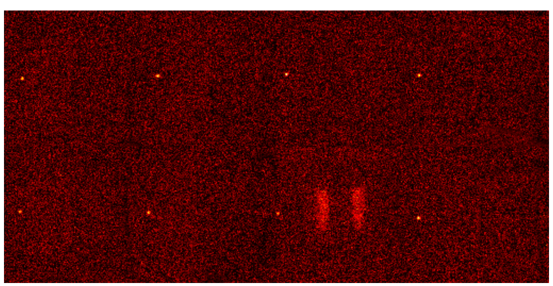


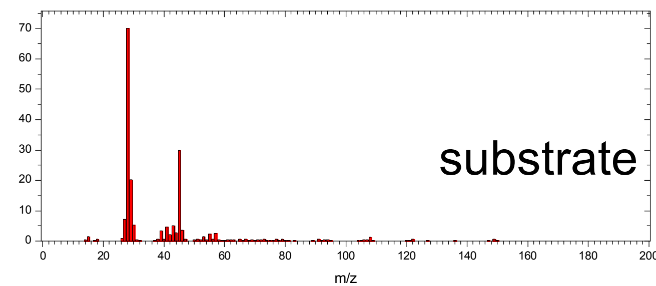


(vapor-deposited fluorocarbon monolayer)









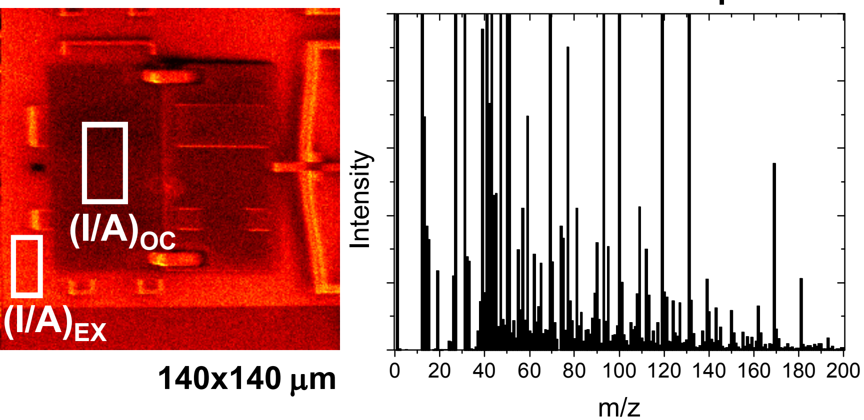
AXSIA is a very efficient data-mining tool, maximizing contrast between areas with different chemistry on the surface

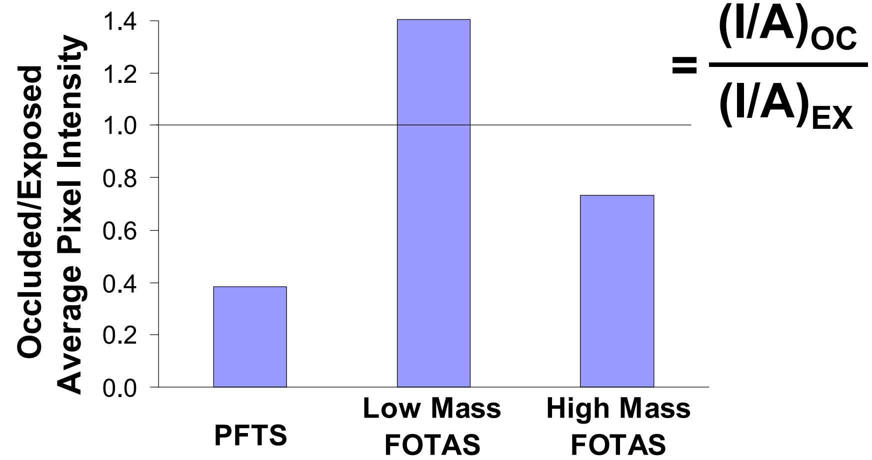
- **capability developed in-house, now applied to surface analysis**

Coverage of as-deposited PFTS and FOTAS

PFTS – liquid deposition

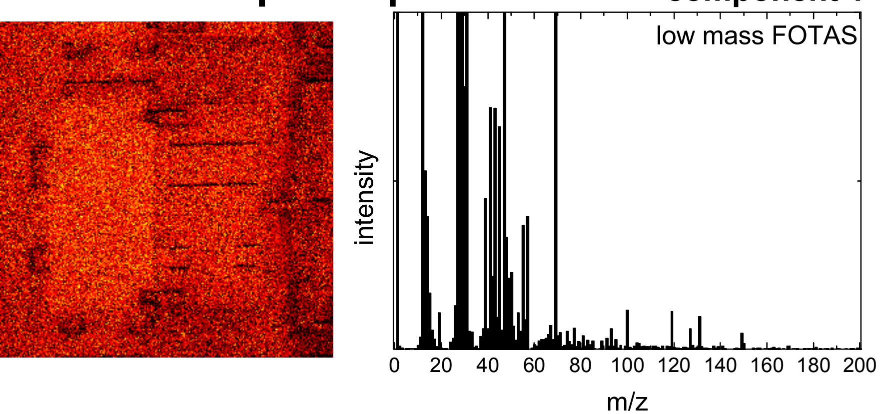
component 1



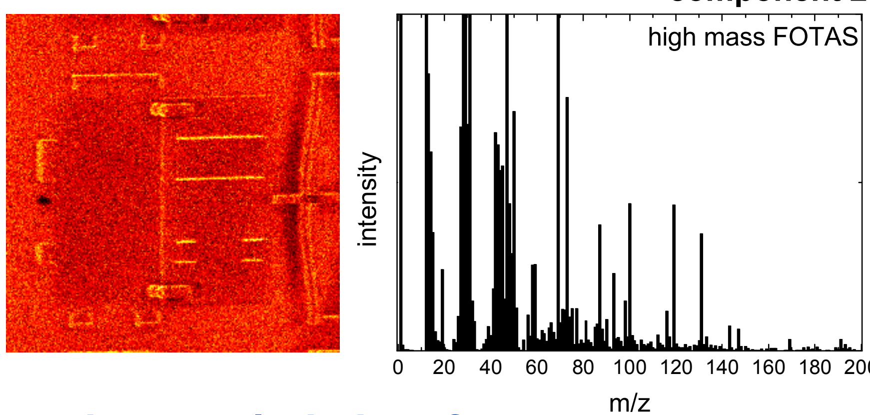


FOTAS – vapor deposition

component 1



component 2



- monolayer coverage is non-uniform on exposed vs. occluded surfaces
- vapor deposition yields improved coverage compared to liquid process
- FOTAS fragmentation varies on exposed vs occluded surfaces

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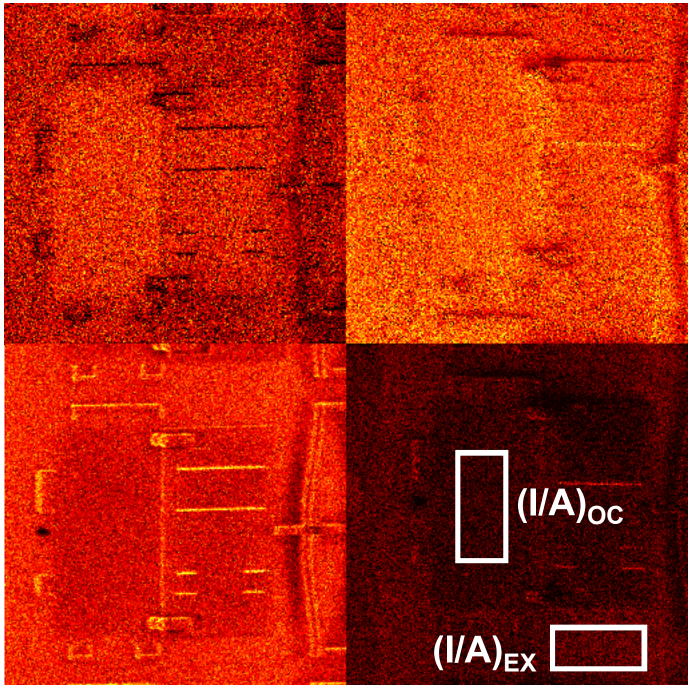
Exposure to water vapor reduces the coverage of the FOTAS monolayer

spectral data processed as a
montage of individual datasets
each image 140x140 μm

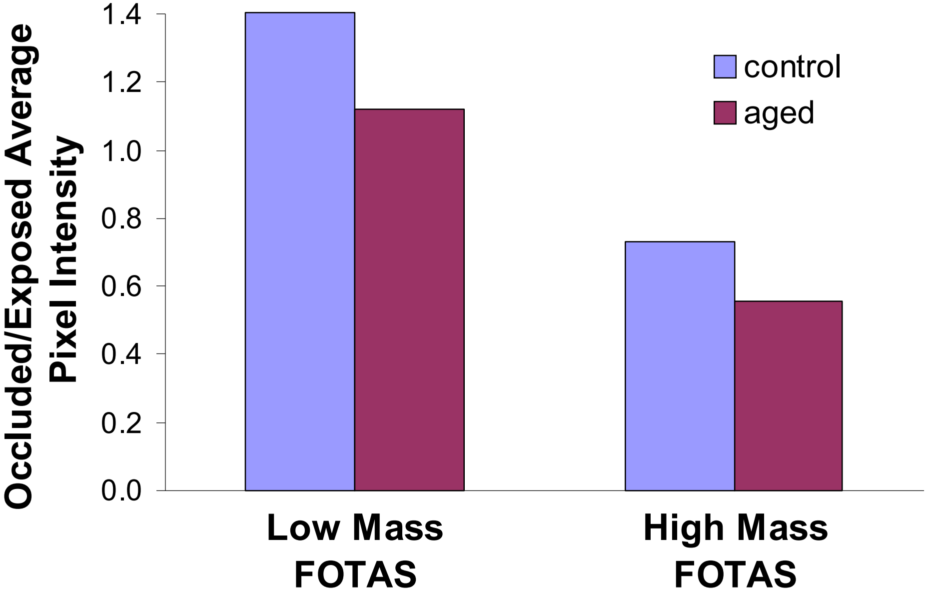
control (stored in N_2) | aged (300ºC, 2000 ppm H_2O, 16 hrs)

low mass FOTAS

high mass FOTAS

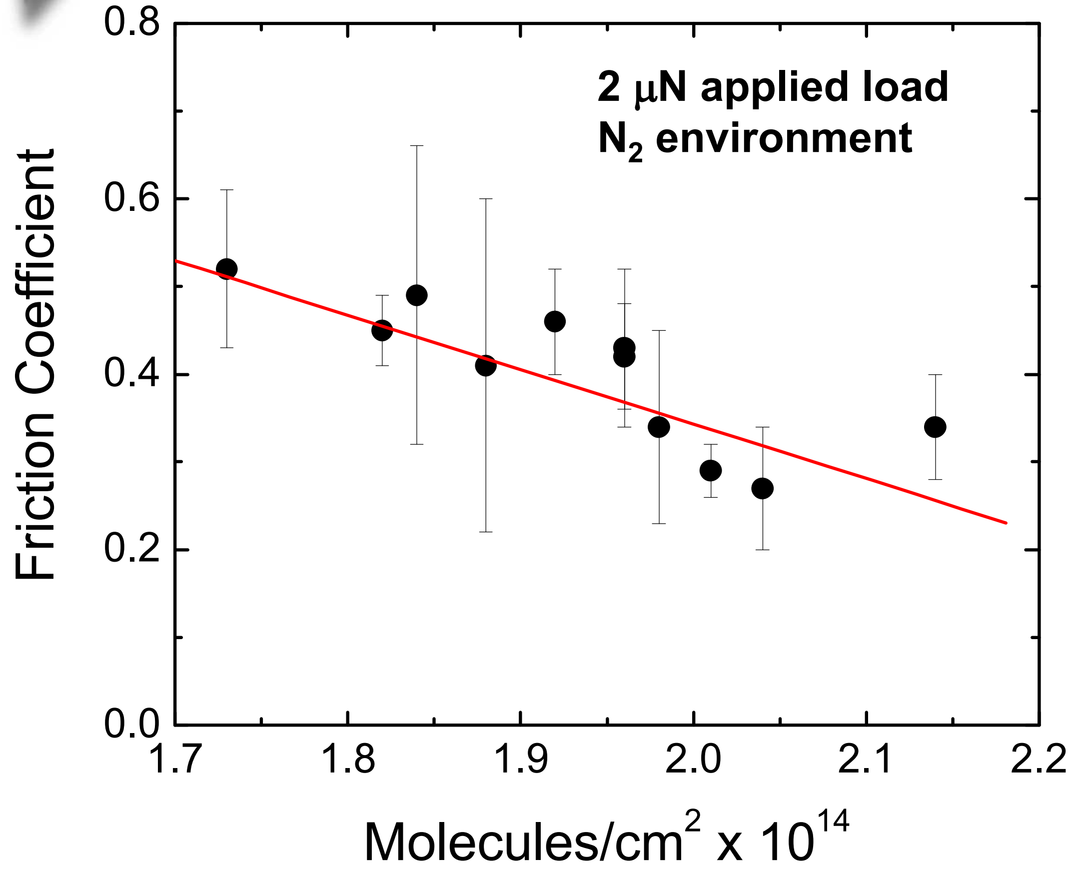


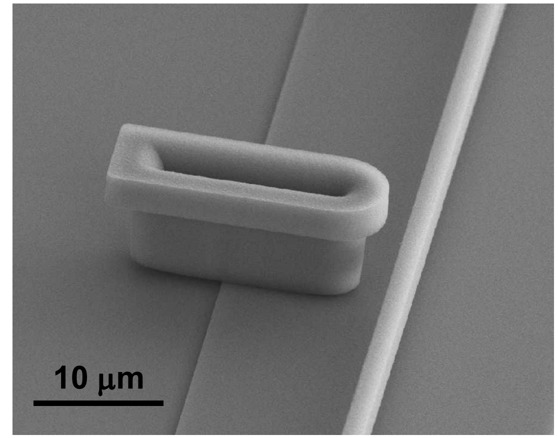
$$= \frac{(I/A)_{OC}}{(I/A)_{EX}}$$

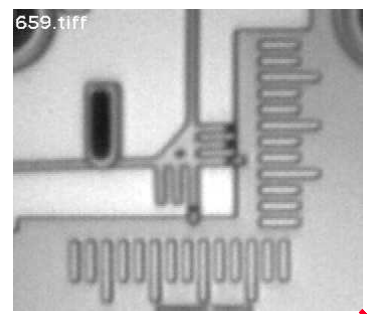


Reaction of FOTAS-coated flaps with water vapor at 300ºC reduces coverage in both exposed and occluded areas

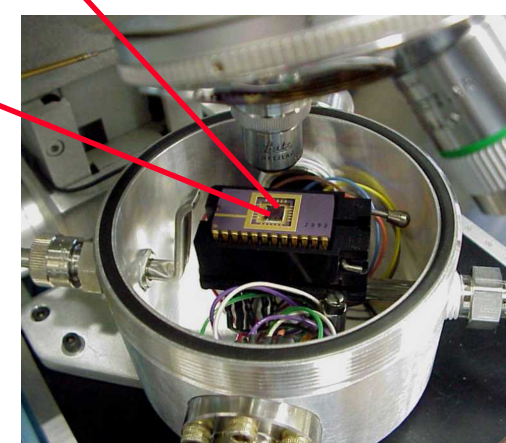
Changes in static friction are due to reduced monolayer coverage







environmental cell

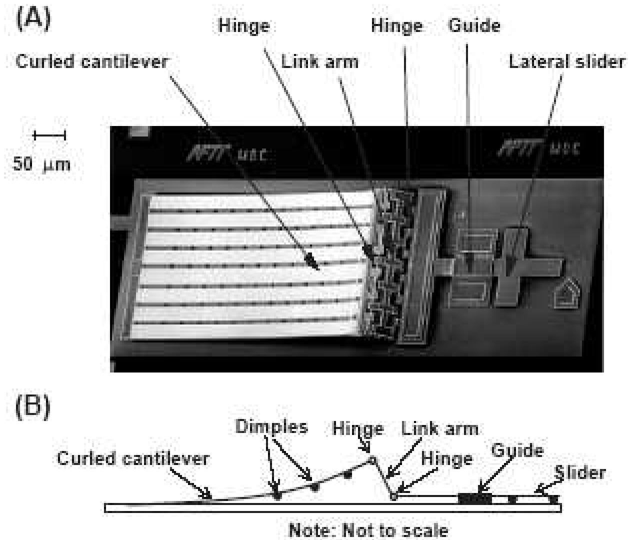


- **hydrolysis leads to loss of chemisorbed monolayer**
- **shear strength decreases as coverage increases**

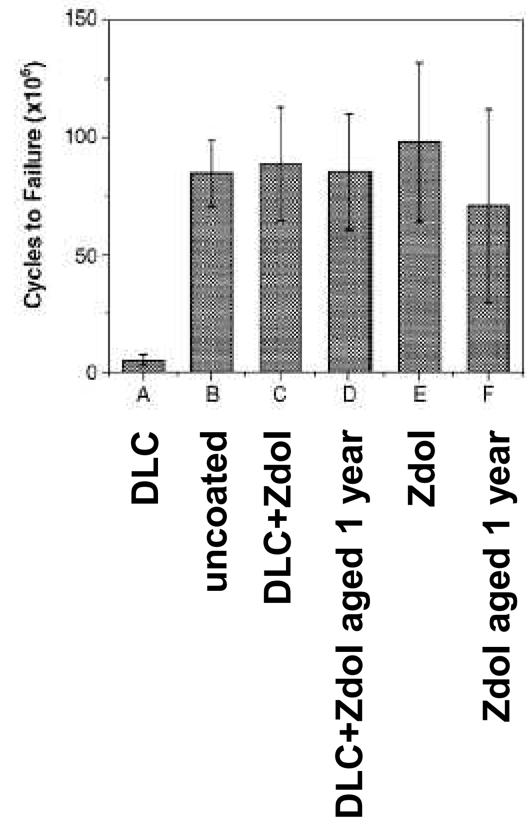
A Mobile Phase Needed to Impart a “Self Healing” Capability to Lubricant Film

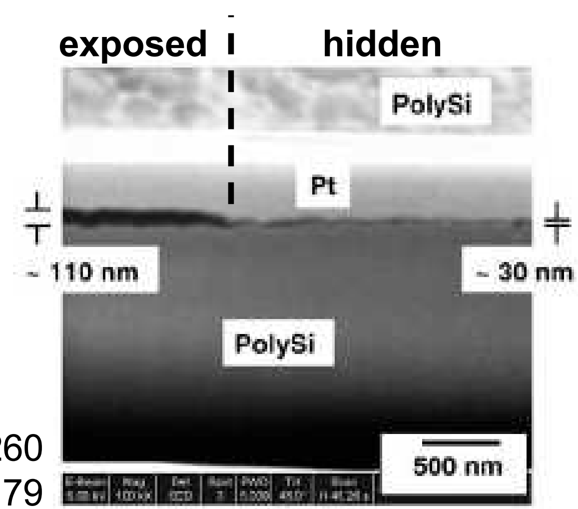
Perfluoropolyether lubricant dramatically improved the operating life of a lateral actuator

- **successful in magnetic recording tribology**
- **carbon film needed to prevent Zdol decomposition and silicon roughening**
- **carbon film present in hidden areas**



Eapen et. al Surf. and Coating Tech. 197 (2005) p. 270





Smallwood et. al Wear 260 (2006) p. 1179

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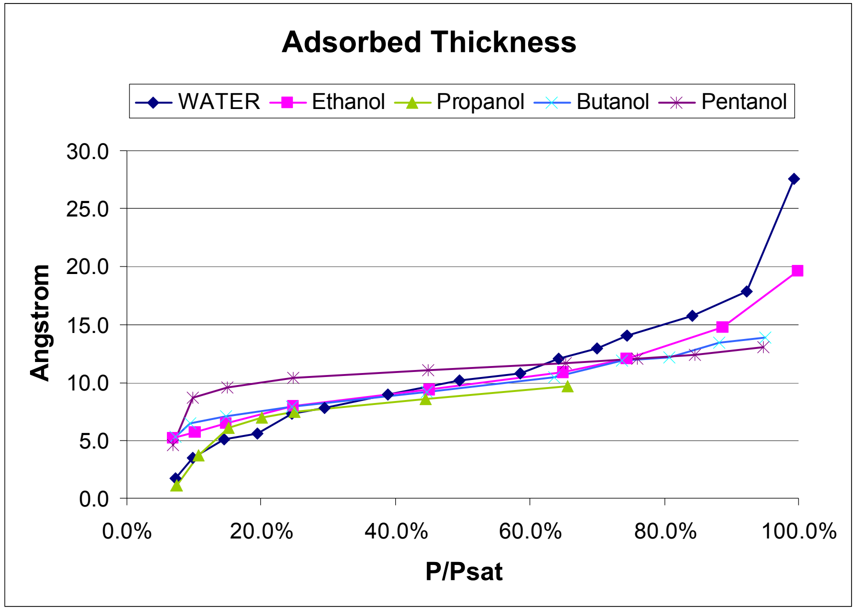
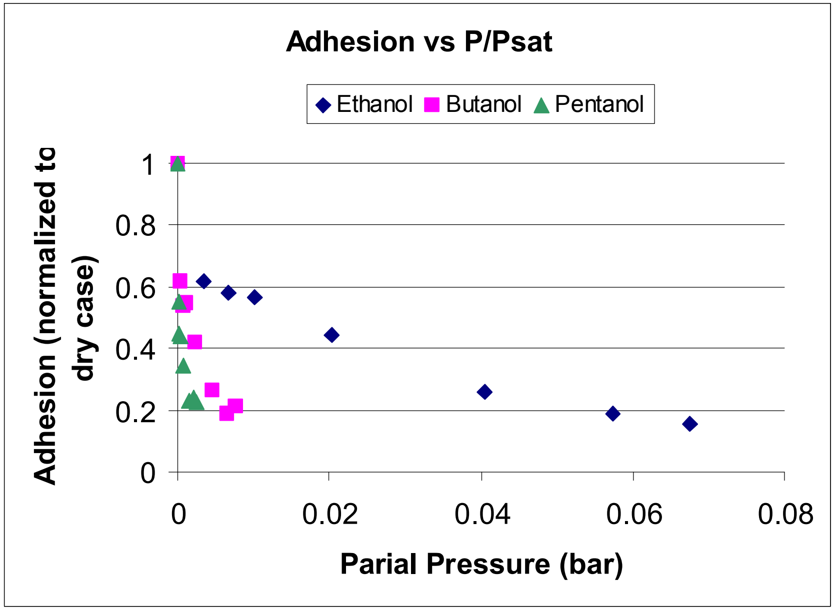
Alcohols Explored for Reducing Adhesion Between Silicon Surfaces

K. Strawhecker, D.B. Asay, J. McKinney and S.H. Kim, Trib. Lett. **19** (2005) 17-21.





ATR-FTIR measurement of adsorbed film thickness

- 1-3 monolayers at $0.1 < P/P_{sat} < 0.9$

AFM measurement of adhesion

- very low concentrations of alcohol in the environment significantly reduce adhesion

Alcohol dissolves surface contaminants and water, creating a lower surface tension film

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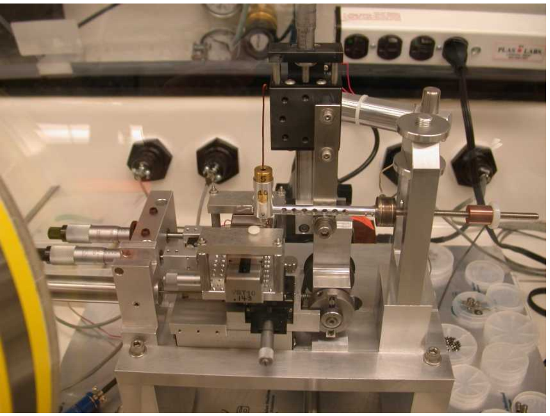
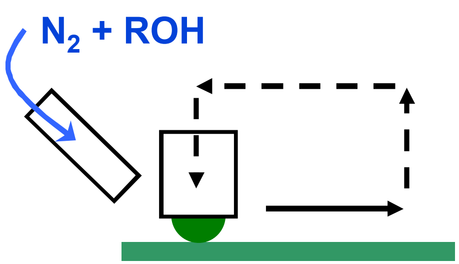
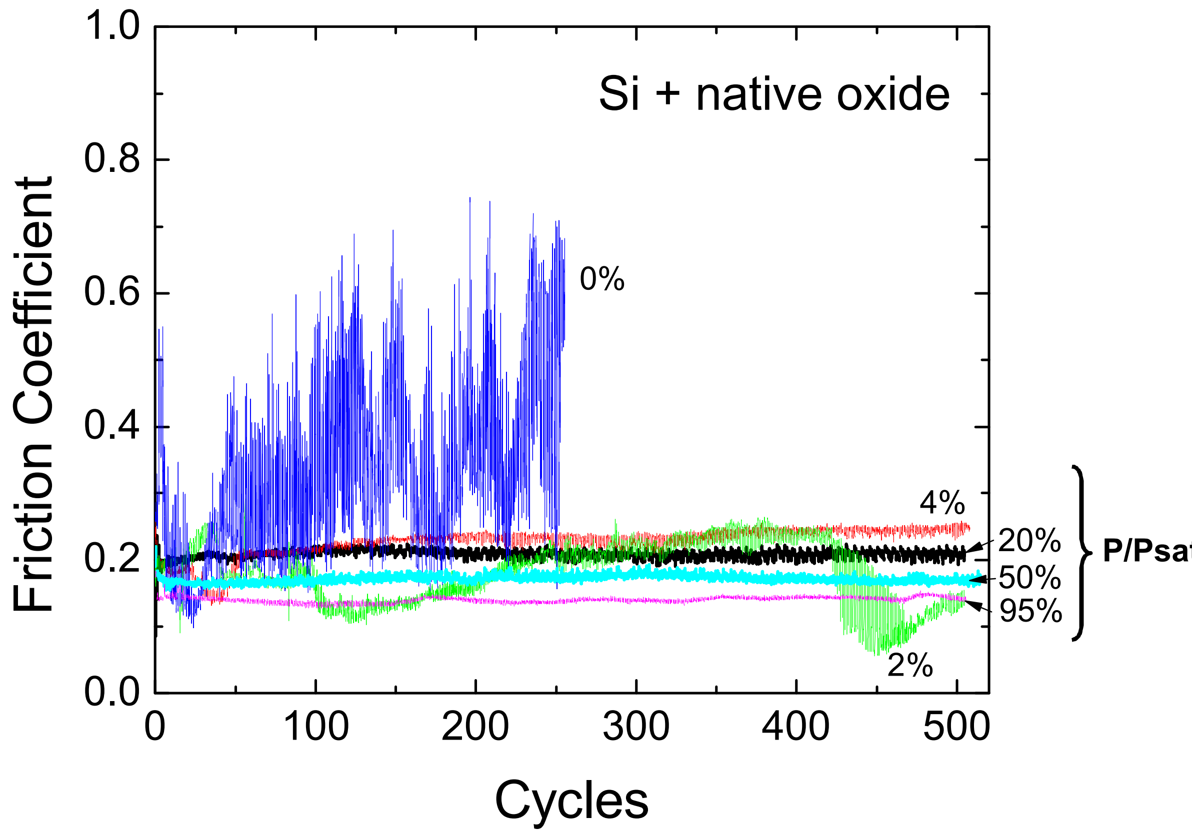
Vapor Phase Lubrication of Silicon Reduces Friction in Macroscale Sliding





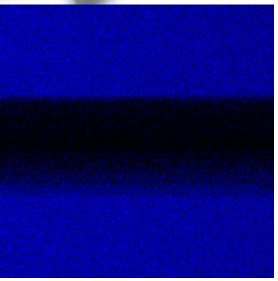


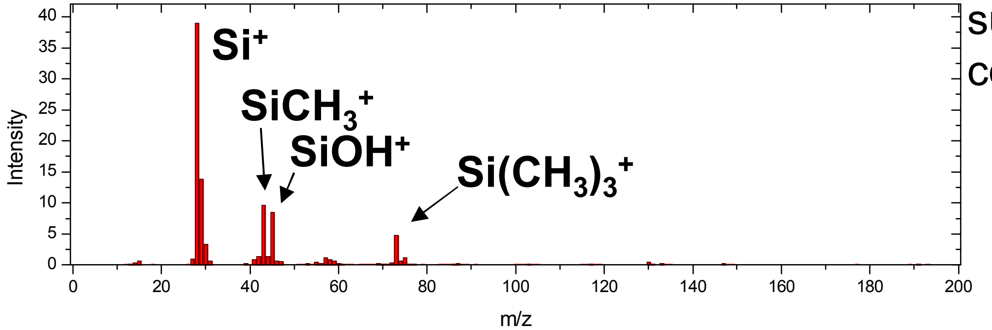
SiO_2 ball on Si + native oxide + FOTAS monolayer

98 mN applied load, 1.5 mm track length, 1 mm/s

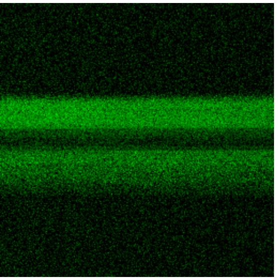
N_2 + ROH (pentanol, Psat = 2200 ppmv at 22ºC)

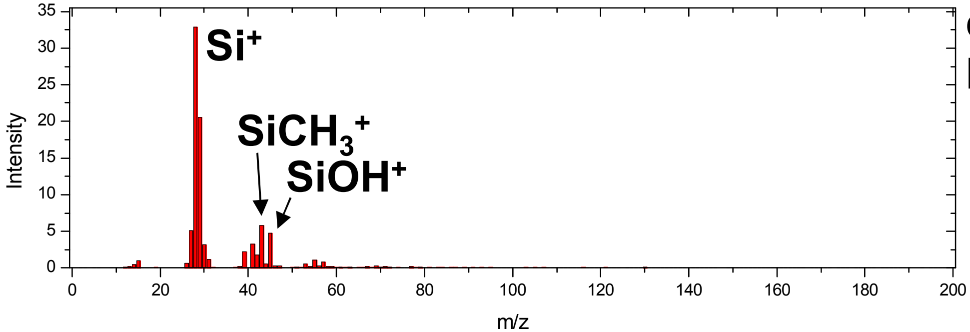
ToF-SIMS With Multivariate Analysis Shows Formation of High MW Product



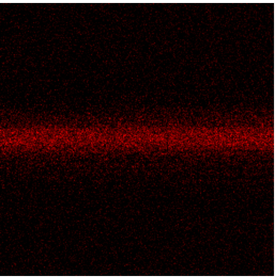


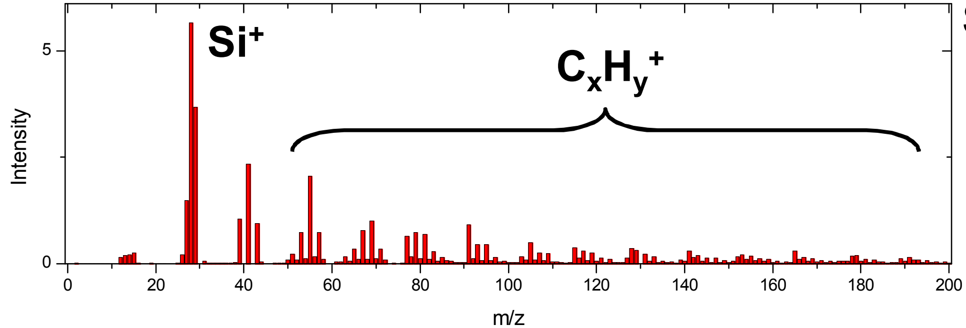
surface oxides and contaminants (silicones)





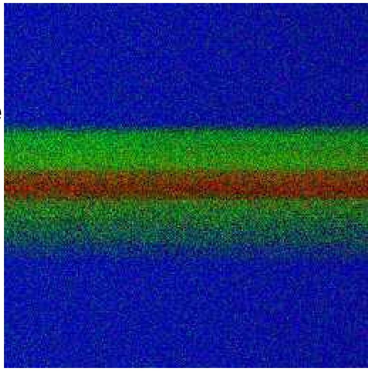
oxidized Si + short chain hydrocarbons





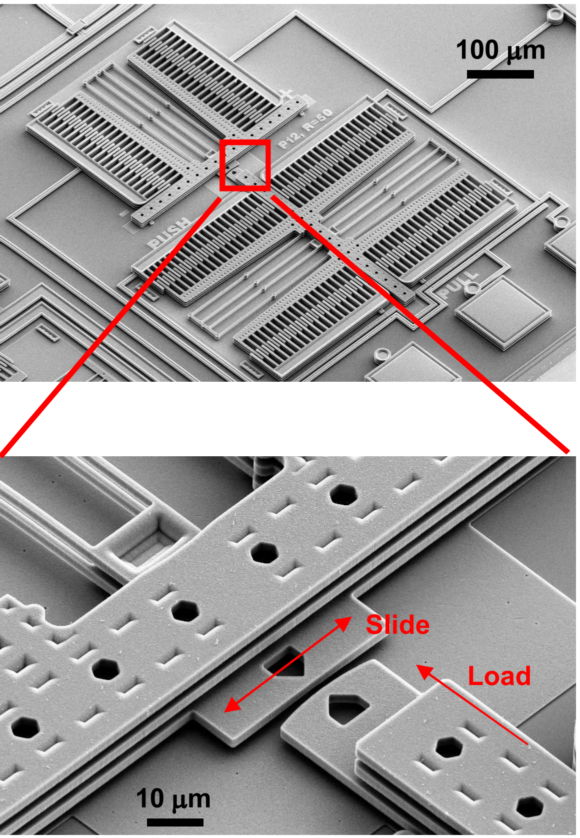
Si + long chain hydrocarbons

composite image



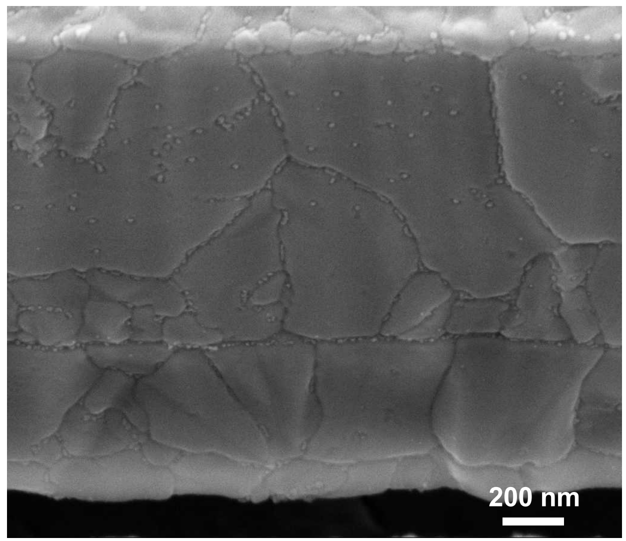
Reaction product forms *when, and where,* it is needed

Wear is Minimized with In Situ Vapor Phase Lubrication

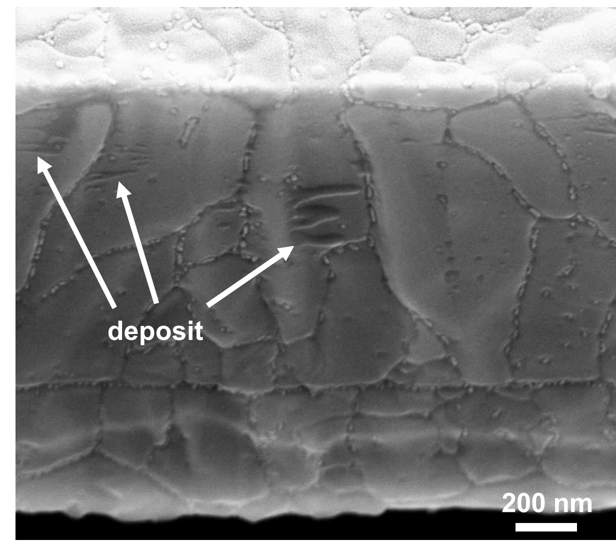


100 Hz
500 nN normal load
N_2 + pentanol, P/Psat = 0.2

Not Tested



after 10^8 cycles



Deposit collected adjacent to asperity locations (real contact) on sidewall of MEMS tribometer

Vapor Phase Lubrication of Silicon by Tribochemical Reactions

S.M. Wiederhorn and D.E. Roberts, *Wear* **32** (1975) 51-72

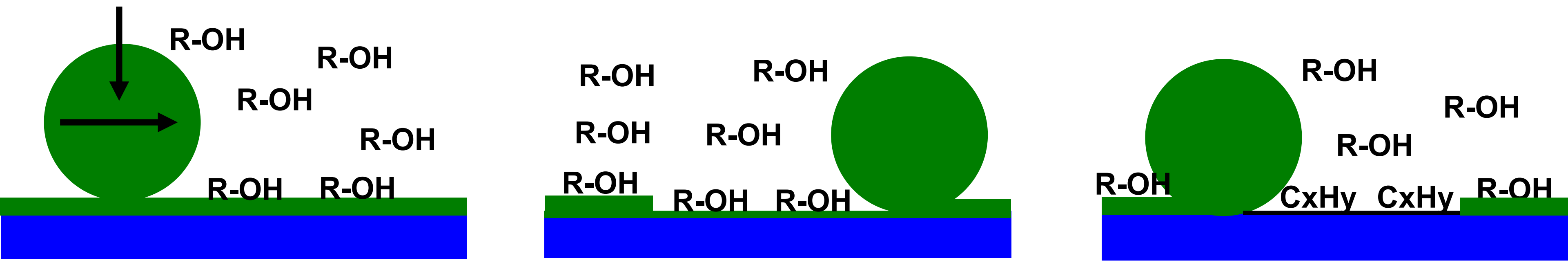
- reduced friction when abrading silicate glass in alcohols

Y. Hibi and Y. Enomoto, *Wear* **231** (1999) 185-194

- alcohols reduce friction when cutting Si_3N_4
- very low wear rate in “higher” alcohols (4<n<11)
- postulate silicon alkoxide and hydrocarbon formation

Y. Hibi, Y. Enomoto and A. Tanaka, *J. Mat. Sci. Lett.* **19** (2000) 1809-1812

- postulate metal alkoxides condense to polymer and act as lubricant



Oxidized surface adsorbs 1-3 monolayers of alcohol

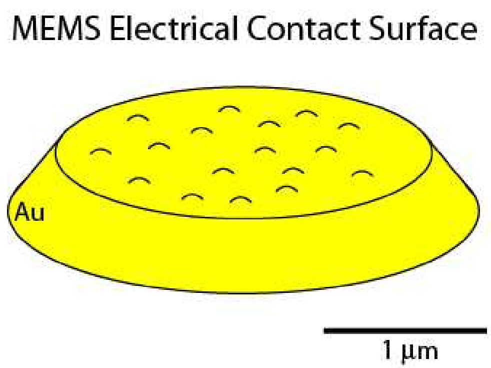
oxide wears, alcohol re-adsorbs

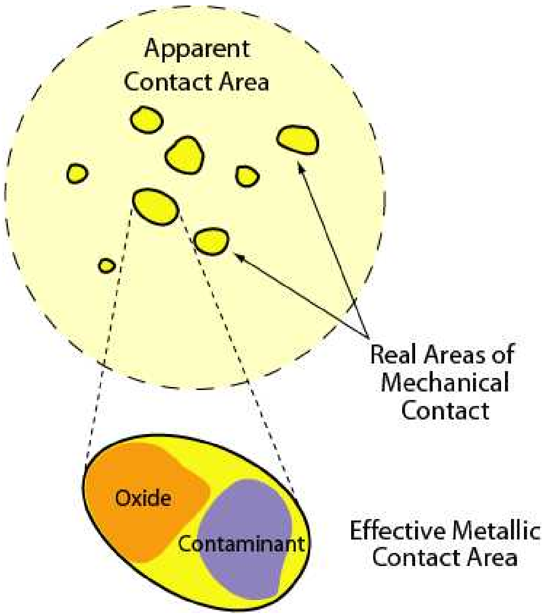
when Si exposed, adsorbed species react to form high MW product

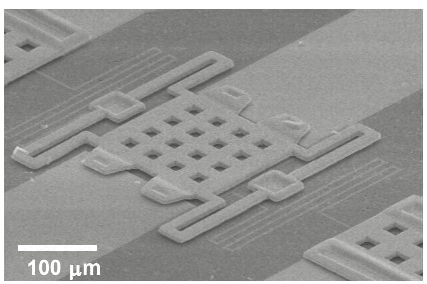
Thermionic emission?

Dangling bonds?

Dynamic Electrical Contacts

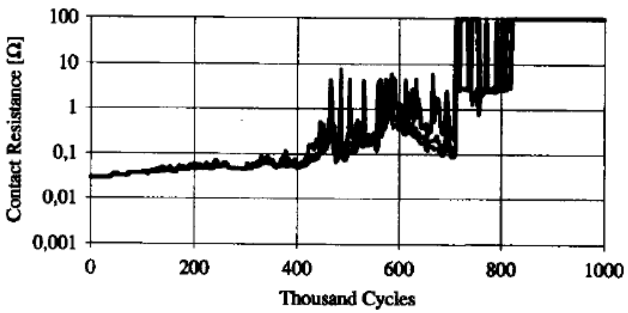






Degradation mechanisms:

- **thermal**
  - **melting**
  - **arcing**
- **physical damage**
  - **adhesion**
  - **delamination**
- **contamination**
  - **oxidation**
  - **segregation**

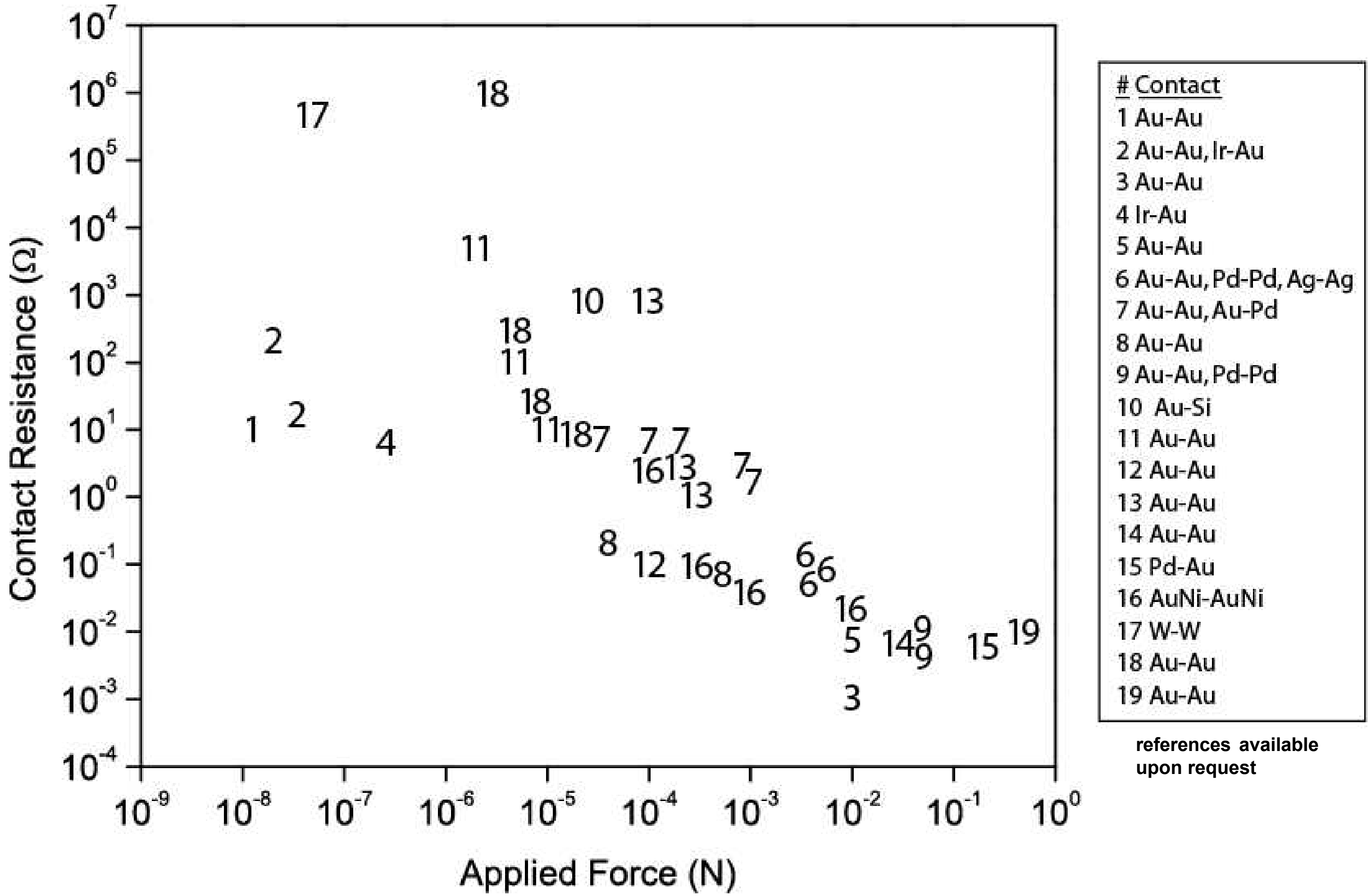


Example: Contact Degradation due to Corrosion [Neufeld and Rieder 1995]

Real contact spots in MEMS can be few in number (<50) and small in size (~100 nm diameter)

MEMS contacts more susceptible to cyclical degradation than macro-scale switches

Electrical Contact Resistance

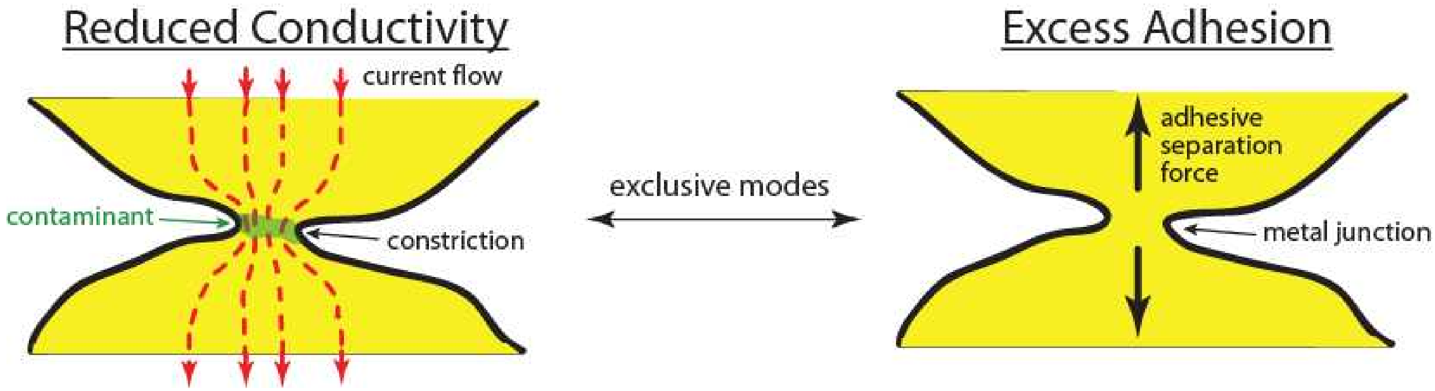


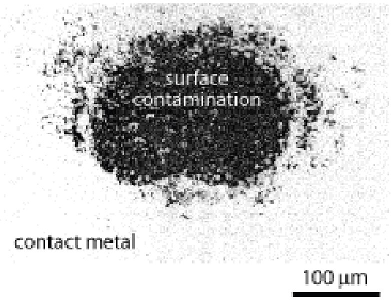
references available upon request

Resistance increases with decreasing contact force

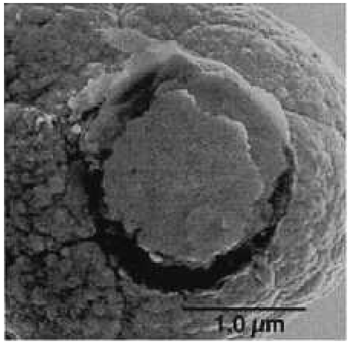
MEMS contact forces ~ 10 – 100 μN

Degradation Mechanisms





Tamai, T., 1995, "Effect of Silicone Vapour and Humidity on Contact Reliability of Micro Relay Contacts," IEEE Transactions on Components, Packaging, and Manufacturing Technology – Part A, 19(3), pp. 329-338.



Hyman, D., and Mehregany, M., 1999, "Contact Physics of Gold Microcontacts for MEMS Switches," IEEE Transactions on Components and Packaging Technology, 22(3), pp. 357-364.

Proper operation of MEMS electrical contacts depends on the balance between

conductivity and separability

of the surfaces

D. Dickrell, U. Florida

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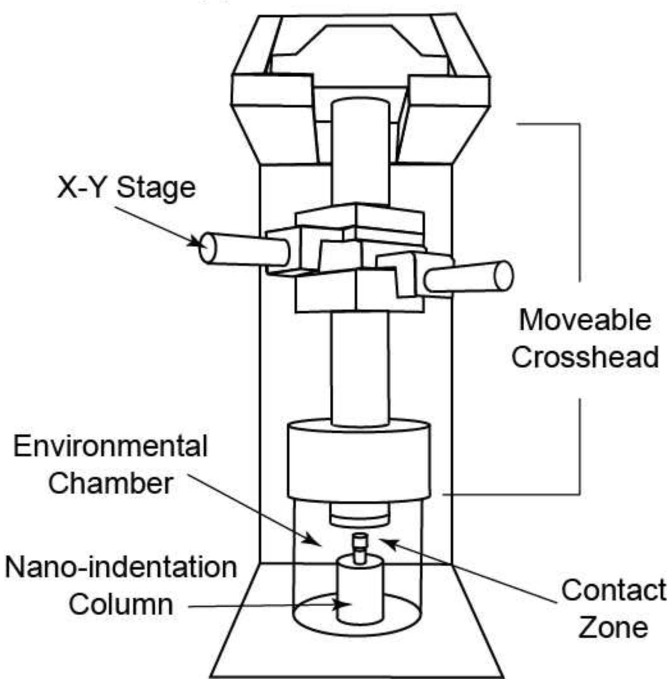
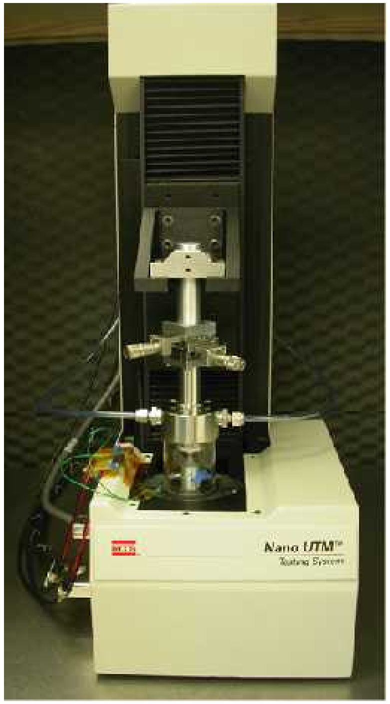
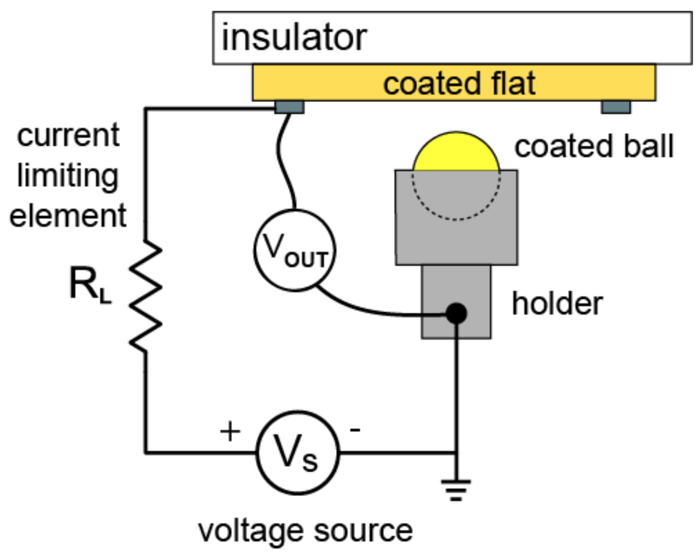
Experimental Set-up

Apparatus Schematic





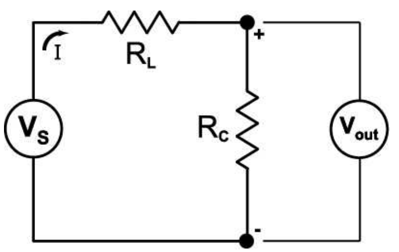
Contact Zone Schematic



MTS Nano-UTM System

Force, displacement, and resistance simultaneously recorded during each contact cycle

F_n = 150 μN
V_s = 3.3 V
R_L = 1.1 kΩ
I = 3 mA



$$R_C = \frac{R_L}{\frac{V_S}{V_{out}} - 1}$$

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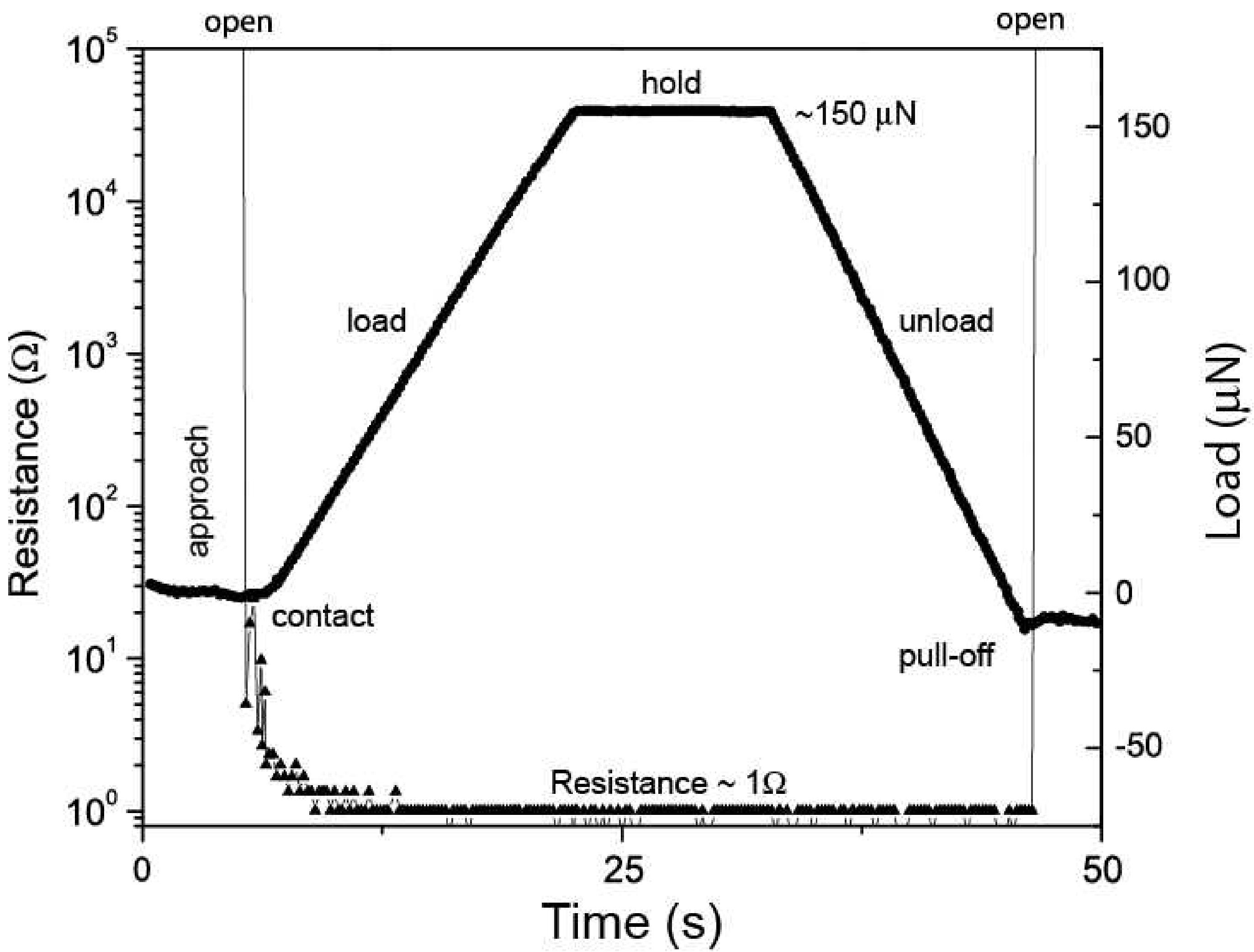
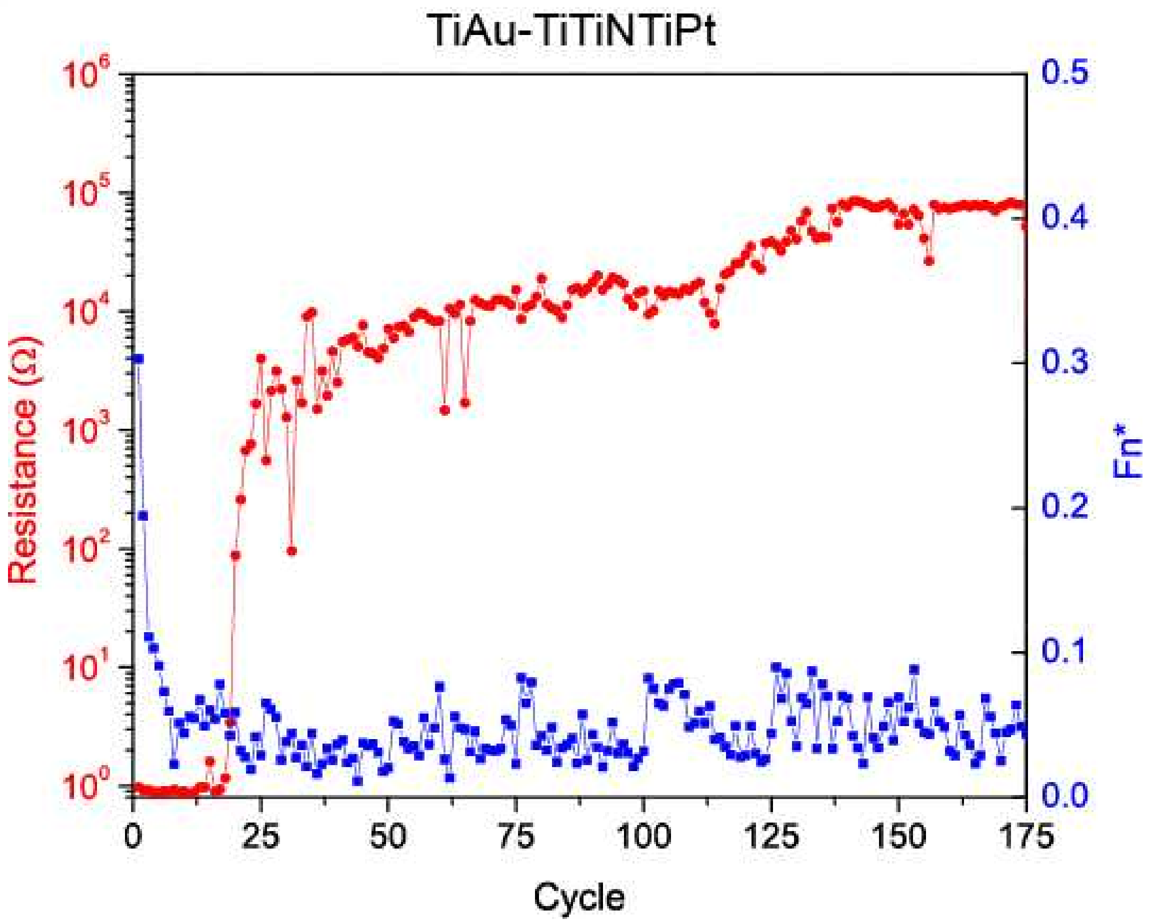
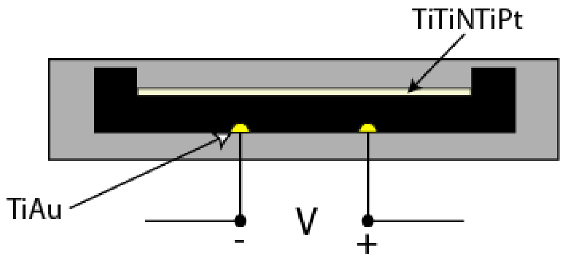
Contact Cycle Example



Cyclic Degradation of Electrical Contact Resistance





Resistance degrades to levels far above initial values in relatively few (<75) repeated contact cycles

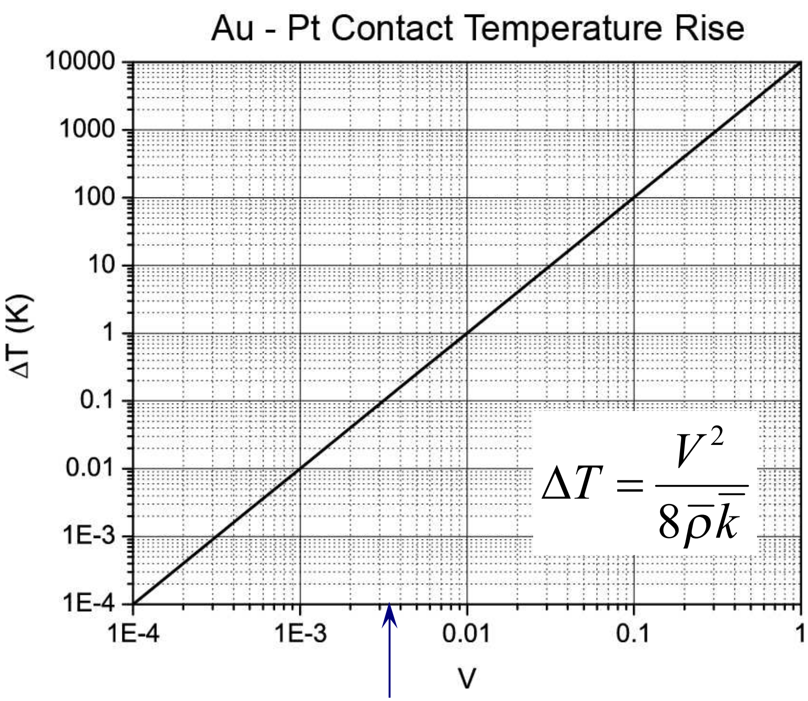
What is the mechanism causing this sudden increase in resistance?

$$F_n^* = \frac{F_{pull-off}}{F_n}$$

Air
F_n = 150 μN
V_s = 3.3 V
I = 3 mA

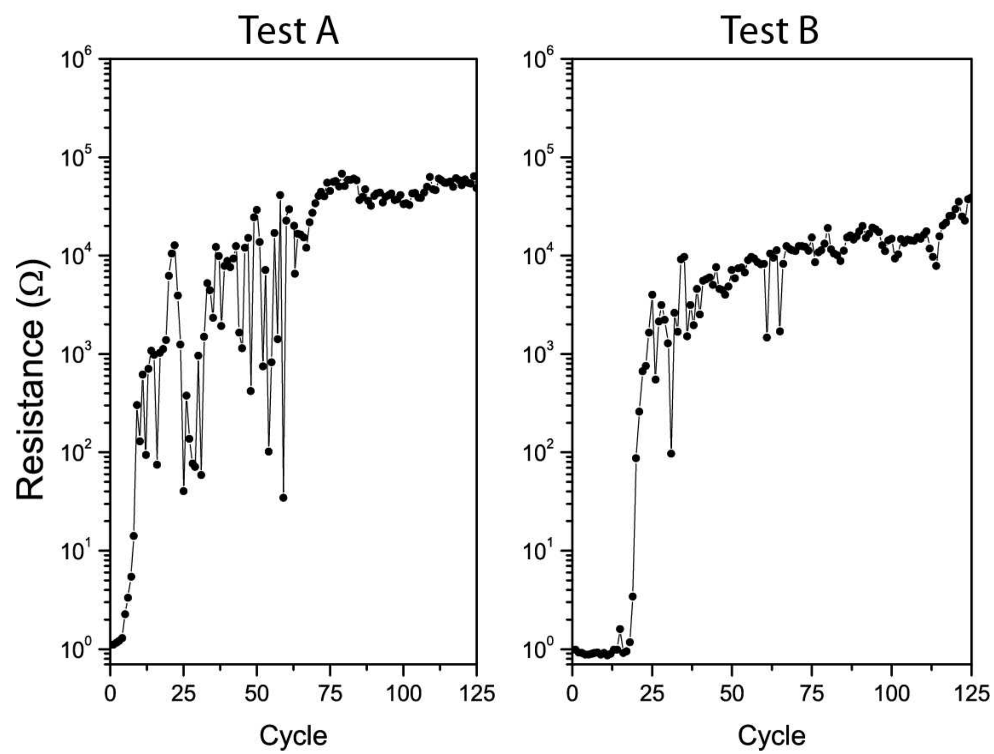
Thermal and Surface Damage Testing

Nominal Temperature Rise



Non-degraded voltage drop across contact (corresponding to Rc = ~ 1 Ω)

Accumulated Mechanical Surface Damage



Test A – Hot-switched from cycle 1
Test B – Contact for 100 cycles with no current present, then hot-switched until degraded

Degradation insensitive to accumulated cold contacts and calculated temperature rise too small to affect surface

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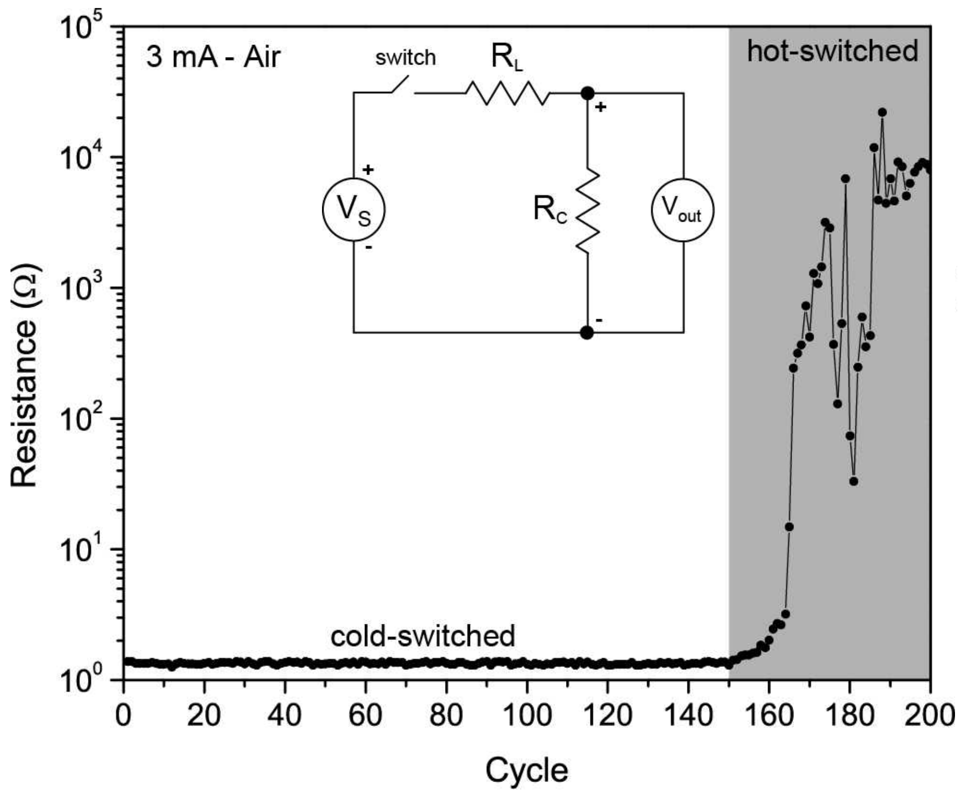
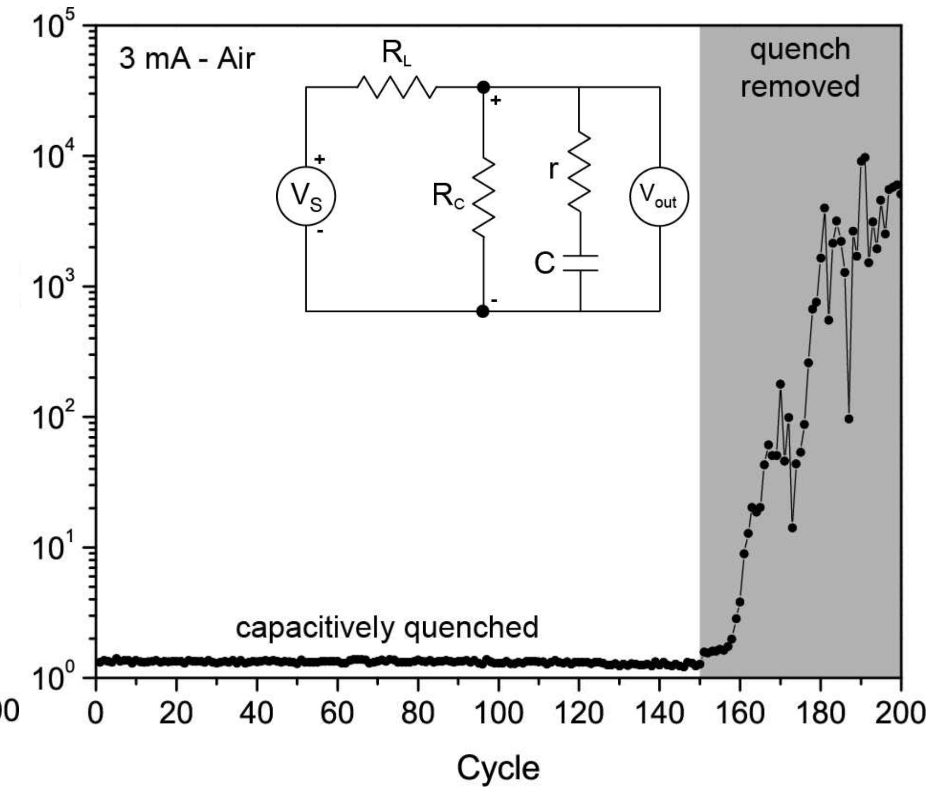
Degradation Sensitivity to Transient Electrical Events at Contact

Hot/Cold-Switch Tests



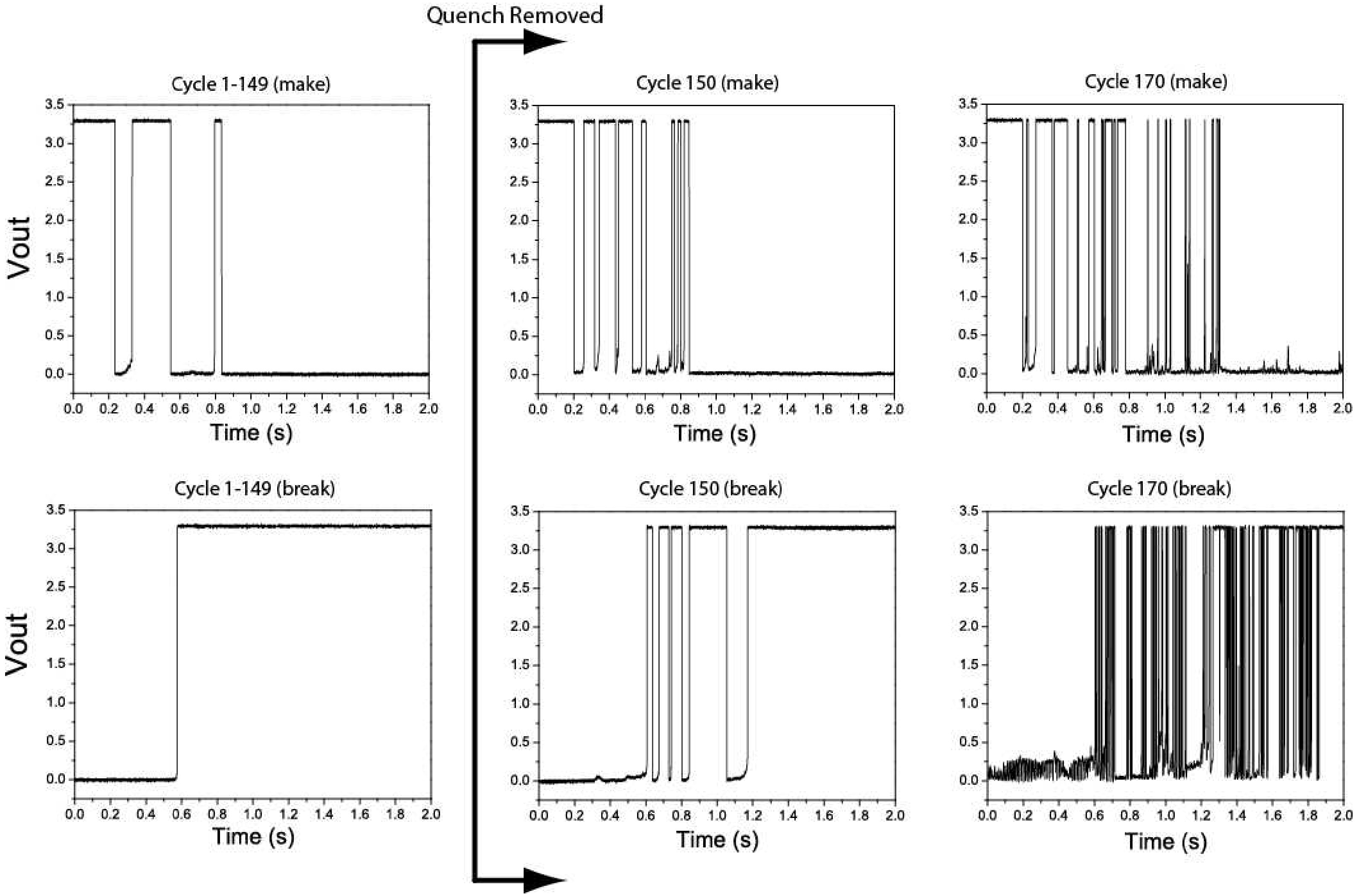
Capacitive Arc-Quench Tests



The presence of electrical energy at contact appears strongly related to resistance degradation

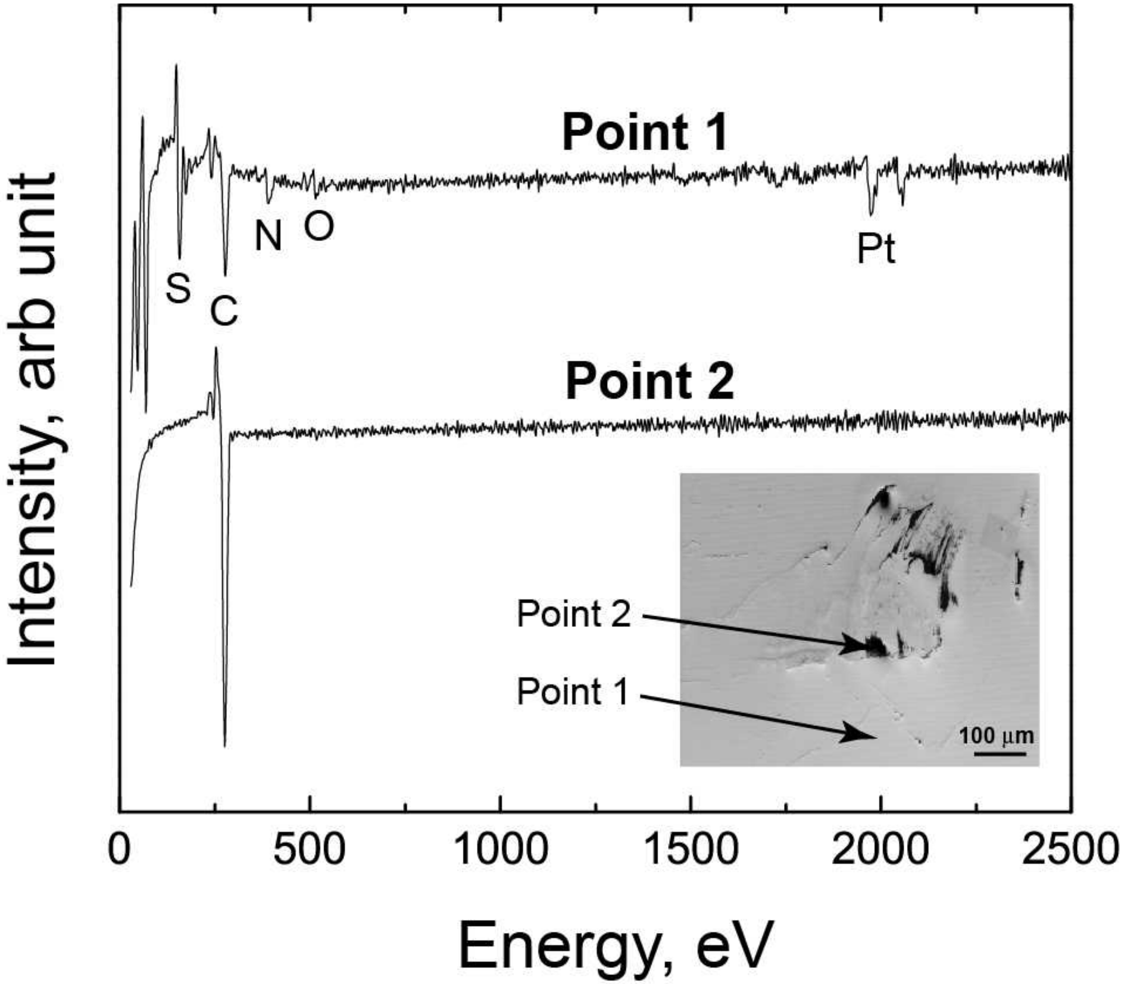
Resistance degradation occurs shortly after the arc-quenching element in parallel to the contact is removed, strongly suggestive that arcing and degradation are related

Contact Oscillograms – Before and After Capacitive Quench Removal



Number and frequency of voltage transients increases when the arc-quenching circuit removed

Auger Electron Spectroscopy Analysis of Suspected Surface Contaminant



Auger Electron Spectroscopy of an apparently clean area (Point 1) showed various surface species, including carbon

Similar analysis of a suspected contamination site (Point 2) on the flat showed essentially pure carbon

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Summary

A robust solution for reliable sliding contacts in silicon MEMS will enable new device concepts to be explored

Alternative materials are being explored for MEMS, but challenges remain

- residual stress and strain gradients must be mitigated
- potential opportunity for integrating carbon films with Si micromachining

Chemisorbed monolayers alone are not durable enough for sliding MEMS contacts

- wear, and aging in storage are main issues

Mobile phases are the most promising for lubrication of MEMS sliding contacts

- surface mobile, relies on diffusion to contact zone
- vapor phase, with formation of reaction product at exposed Si

Electrical contacts in MEMS require balance between low resistance (high contact stress) and low adhesion (low contact stress)

- adsorption and decomposition of hydrocarbons on contacts during long term storage leads to increased contact resistance
- optimized film structure (passivating yet conductive) could lead to mechanically robust electrical contacts for MEMS

Acknowledgements

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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