Surface Chemistry of Glass:
Interfacial water and mechanochemical properties

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Engineering Conferences International
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- Laura Bradley, Zach Dilworth – undergraduate REU through support from NSF IMI for New Functionality in Glass (Grant No. DMR-0844014).

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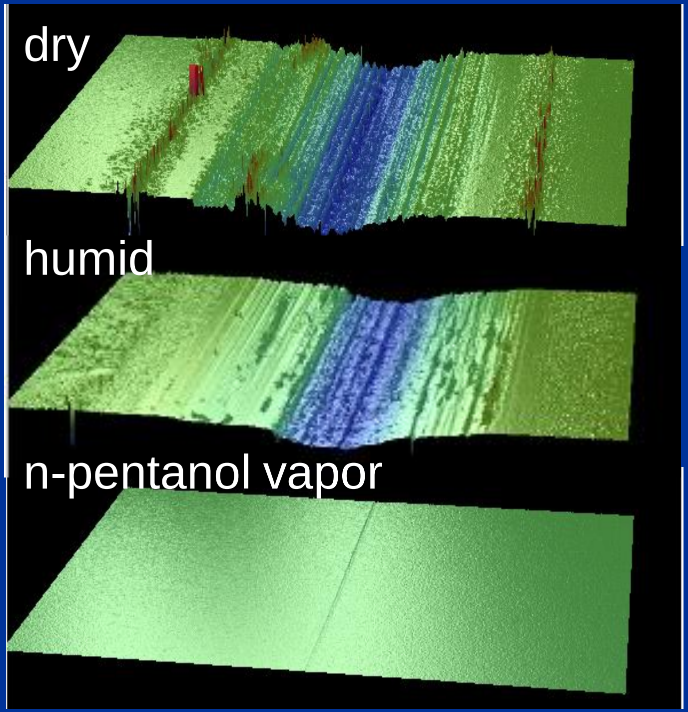
Surface properties in vacuum conditions
are
intrinsic properties of materials;

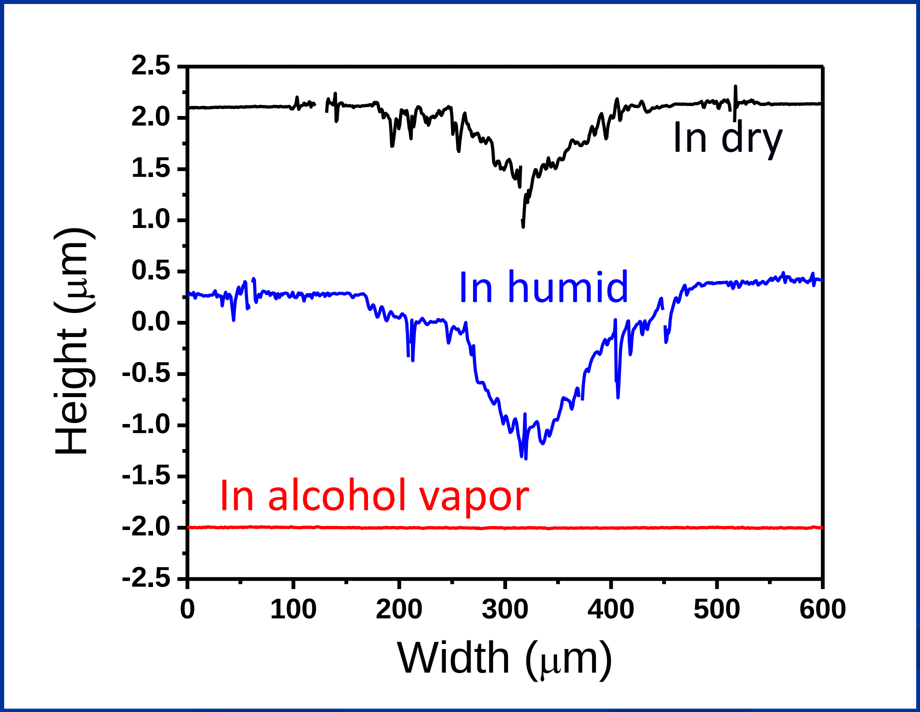
Effects of vapor adsorption on SiO_2/Si wear

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

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

Optical profilometry

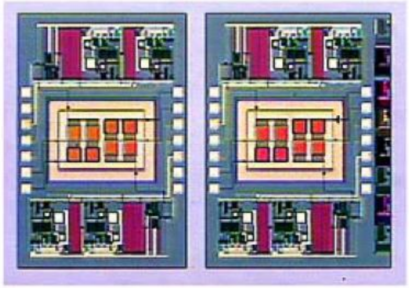




Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* **2009**, *25*, 13052–13061

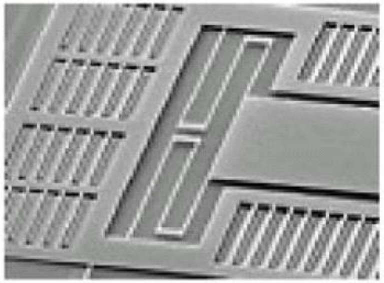
MEMS Reliability Taxonomy

Class I
No Moving parts



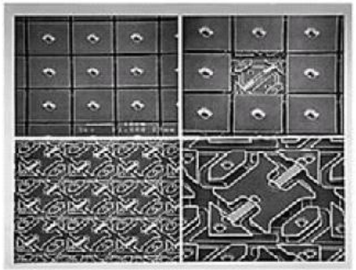
Accelerometers
Pressure Sensors
Ink Jet Print Heads
Strain Gauge

Class II
Moving Parts, No Rubbing or Impacting Surfaces



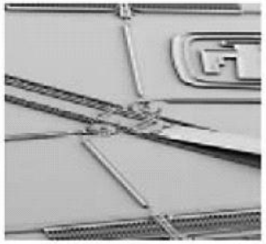
Gyros
Comb Drives
Resonators
Filters

Class III
Moving Parts, Impacting Surfaces



TI DMD
Relays
Valves
Pumps

Class IV
Moving Parts, Impacting and Rubbing Surfaces

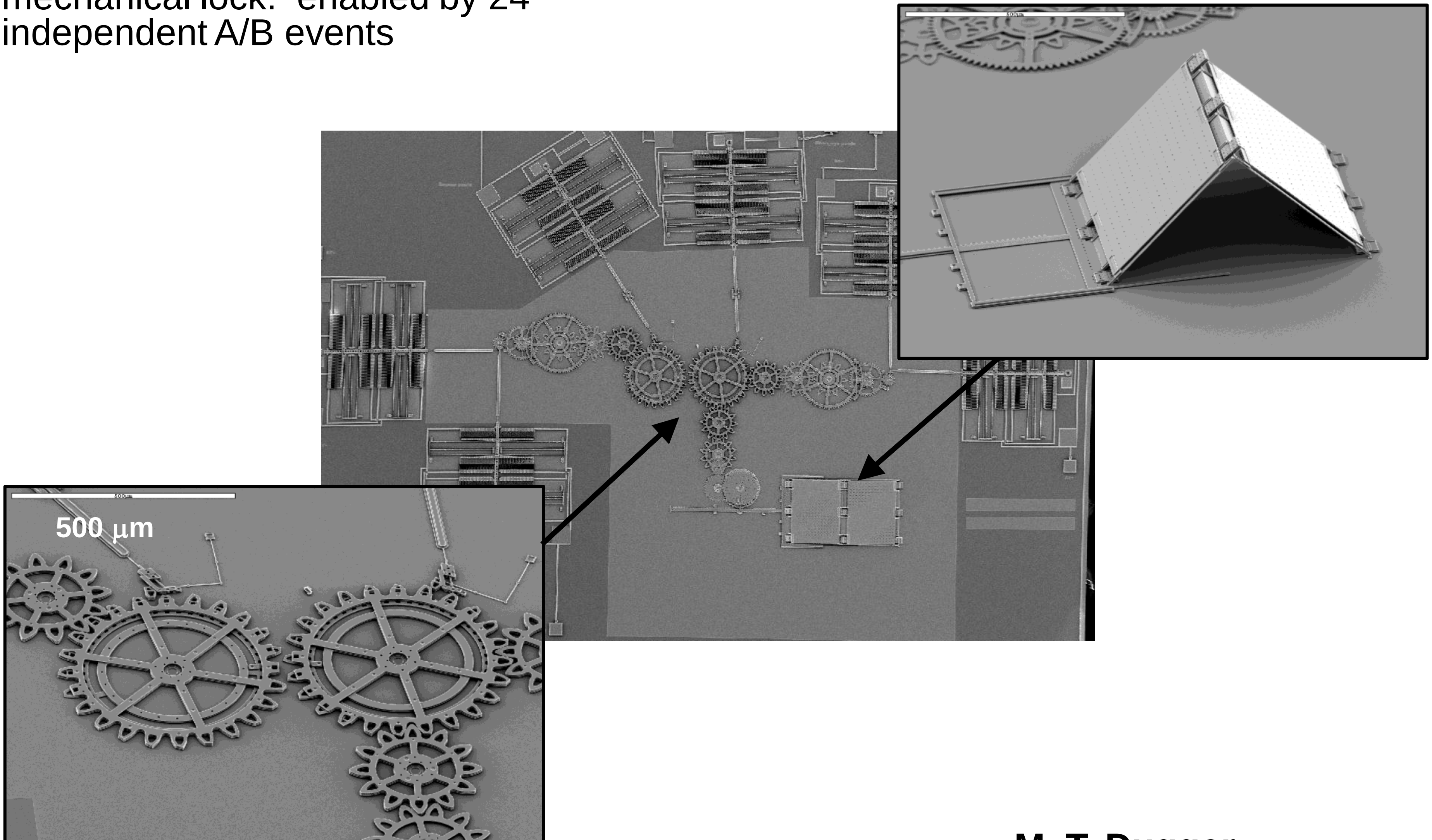


Optical Switches
Corner Cube Refl.
Shutters
Scanners
Locks
Discriminators

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

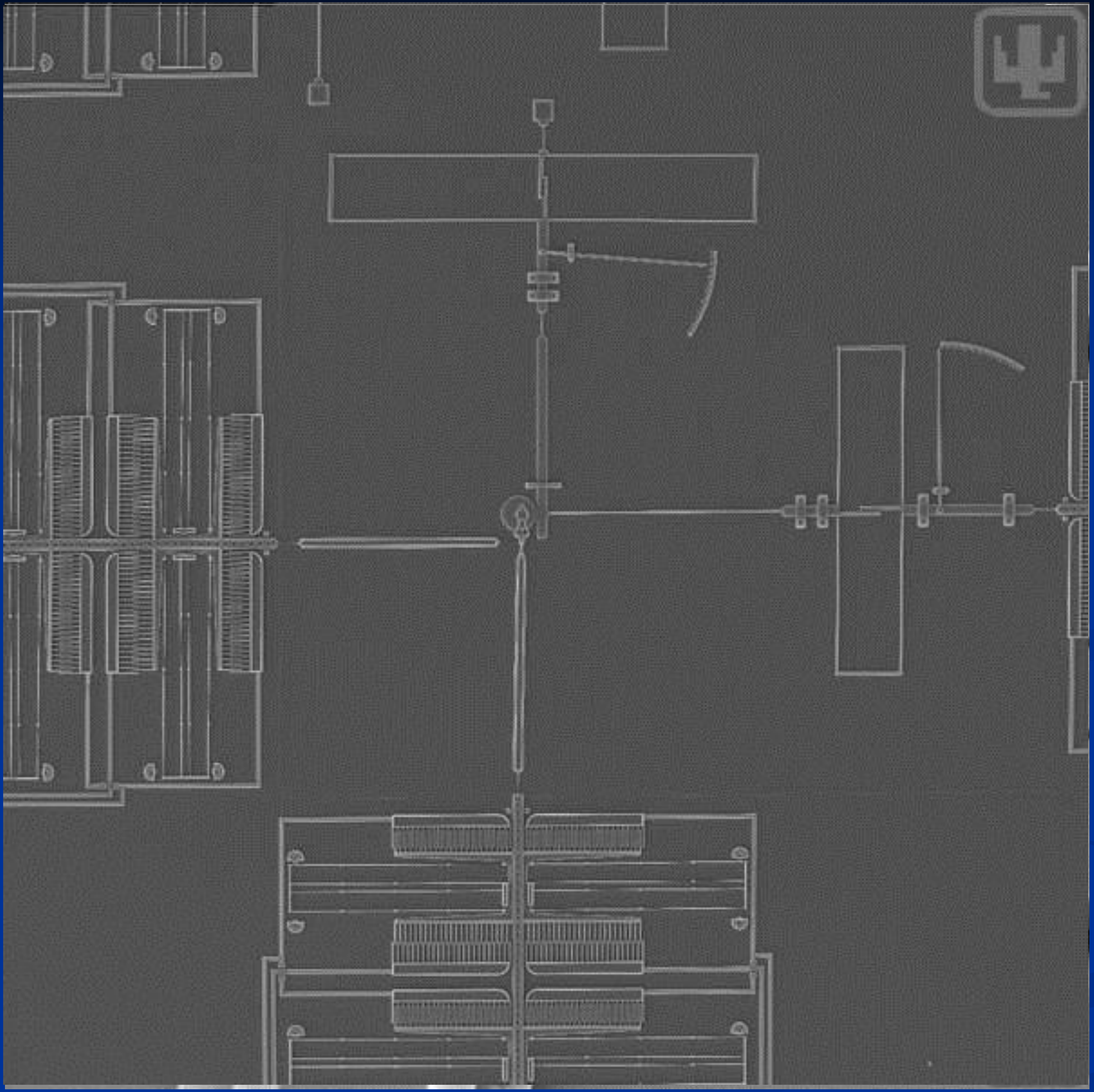
Unreliable Dynamic Interfaces have Limited the Development of Complex MEMS

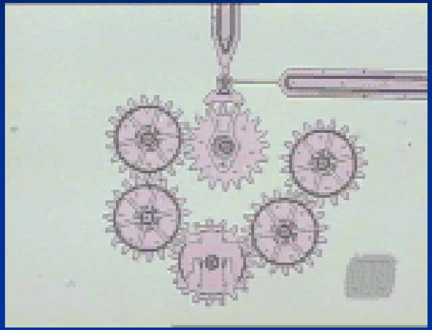
mechanical lock: enabled by 24 independent A/B events

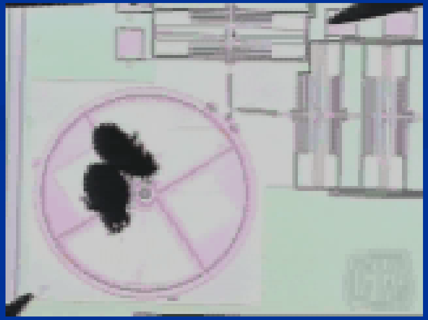


M. T. Dugger

Sandia National Laboratories





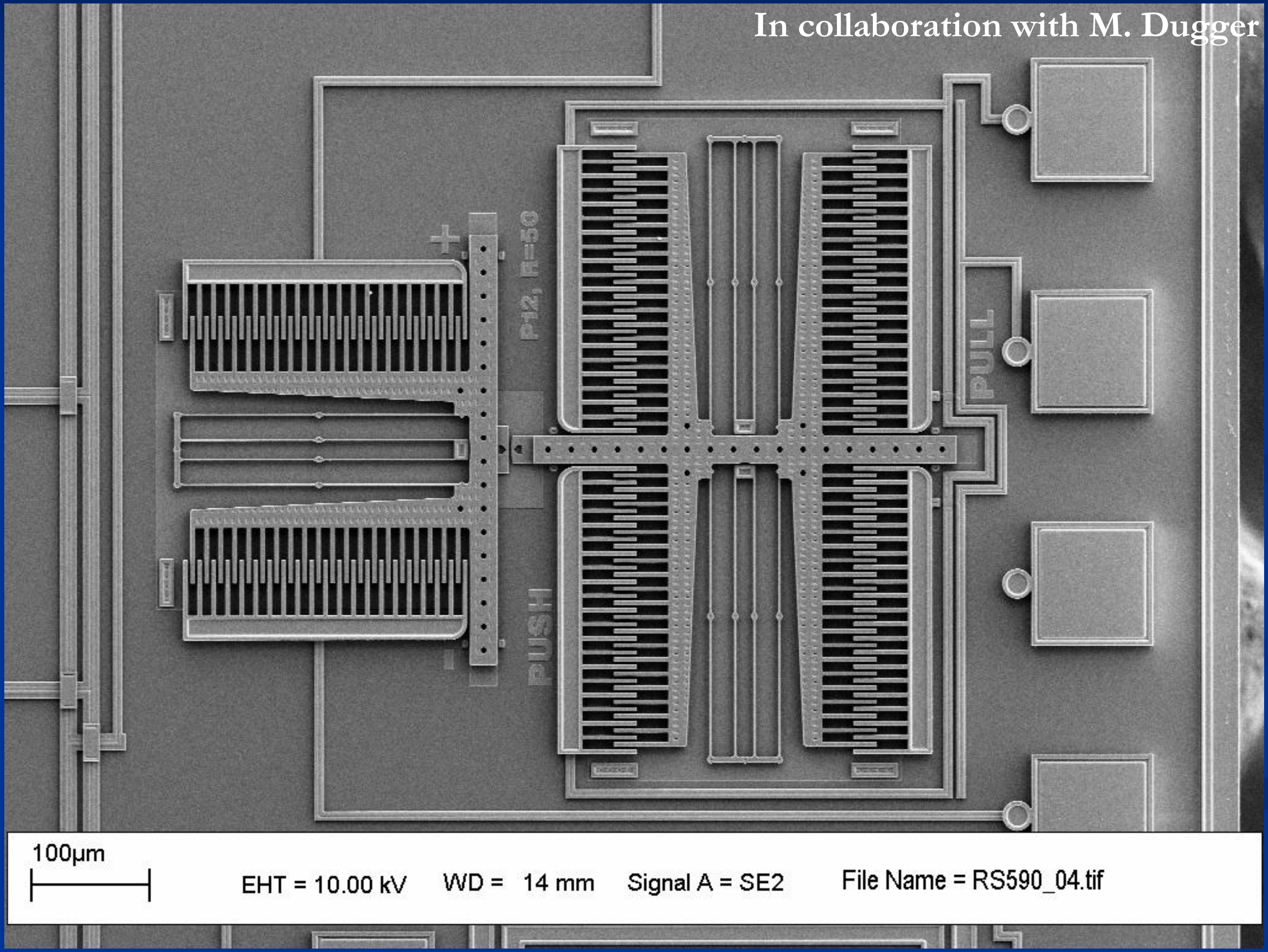


"Courtesy Sandia National Laboratories, SUMMiT™ Technologies, www.sandia.gov/mstc"

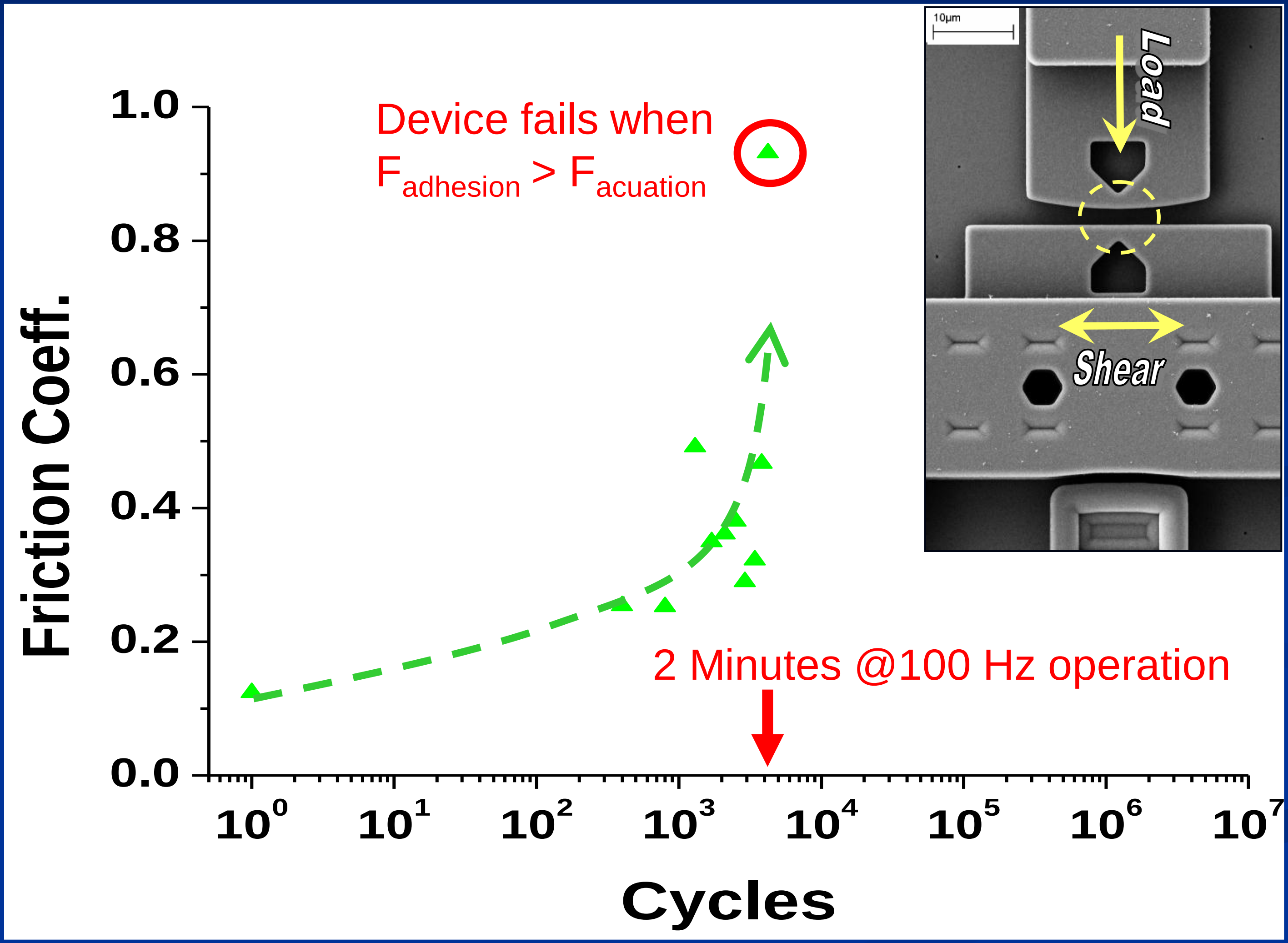
MEMS side-wall tribometer

Initially coated with “lubricious” fluorinated self-assembled monolayer

In collaboration with M. Dugger (Sandia)



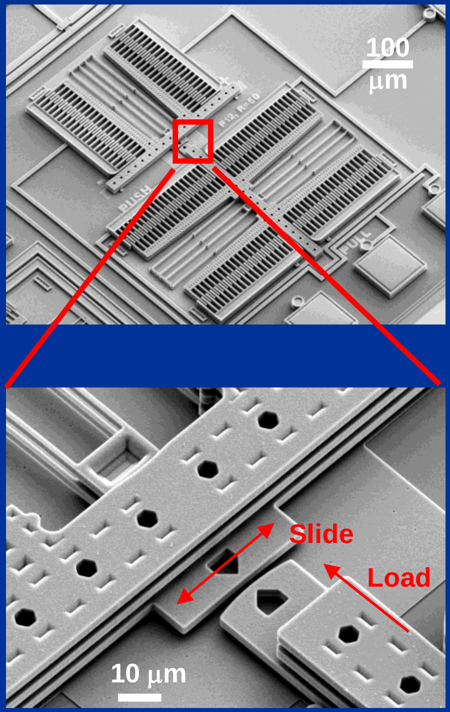
Device fails once the lubricious coating layer is worn off and the adhesion of the newly exposed bare surfaces becomes larger than the actuation force.

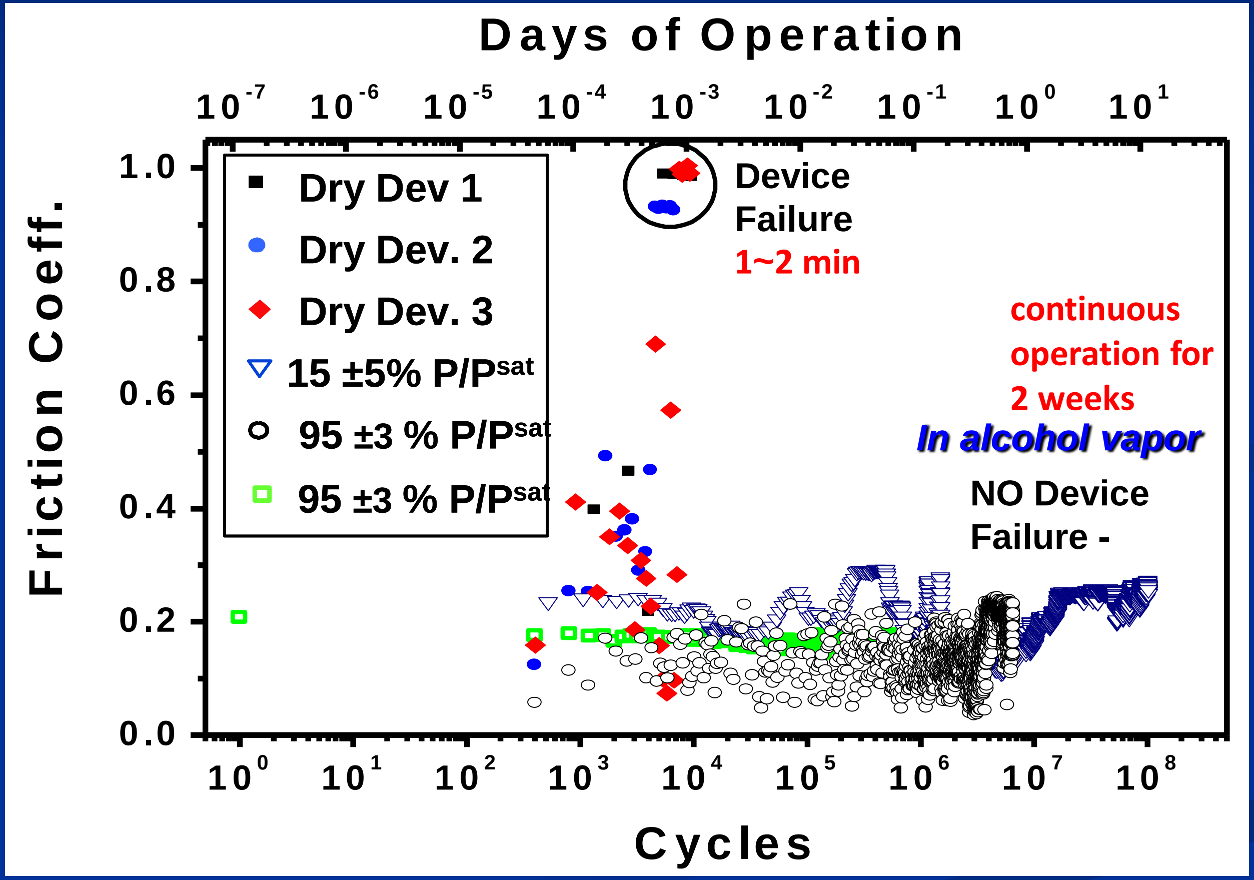


D. B. Asay, M. T. Dugger, and S. H. Kim, *Tribol. Lett.* **2008**, 29, 67.

In the presence of alcohol vapor, the device does not fail …

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.

Micro-scale lubrication with a molecular adsorbate film

(12) **United States Patent**
Dugger et al.

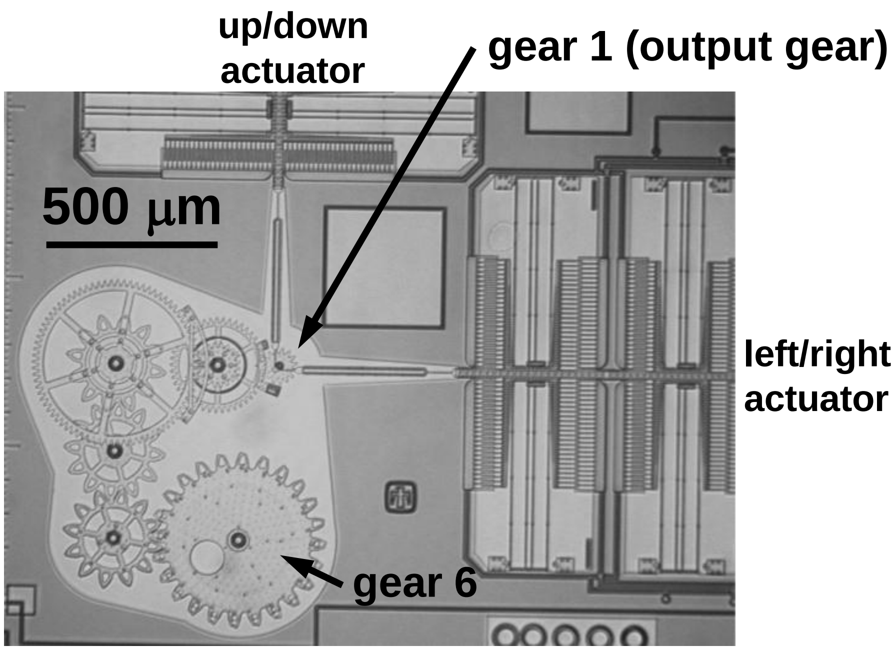
(10) **Patent No.:** **US 8,071,164 B1**
(45) **Date of Patent:** **Dec. 6, 2011**

(54) **METHOD FOR LUBRICATING CONTACTING SURFACES**

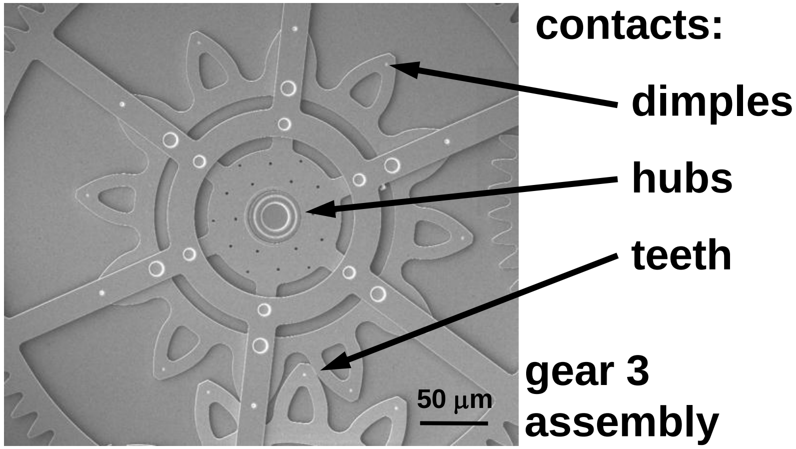
(75) Inventors: **Michael T. Dugger**, Tijeras, NM (US); **James A. Ohlhausen**, Albuquerque, NM (US); **David B. Asay**, Boalsburg, PA (US); **Seong H. Kim**, State College, PA (US)

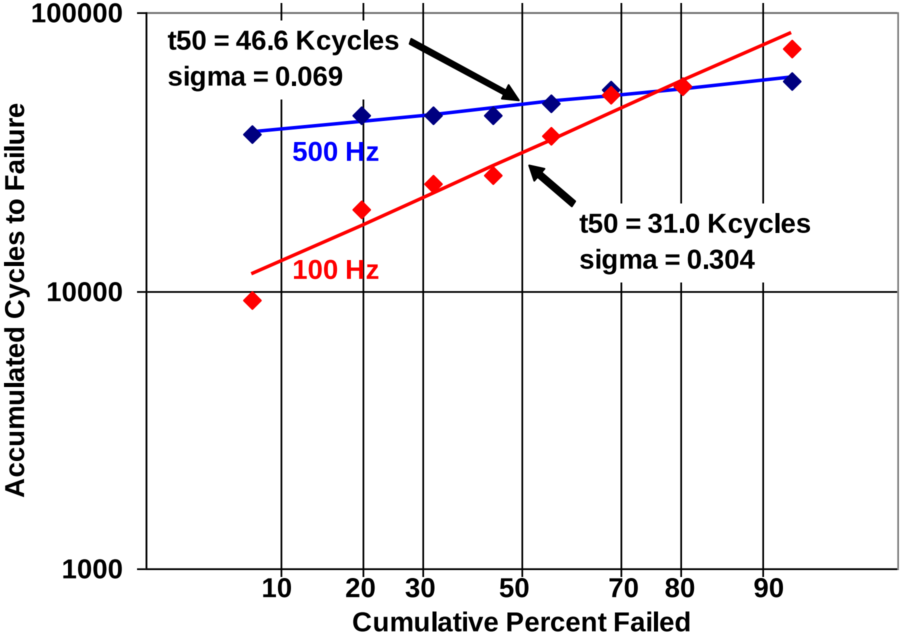
Increased Operating Life of Gear Train with Vapor Phase Lubrication

M. T. Dugger



gear train on aging module





FOTAS monolayer alone, $t_{50} = 4.7 \times 10^4$

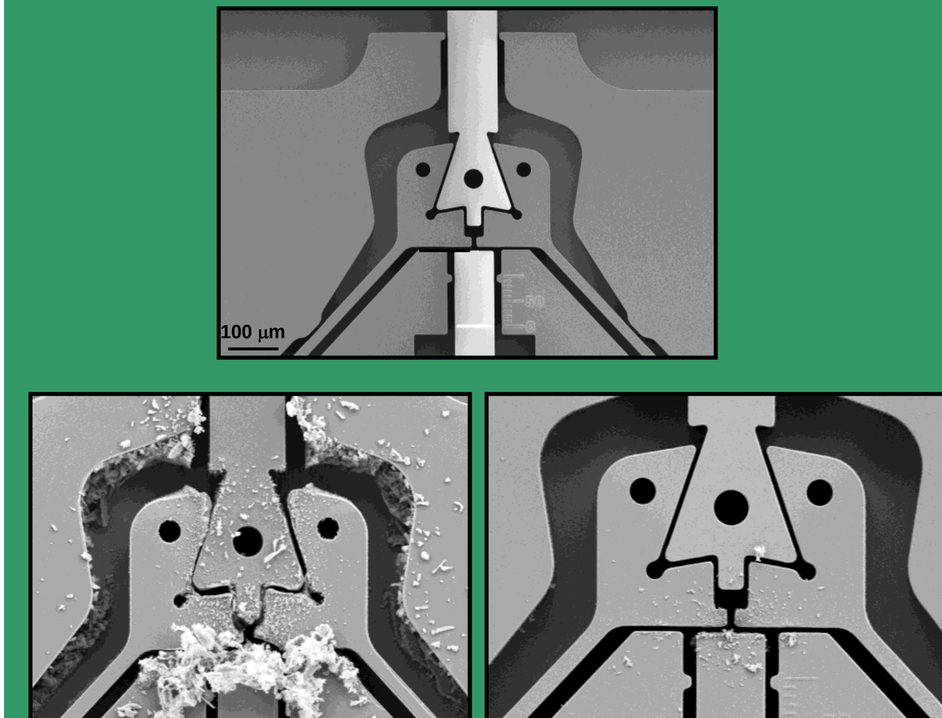
With VPL, device was stopped at 4.8×10^8 cycles *without failure*

- **1000 ppm pentanol, <100 ppm H_2O**

VPL is Effective on MEMS Devices with Thermal Actuators

M. T. Dugger

single crystal silicon Fiber Switch



$5x10^6$ cycles in air

$5x10^6$ cycles in 20% Psat pentanol

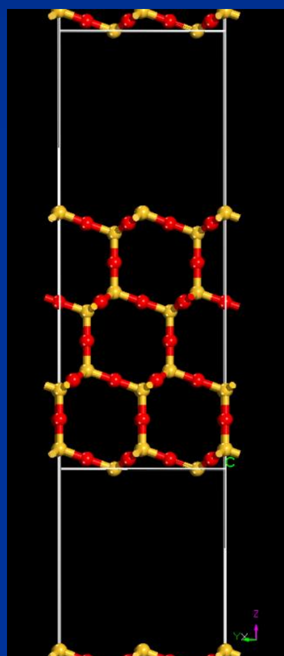
VPL with pentanol produces extraordinary operating life in a variety of MEMS devices

Understanding accelerated wear of SiO_2 by water and wear prevention by alcohol

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

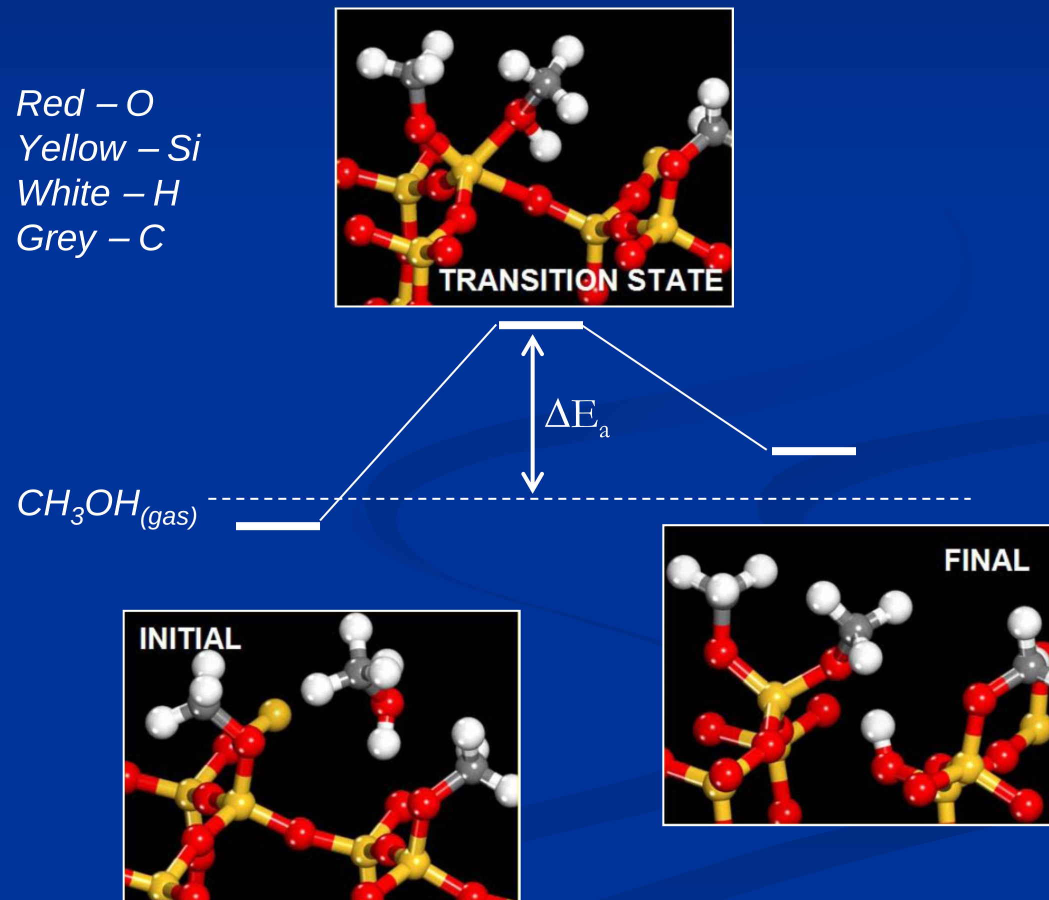
Model System:

β-cristobalite (111)



Stable & low density form of SiO_2

Si-O-Si Rupture via Methanol

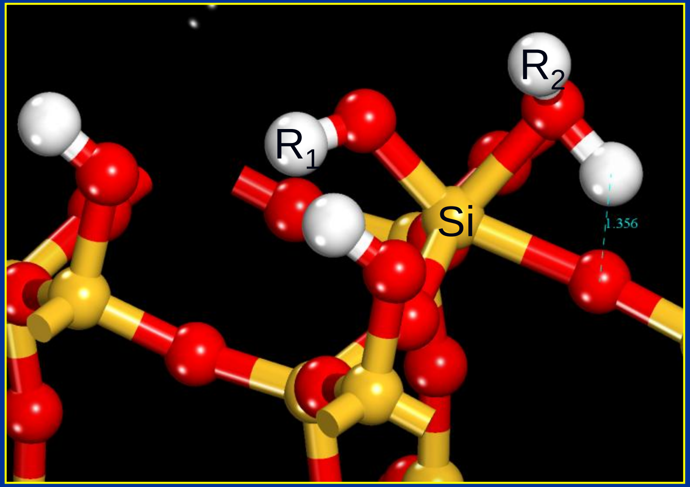


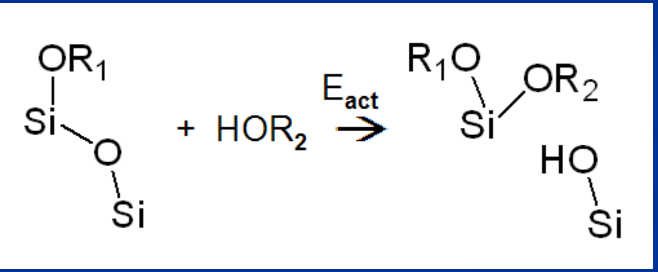
Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* **2009**, *25*, 13052–13061

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





R_1	R_2	E_a (kJ/mol)
H	H	114
CH_3	H	151
H	CH_3	112
CH_3	CH_3	154
propyl	propyl	224

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

Barnette, Asay, Kim, Guyer, Lim, Janik, and Kim, *Langmuir* **2009**, *25*, 13052–13061

“Amorphous oxide of Si is boring; multicomponent silicate glasses are more complicated & interesting”

Water adsorption and penetration can cause ion-exchange with mobile/leachable ions and hydrolysis of Si-O-Si network

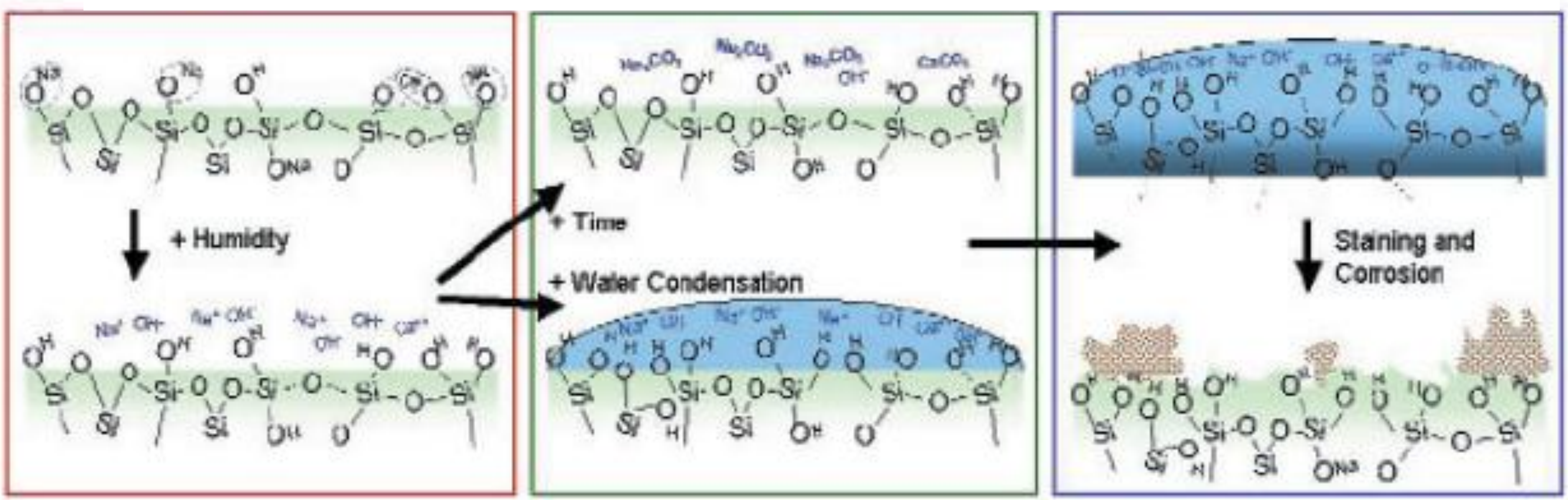
$$\equiv Si\text{-}O^{-}\,Na^{+} + H_2O \longrightarrow \equiv Si\text{-}OH + Na^{+} + OH^{-}$$

$$\equiv Si\text{-}O\text{-}Si\equiv + OH^{-} \longrightarrow \equiv Si\text{-}OH + \equiv Si\text{-}O^{-}$$

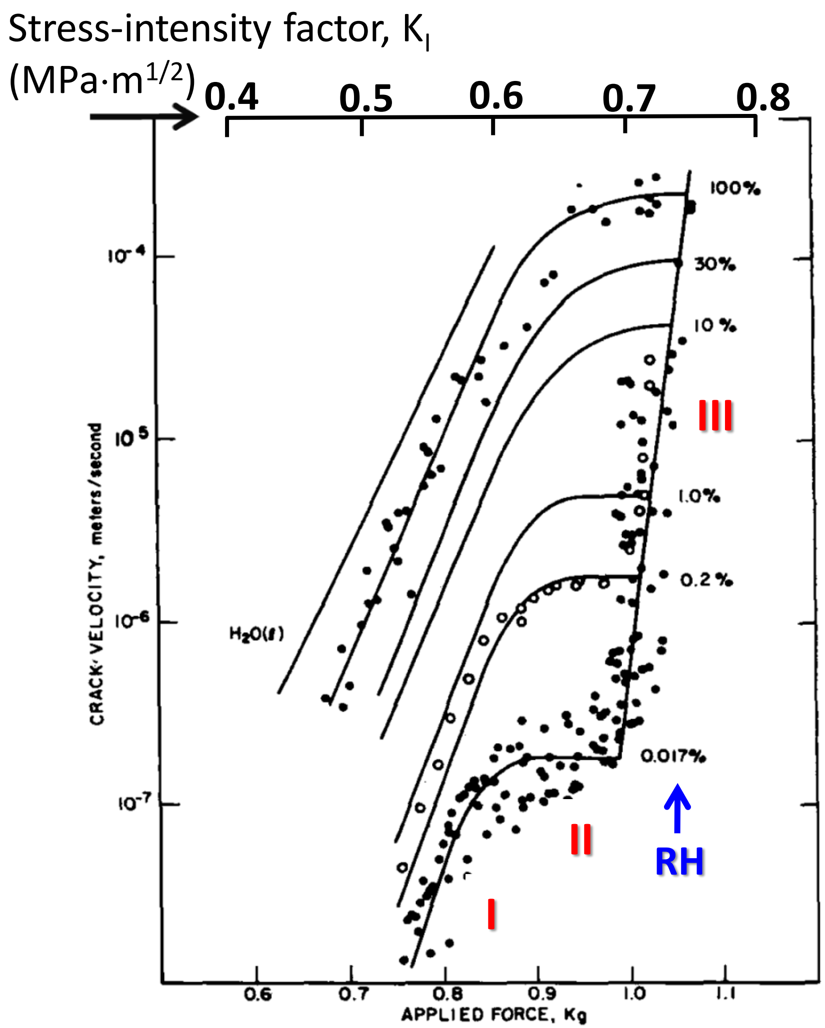
$$\equiv Si\text{-}O^{-} + H_2O \longrightarrow \equiv Si\text{-}OH + OH^{-}$$

$$\equiv Si\text{-}O\text{-}Si\equiv + H_2O \longrightarrow \equiv Si\text{-}OH + HO\text{-}Si\equiv$$

R.A.Schaut, C.G.Pantano. 2005



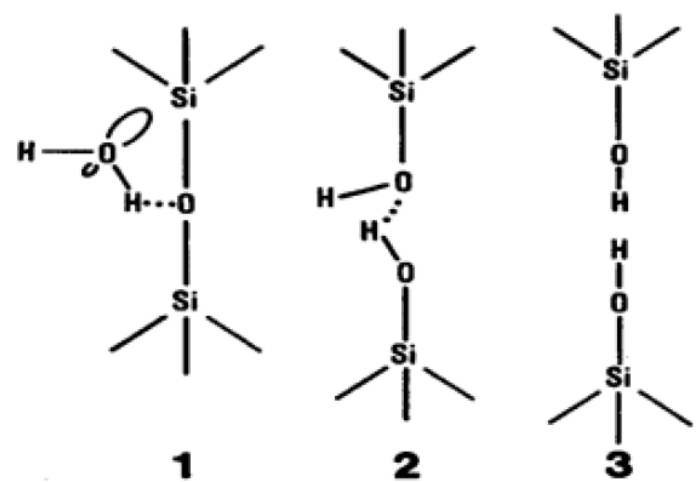
Influence of water vapor on crack propagation in soda lime glass



S. M. Wiederhorn
J. Am. Ceram. Soc. **50**, 407-414 (1967)

Charles & Hillig Theory

Molecules possessing proton donor sites and lone-pair orbitals can enhance the crack growth rate by coupling across the Si-O bond to form an activated complex…

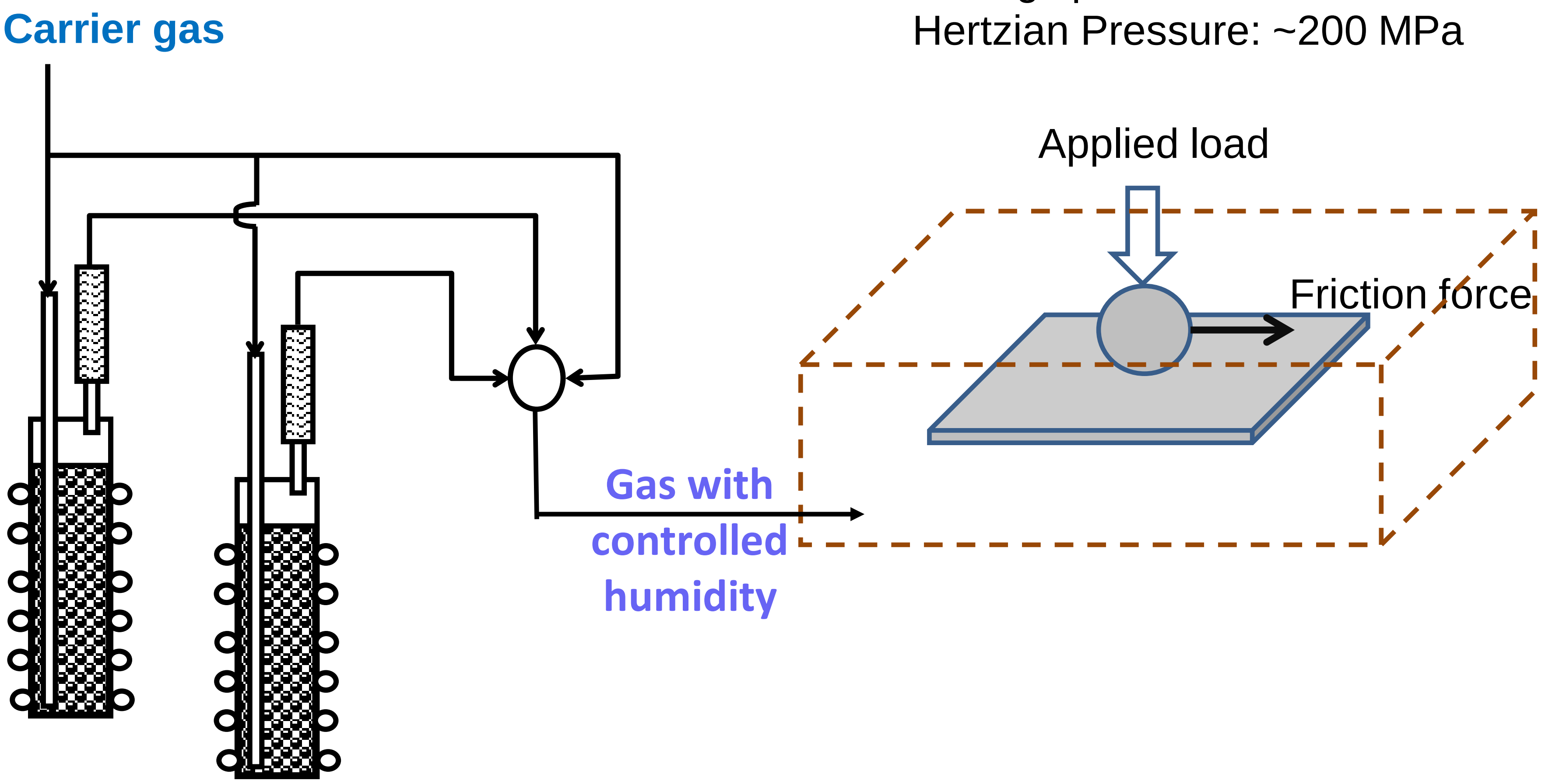


Freiman, Wiederhorn, & Mecholsky,
J. Am. Ceram. Soc. **92**, 1371 (2009)

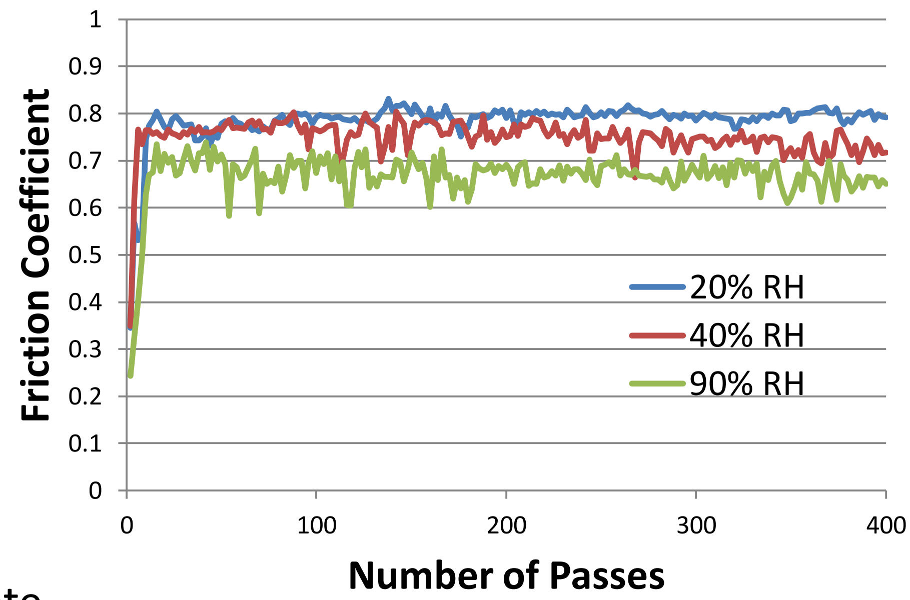
How does water adsorption affect scratch behaviors of glass?

Scratching glass surface in humid conditions

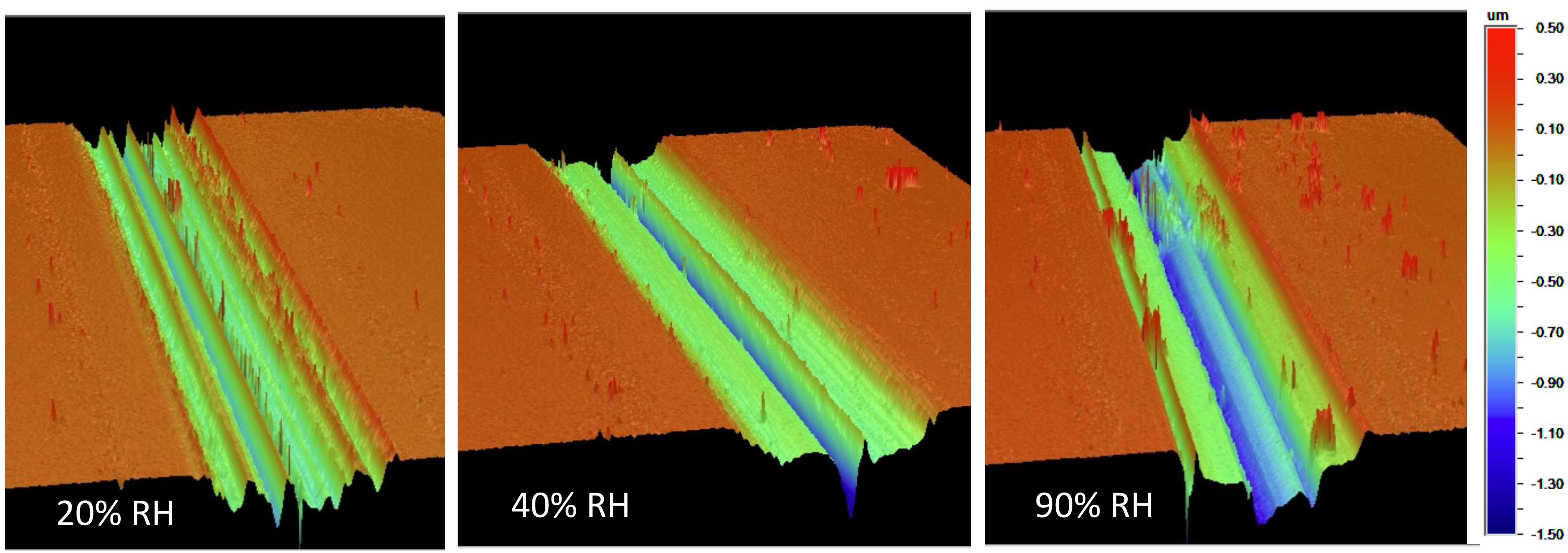
Load: 0.2 N
Sliding speed:~4.2mm/s
Hertzian Pressure: ~200 MPa



Humidity dependence of wear of *fused quartz* surface rubbed with *pyrex ball*

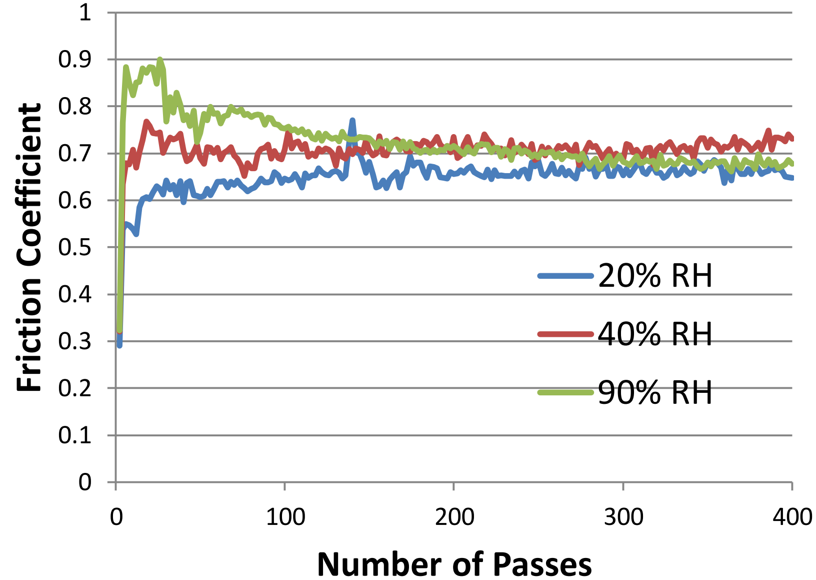


Optical profilometry images of the substrate

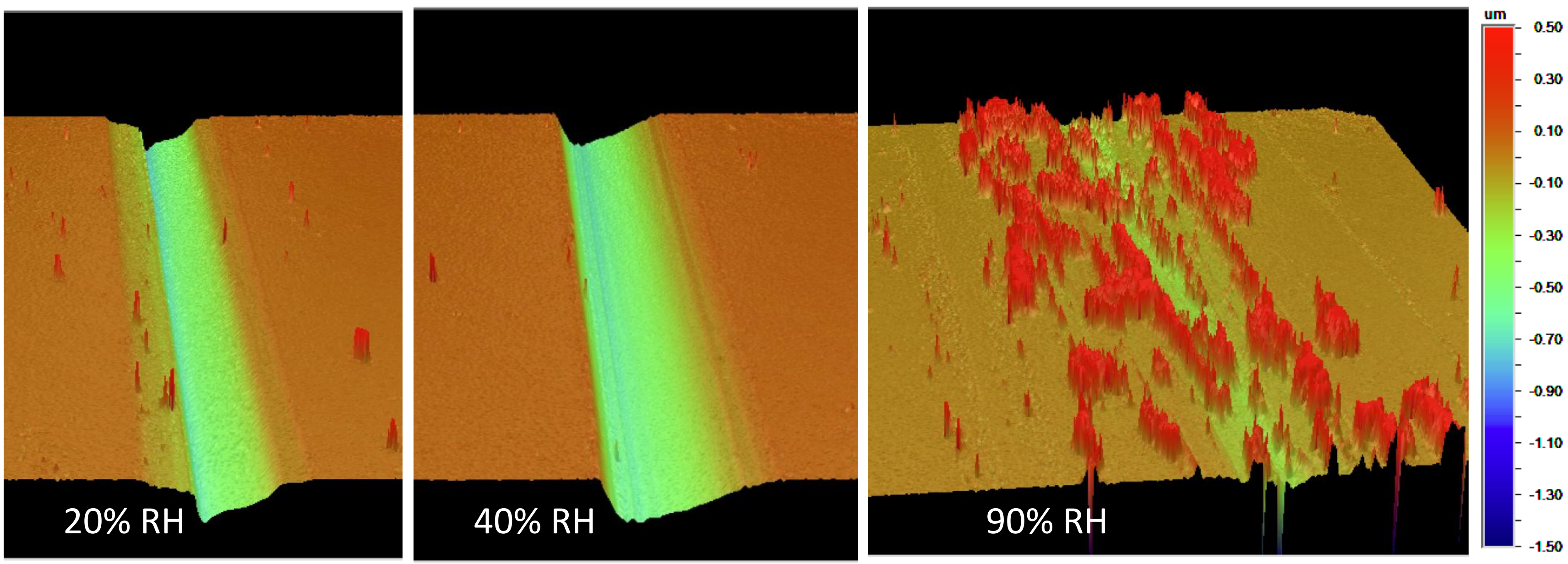


Total displaced volume	$-21000\ \mu m^3$	$-30000\ \mu m^3$	$-32000\ \mu m^3$

Humidity dependence of wear of *soda lime glass* surface rubbed with *pyrex ball*



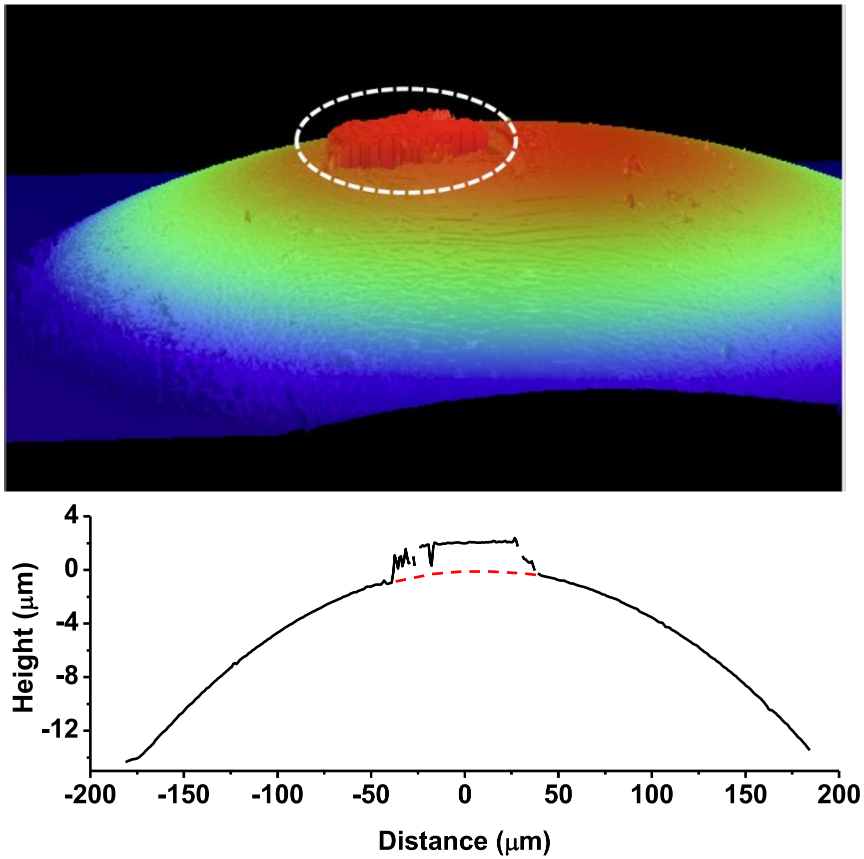
Optical profilometry images of the substrate



Total displaced volume	$-13000\ \mu m^3$	$-18500\ \mu m^3$	$+25000\ \mu m^3$

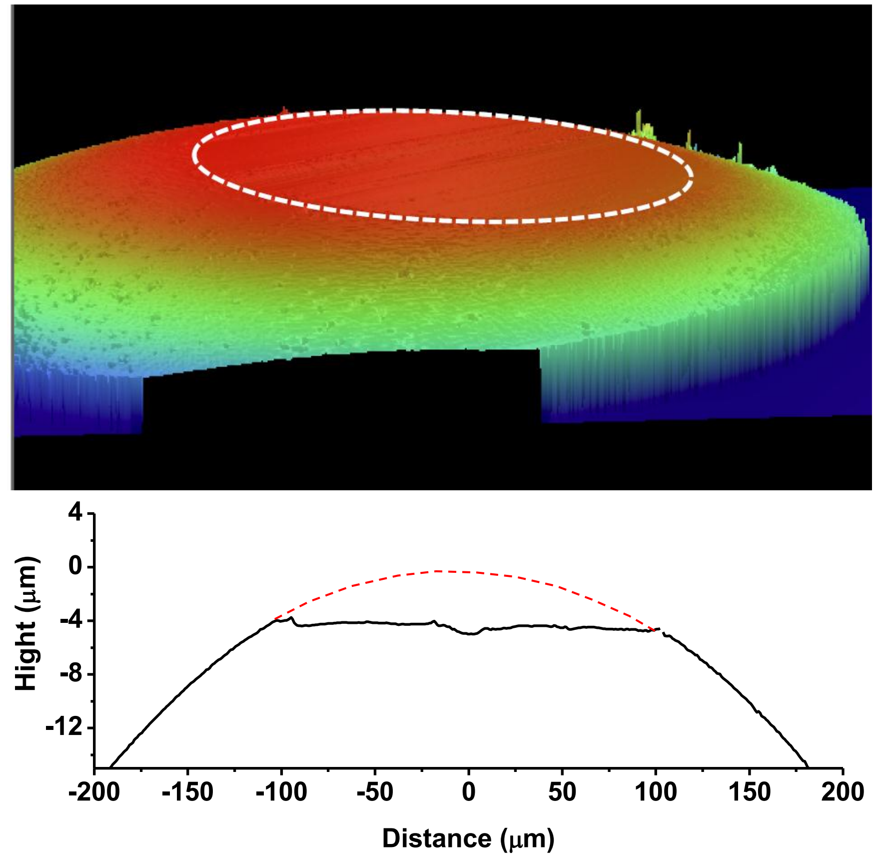
Optical profilometry image of pyrex ball rubbed in 20% RH

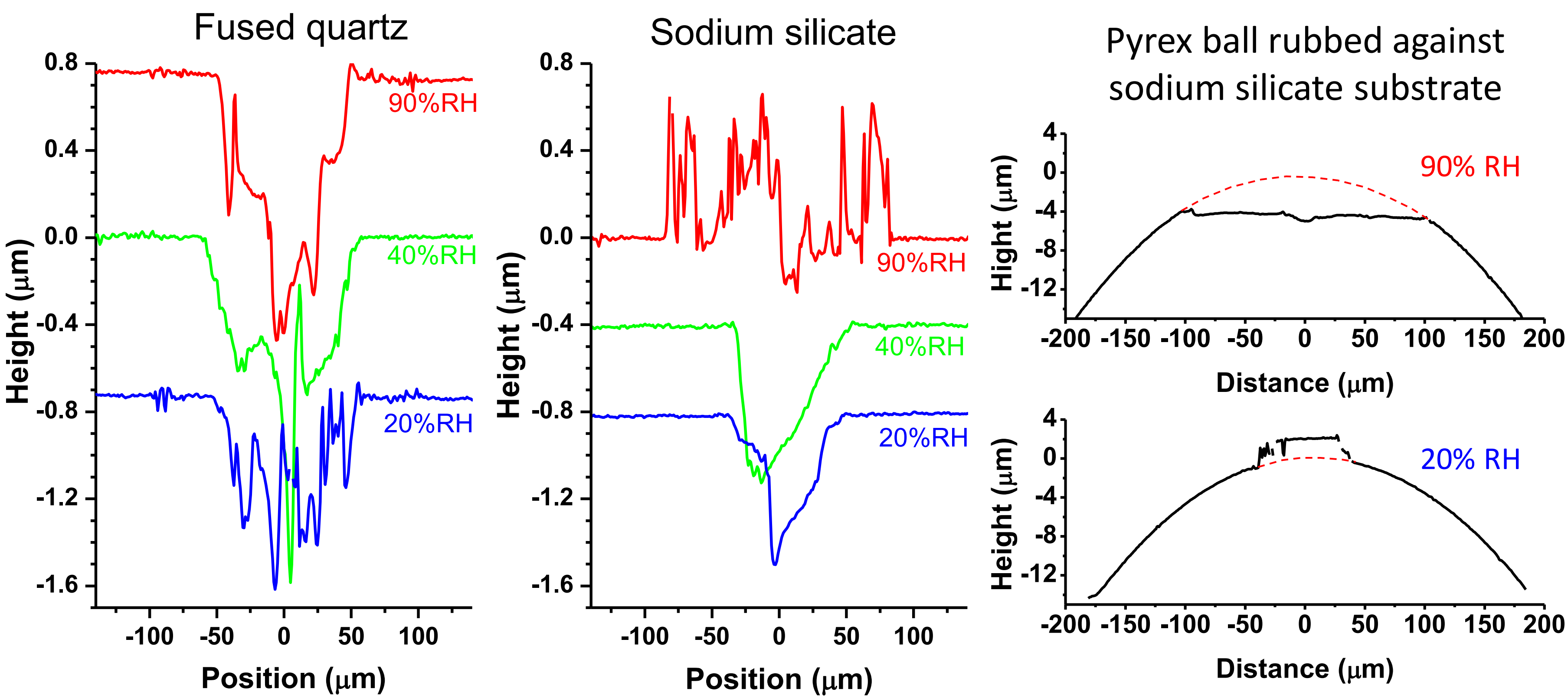
→ Deposition of substrate wear debris



Optical profilometry image of pyrex ball rubbed in 90% RH

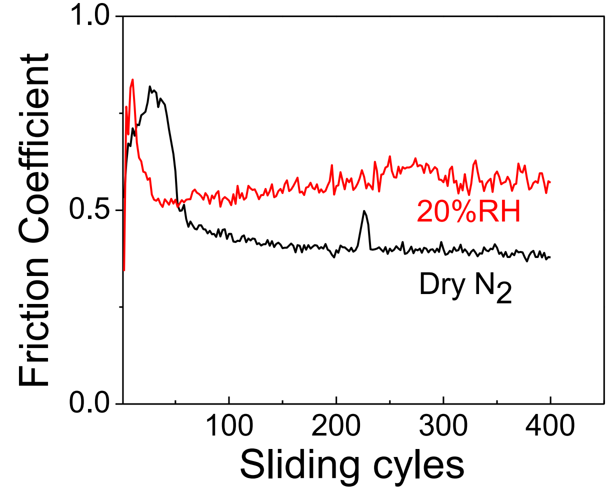
→ Wear of ball



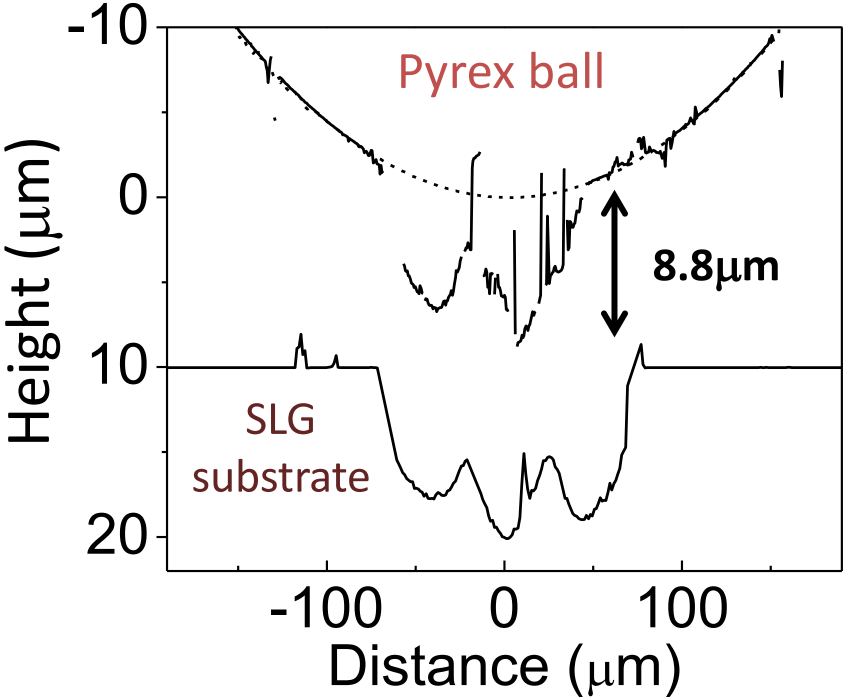


L. Bradley, Z. Dilworth,,, C. G. Pantano, & S. H. Kim "Hydronium Ions in Soda-lime Silicate Glass Surfaces" *J. Am. Ceram. Soc.* (DOI: 10.1111/jace.12136)
(Article first published online: 24 DEC 2012)

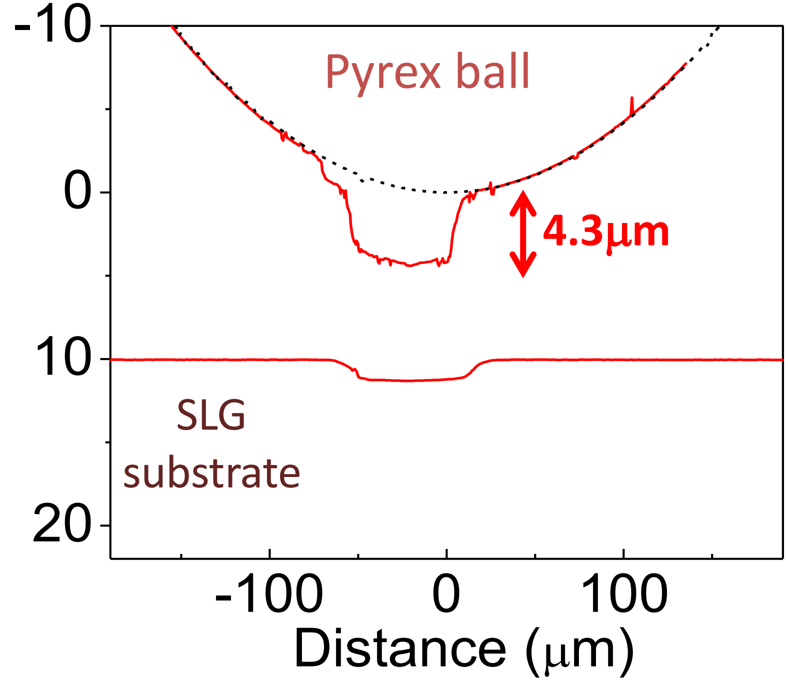
A small increase in humidity from dry air drastically change the surface scratch behavior of glass



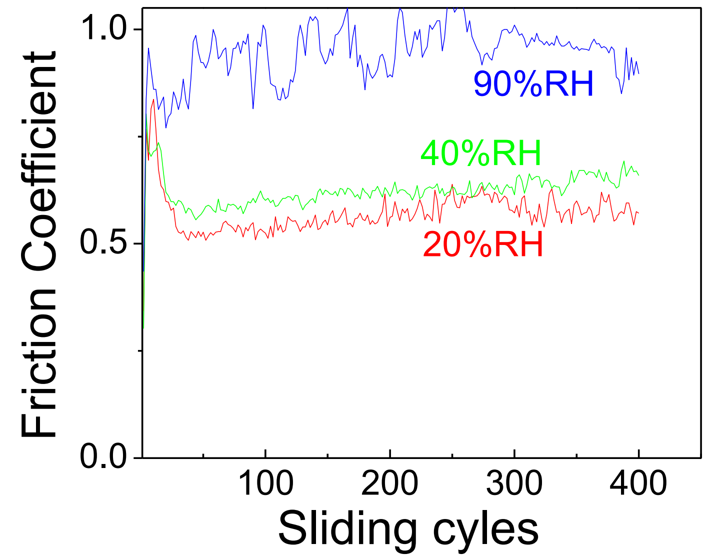
In dry N_2

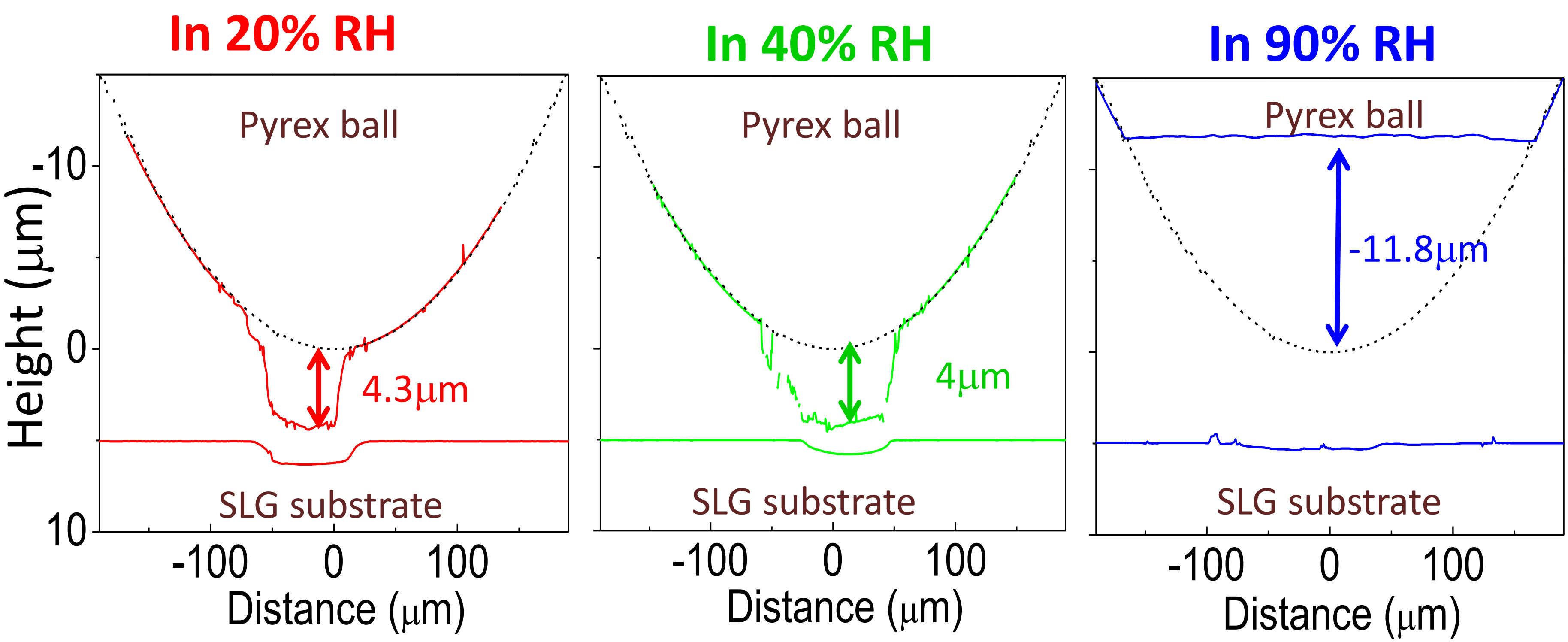


In 20% RH



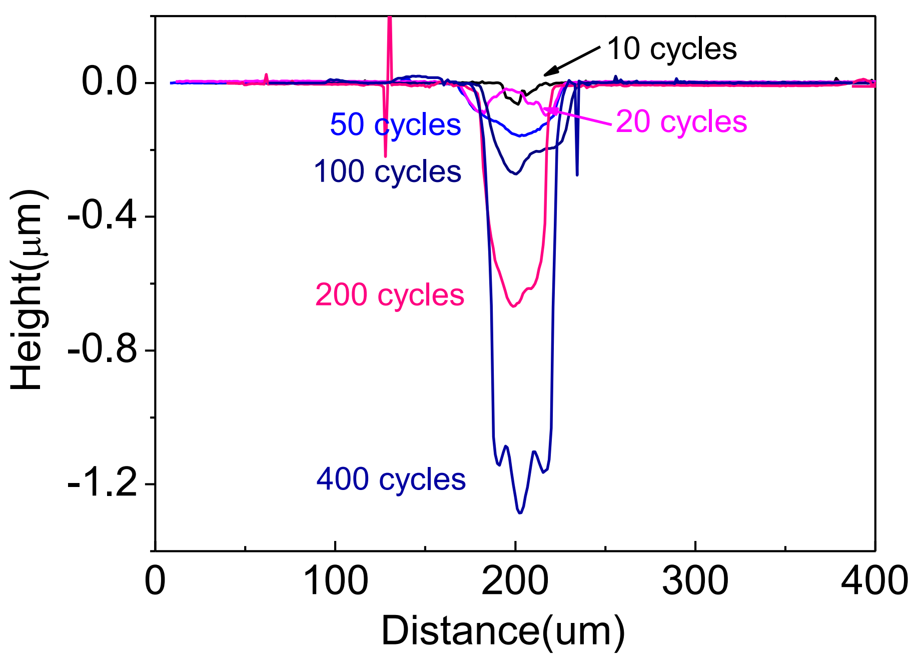
As RH approaches saturation, the SLG surface becomes "wear-resistant"…

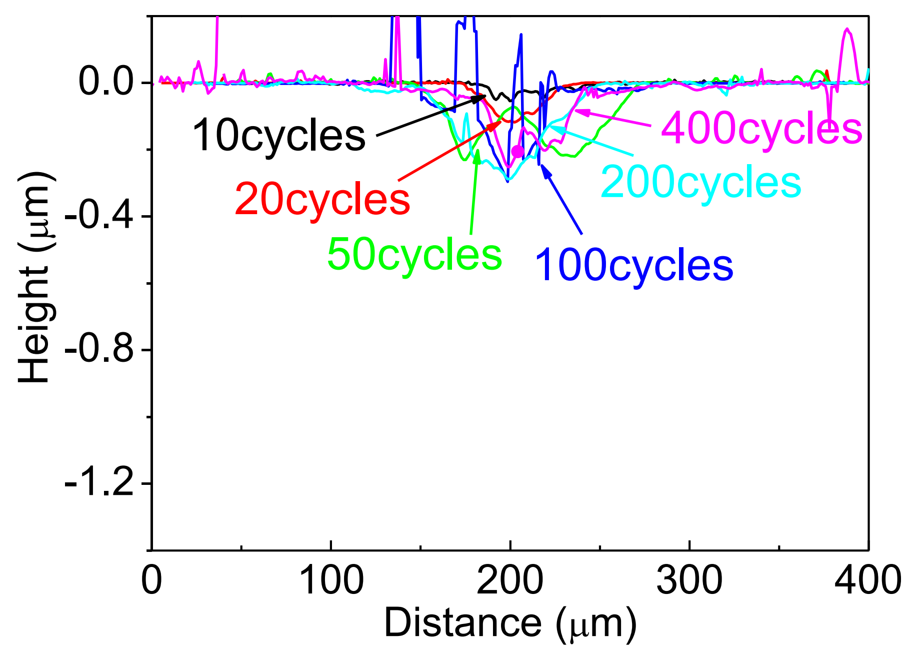




In 20% RH, the wear of the SLG substrate continues as the # of scratch cycles increases

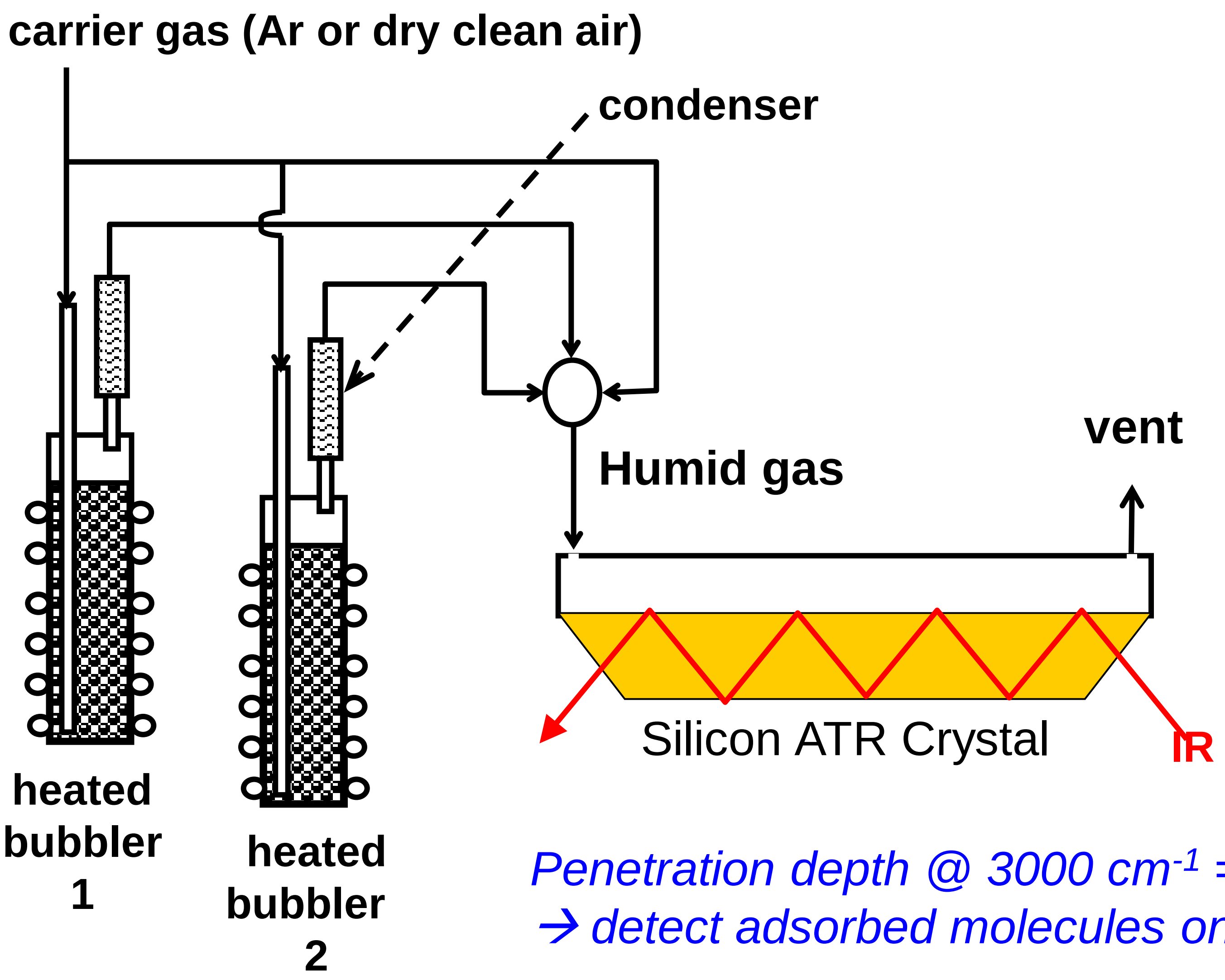
In 90% RH, the damage to the SLG substrate is made initially by a few asperity contacts; but it does not grow.





Water adsorption on glass surface matters…

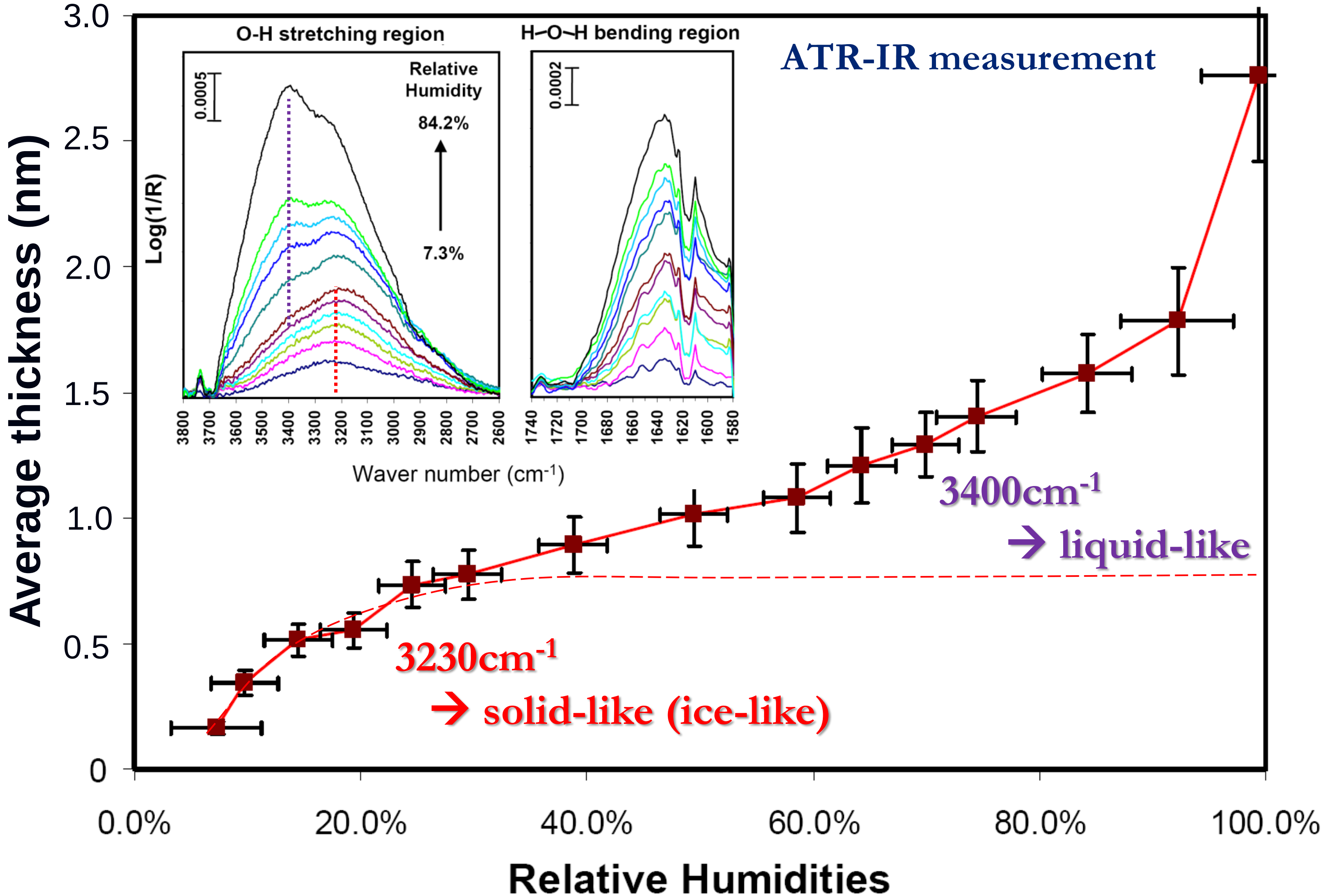
If the substrate is SiO_2, it's easy to measure water adsorption isotherm…



Penetration depth @ 3000 cm^{-1} = ~ 300 nm

→ detect adsorbed molecules only

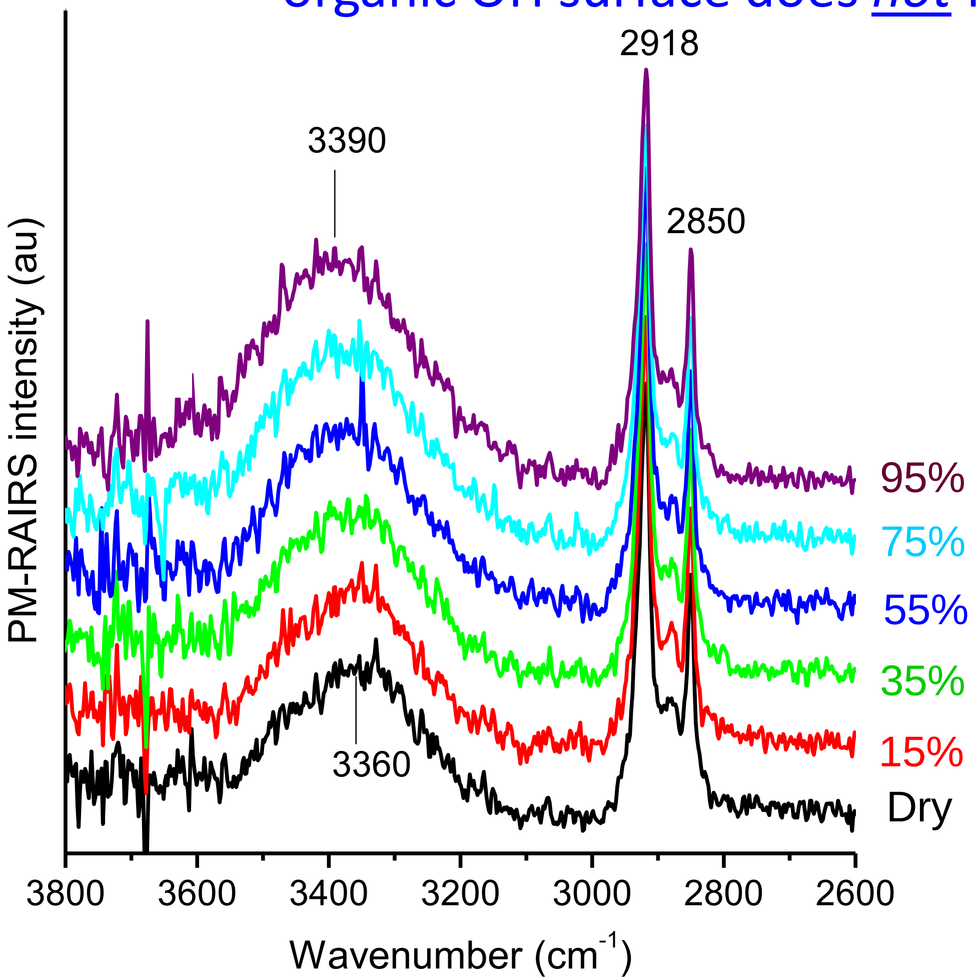
Water adsorption on SiO_2 in humid ambience

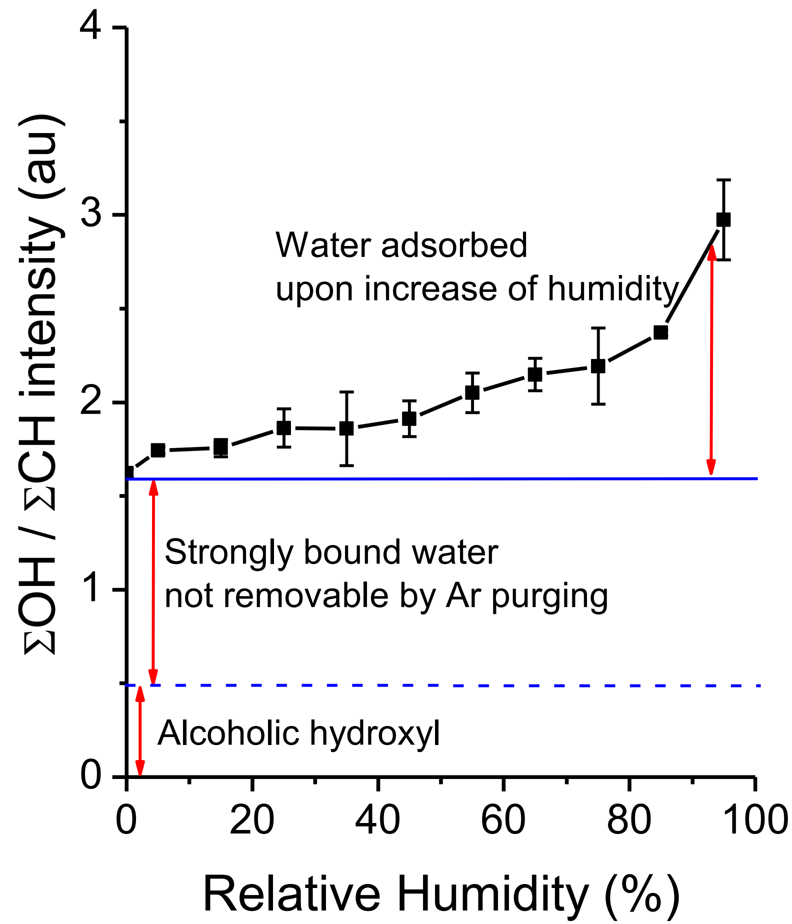


D. B. Asay and S. H. Kim, *J. Phys. Chem. B* **2005,** *109*, 16760

Water contact angle alone cannot tell you much about the structure of water on the solid surface.

Water adsorption on OH-SAM on Au; the “strongly bound” water on organic OH surface does *not* form ice-like structure

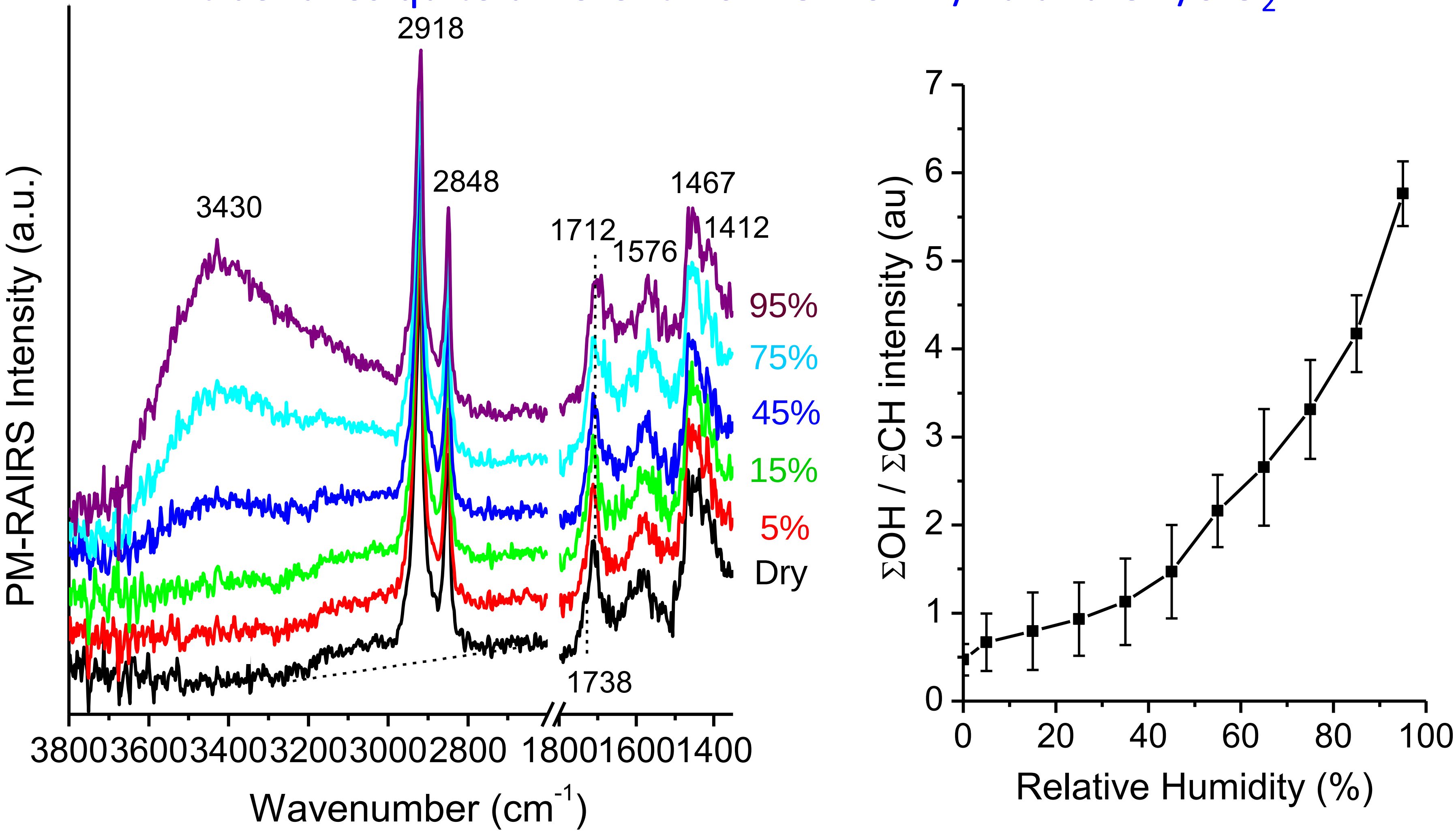




A. Tu, H. R. Kwak, A. L. Barnette, S. H. Kim, *Langmuir* **2012**, *28*, 15263–15269.

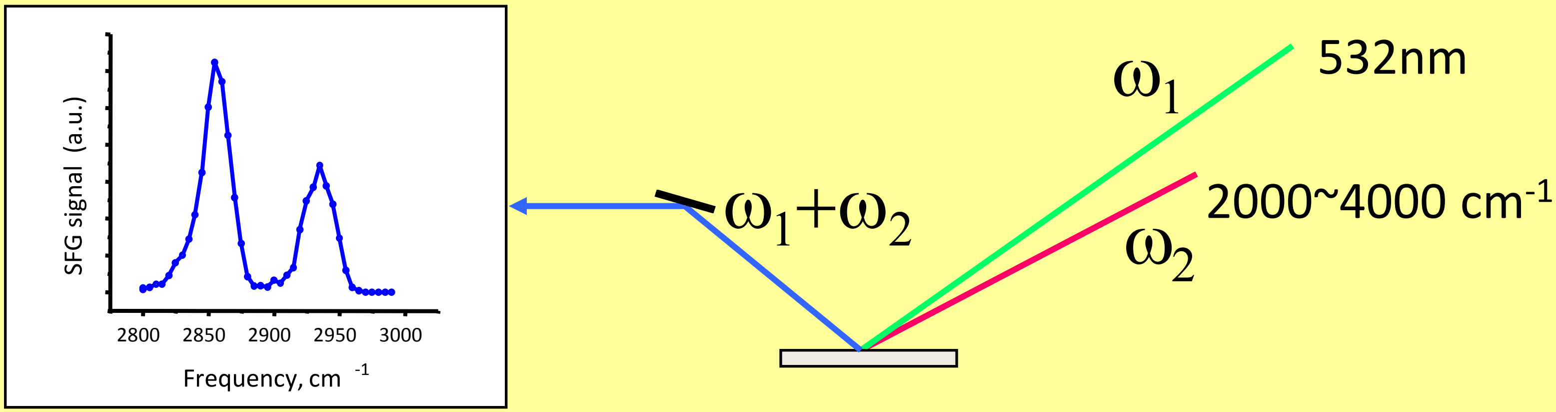
Water contact angle alone cannot tell you much about the structure of water on the solid surface.

Although COOH-SAM/Au also show a water contact angle is <5°, it behaves quite different from OH-SAM/Au and OH/SiO_2.



A. Tu, H. R. Kwak, A. L. Barnette, S. H. Kim, *Langmuir* **2012**, *28*, 15263–15269.

Sum-Frequency-Generation (SFG) Vibration Spectroscopy



$$I(\omega_{SFG}) \propto \left|\chi_{eff}^{(2)}\right|^2 I(\omega_{VIS}) I(\omega_{IR})$$

SFG occurs at the interface or in the bulk with *no inversion symmetry* $\left|\chi^{(2)}\right|^2 \neq 0$

To generate SFG signals: $I(\omega_{SFG}) \propto |\chi_{eff}{}^{(2)}|^2 I(\omega_{VIS}) I(\omega_{IR})$

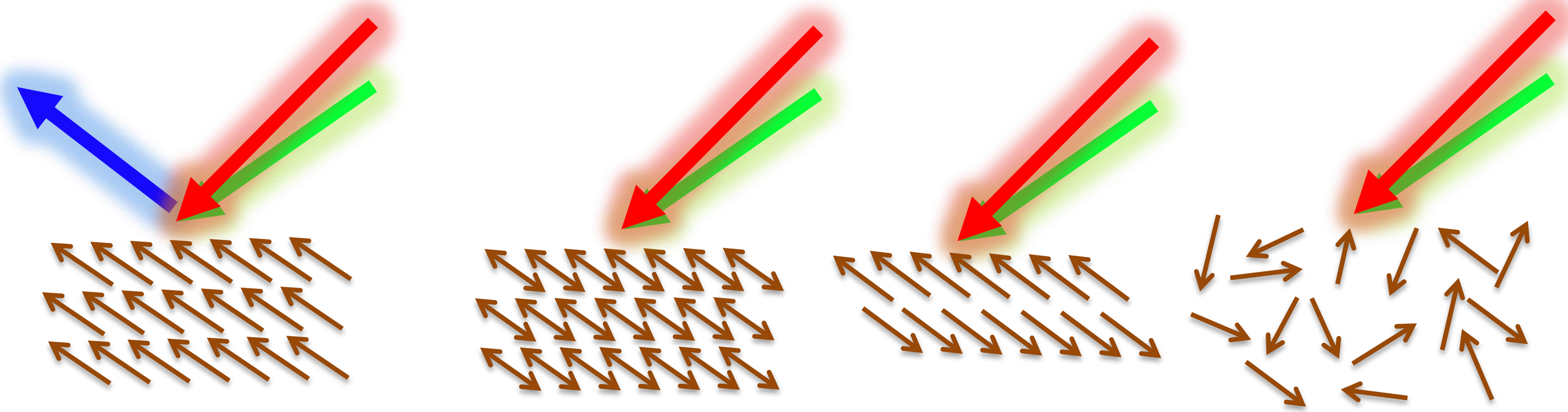
$\chi_{eff}{}^{(2)} \neq 0$

No inversion symmetry in both molecular and optical length scales

$$\underbrace{\chi_{eff}{}^{(2)} = 0}$$

Inversion symmetry

Random



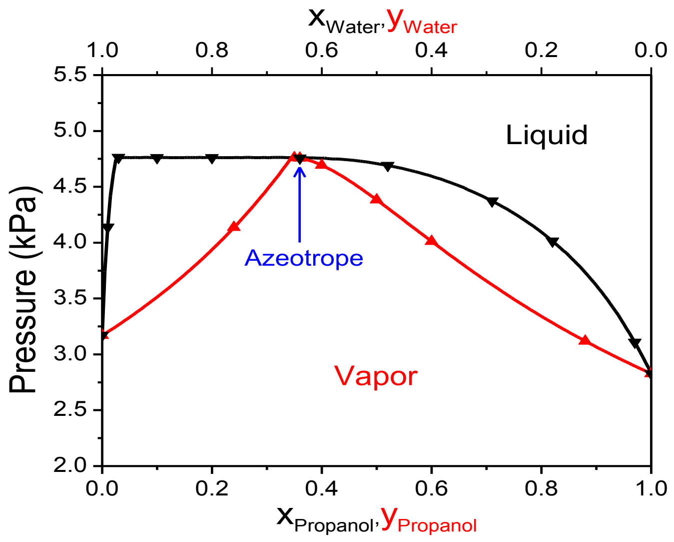
Piezoelectric crystals
Crystalline biopolymers
Interfaces

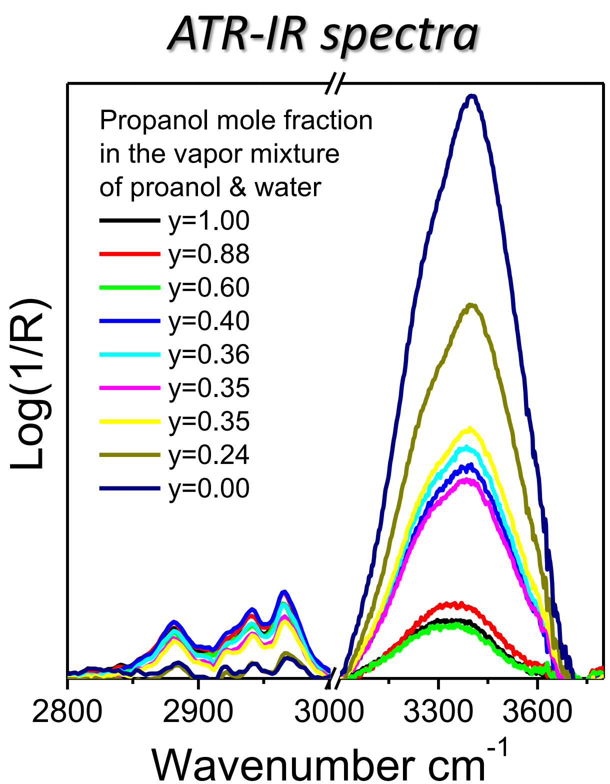
Centrosymmetric crystals
(such as NaCl)
Symmetrically arranged groups
(such as CH_2 in well-packed SAM or lipid bilayer)

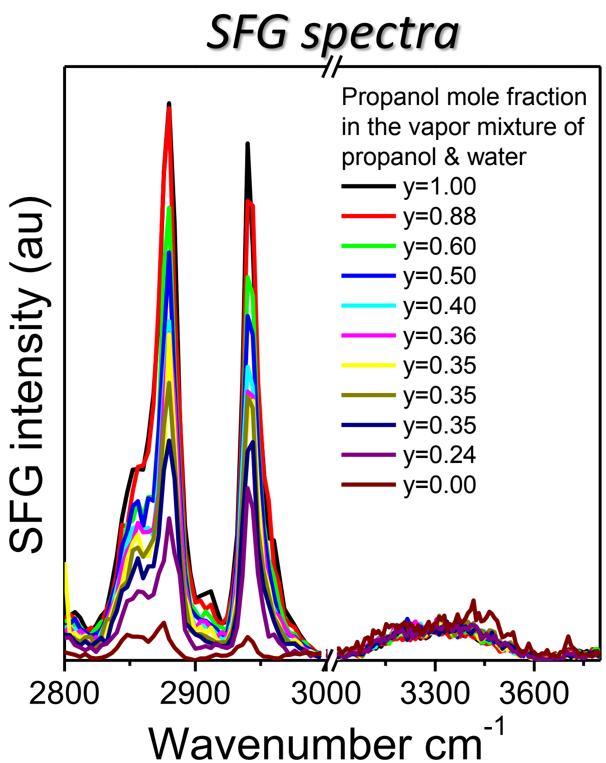
Amorphous polymers
Bulk water & ***vapor***
Glass

Co-adsorption of water & alcohol on SiO_2

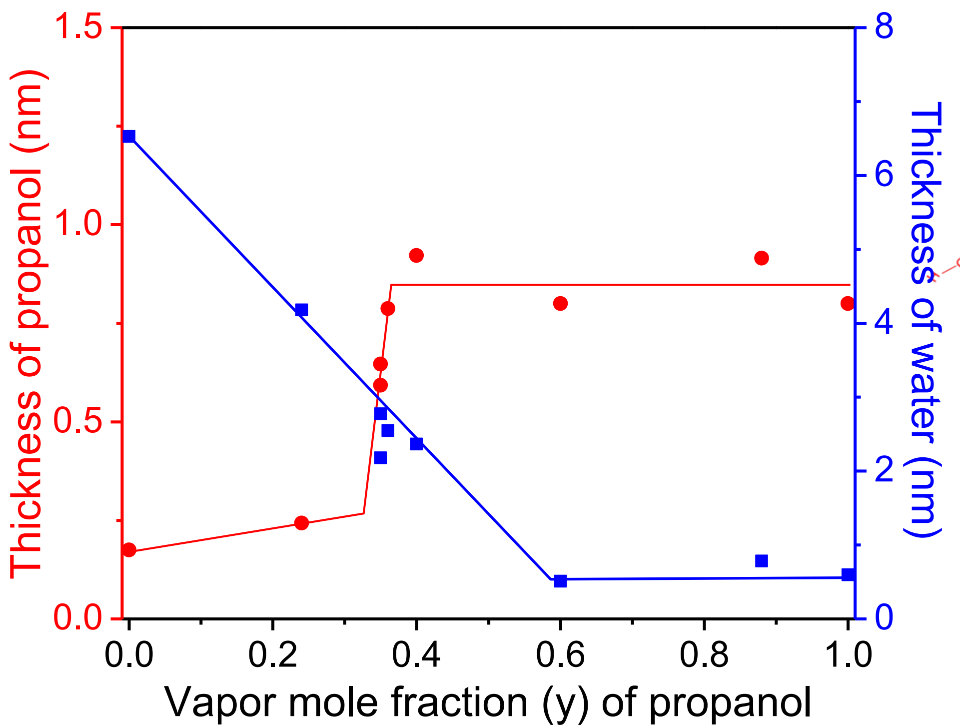
A. L. Barnette and S. H. Kim,
J. Phys. Chem. C **2012**, 116, 9909-9916.

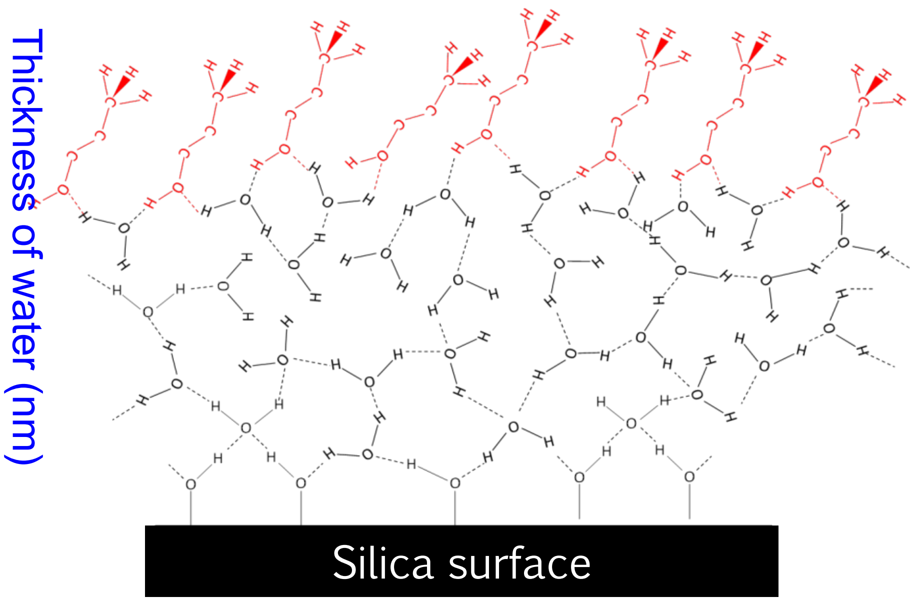






Co-adsorption of water & alcohol on SiO_2

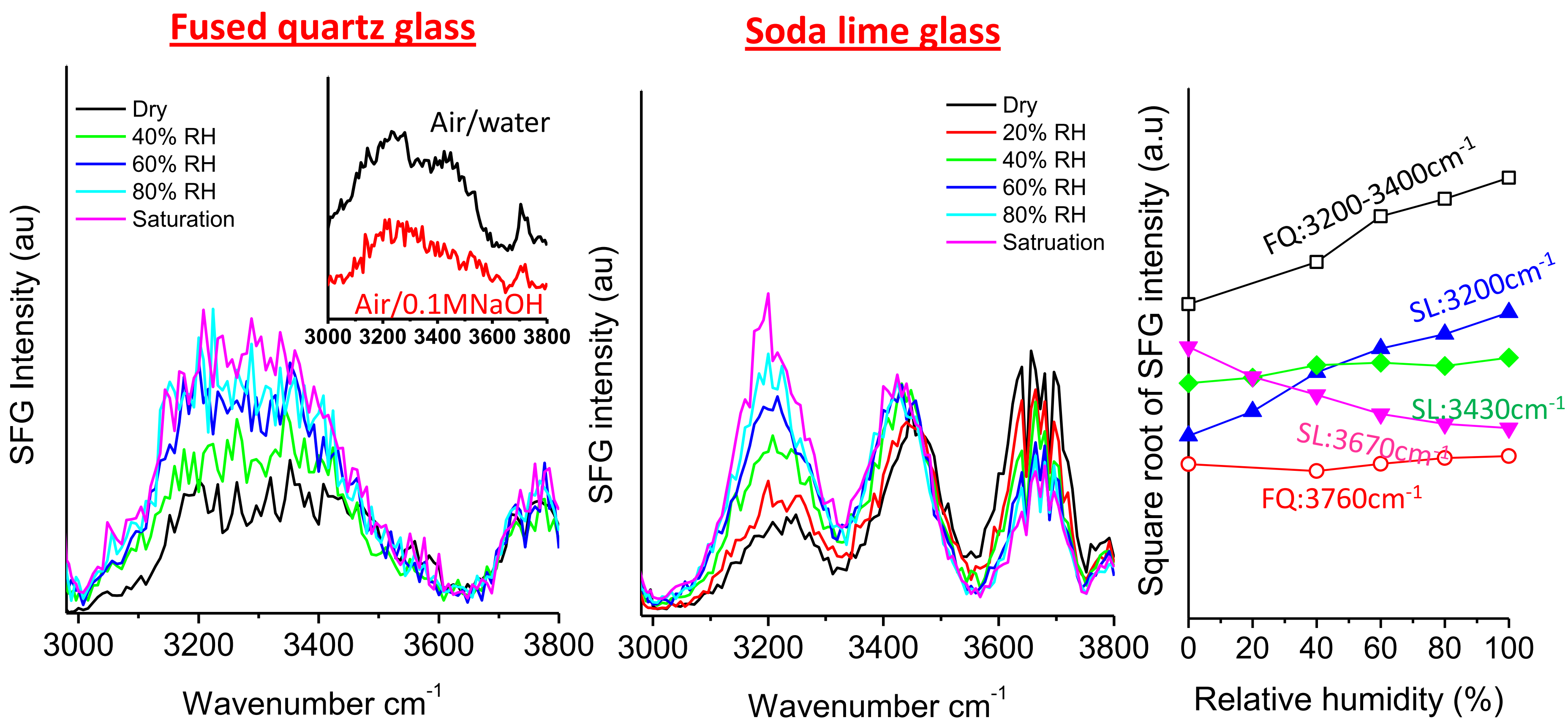




A. L. Barnette and S. H. Kim *J. Phys. Chem. C* **2012**, *116*, 9909−9916

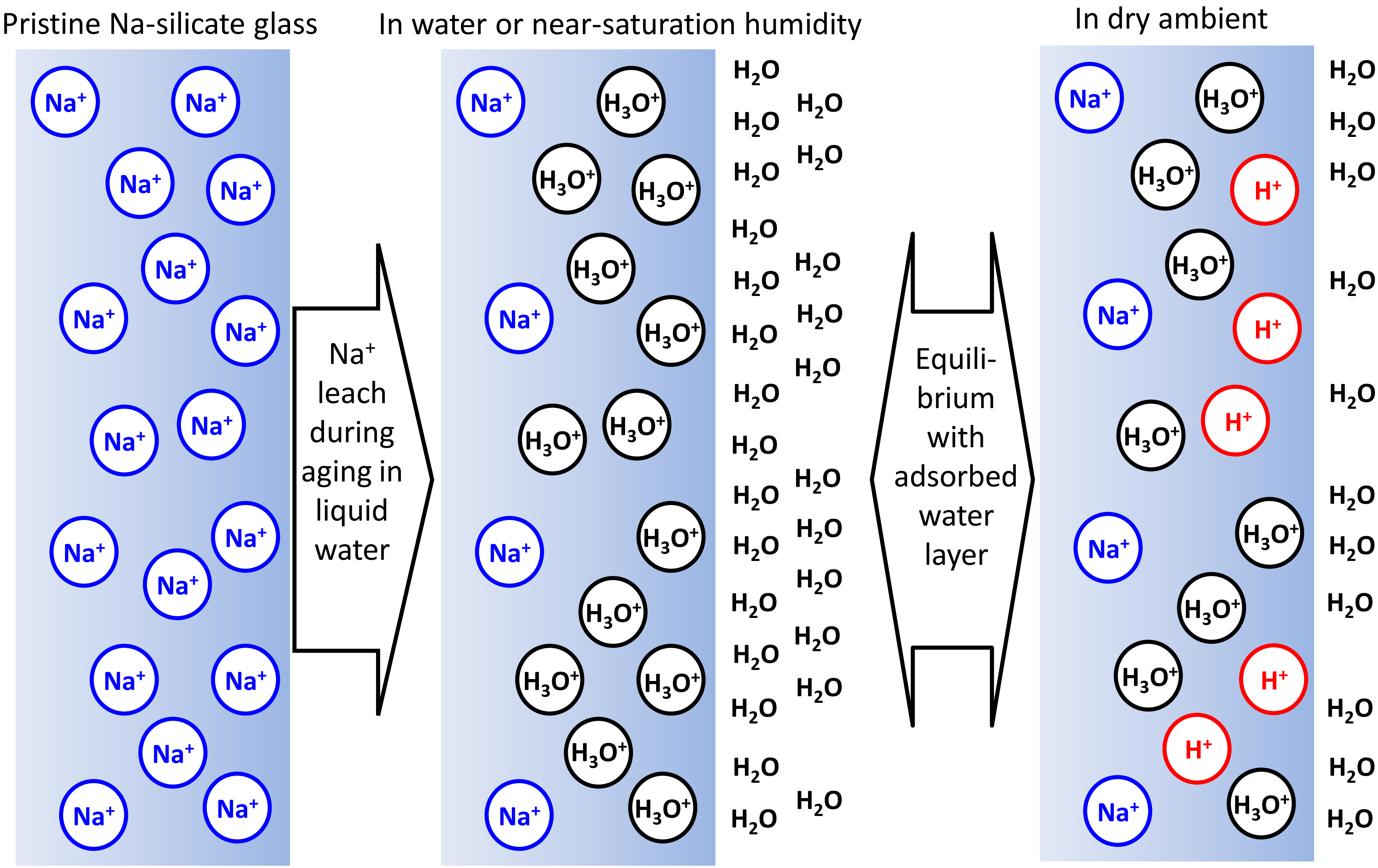
Water adsorption on Glass as ftn of RH

(glass cleaning = ethanol rinsed, and then soaked/aged in water for 3 hr)



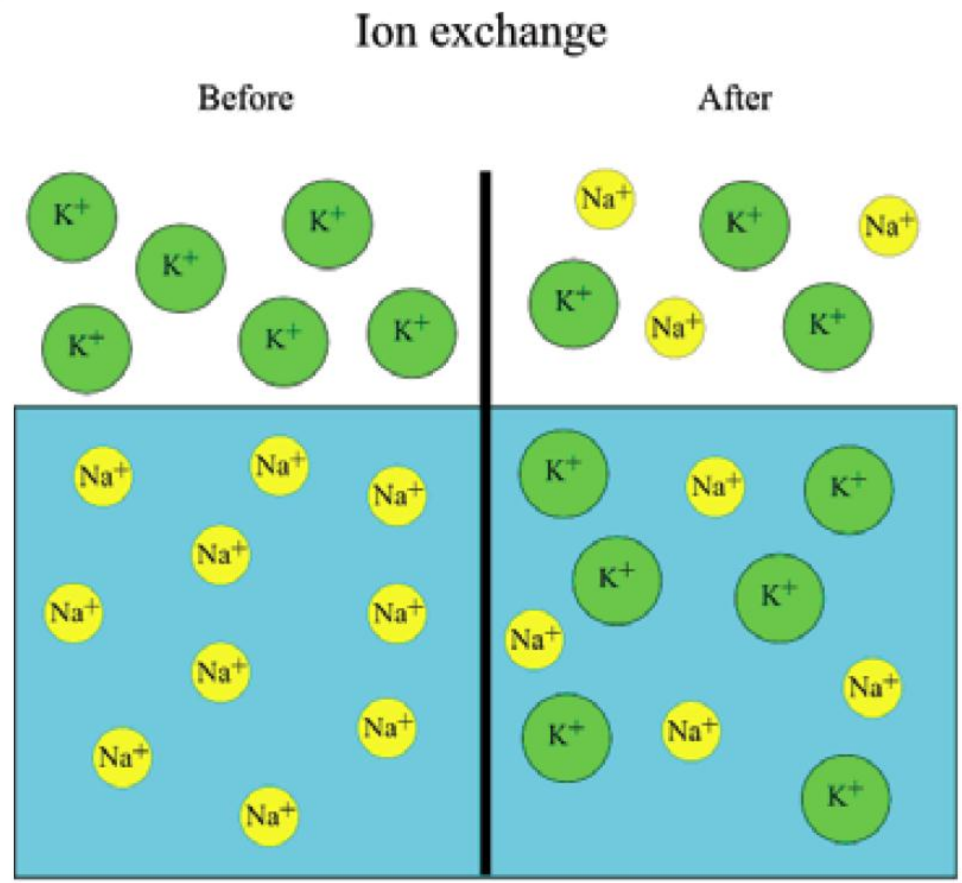
L. Bradley, Z. Dilworth,,, C. G. Pantano, & S. H. Kim
"Hydronium Ions in Soda-lime Silicate Glass Surfaces"
J. Am. Ceram. Soc. (DOI: 10.1111/jace.12136)
(Article first published online: 24 DEC 2012)

The water molecules diffusing into the glass surface may find protons in the Na^+-leached sites and form hydronium ions.

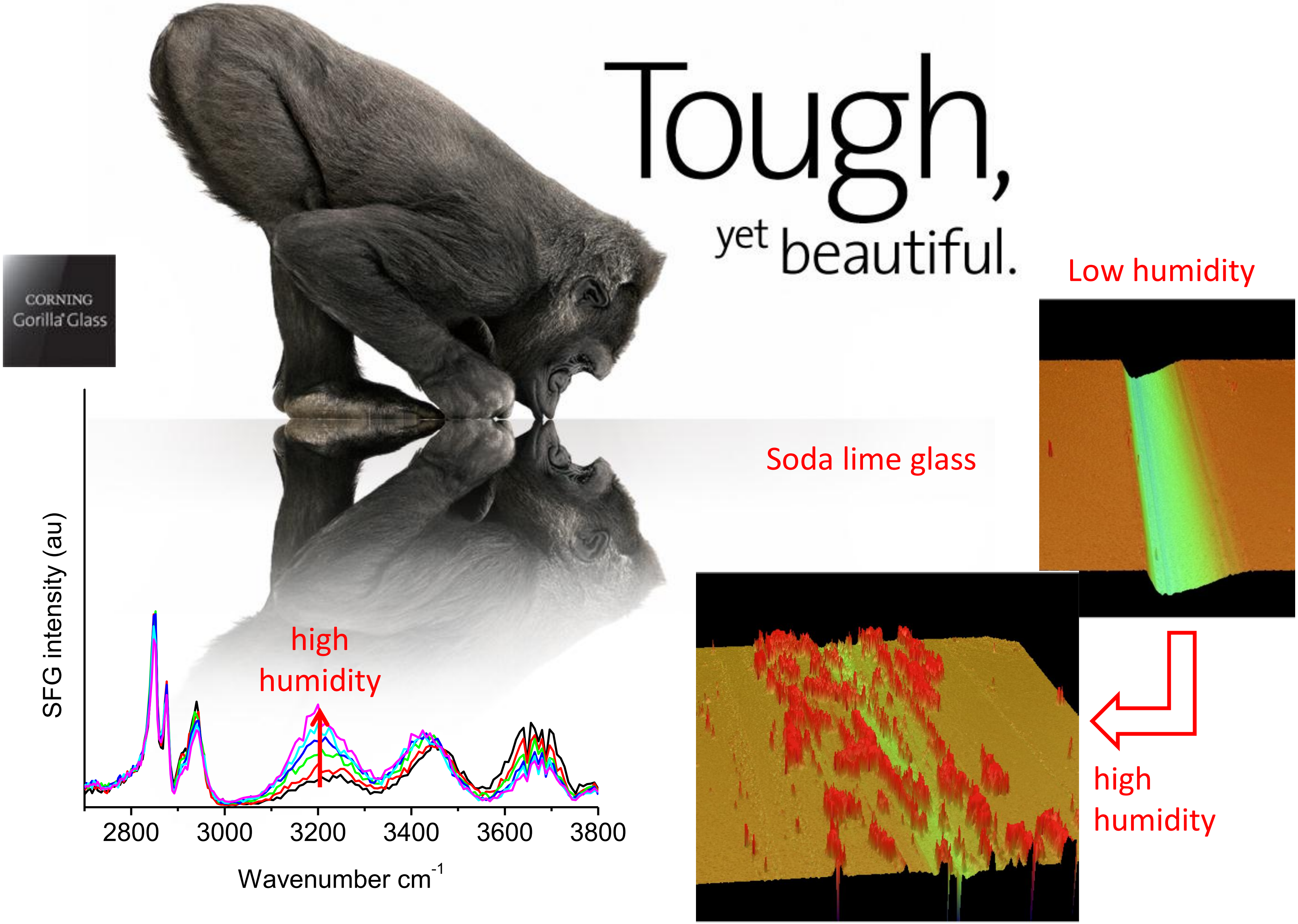


CORNING
Gorilla Glass

Na^+ = 0.1nm
K^+ = 0.14nm
H_3O^+ = 0.14nm



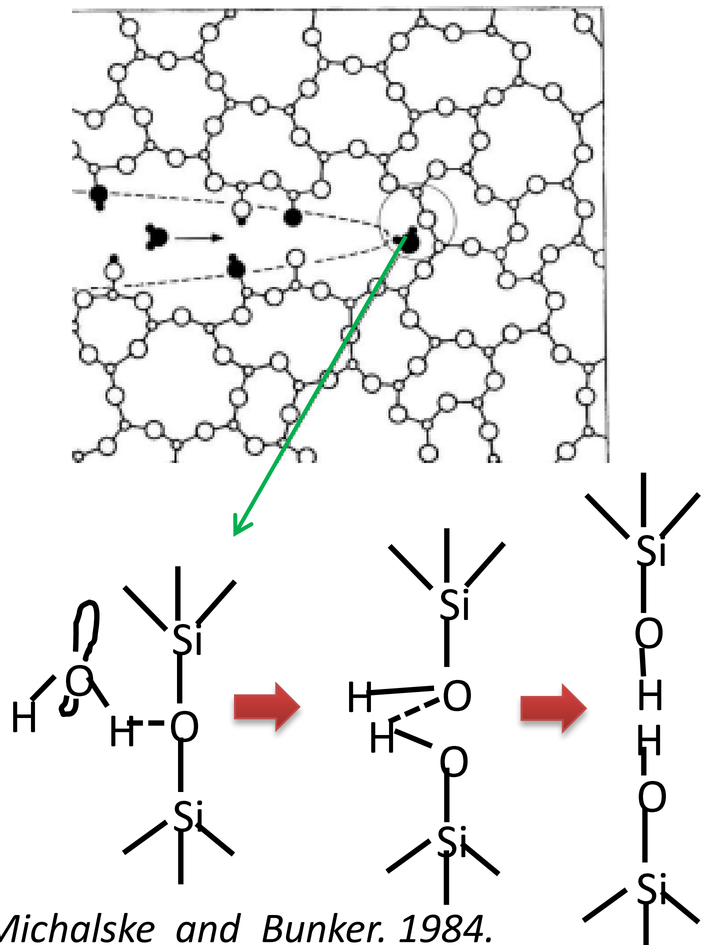
Arun K. Varshneya et al. 2010



Laura Bradley, Zach Dilworth, et al. *J. Am. Ceram. Soc.* (DOI: 10.1111/jace.12136)

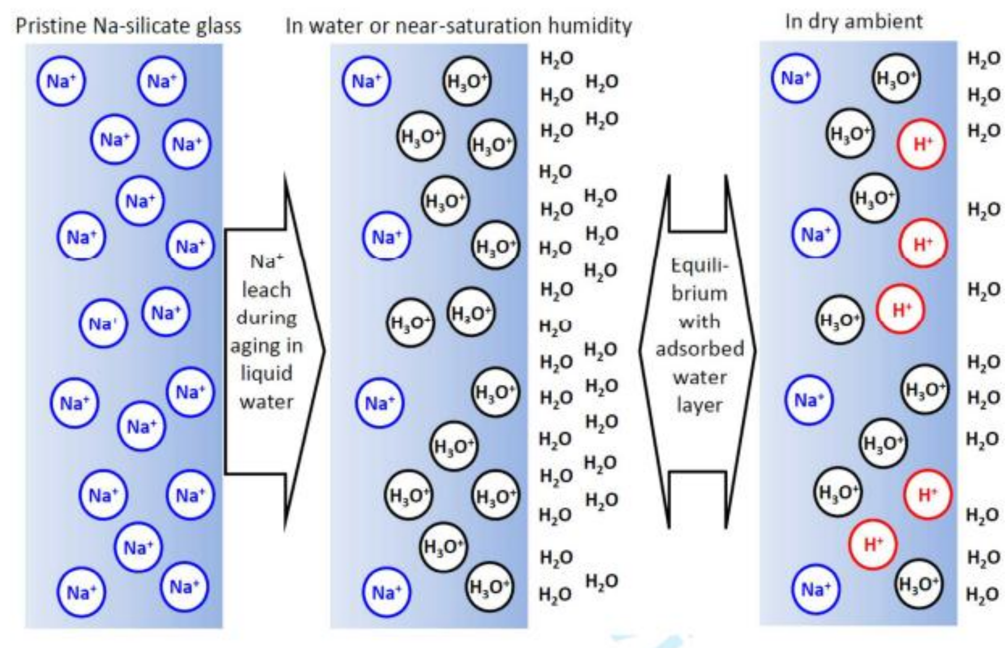
Water ingression into glass

Hydrolysis & network corrosion



Michalske and Bunker. 1984.

Solvation of H^+ in the leached Na^+ site forming H_3O^+

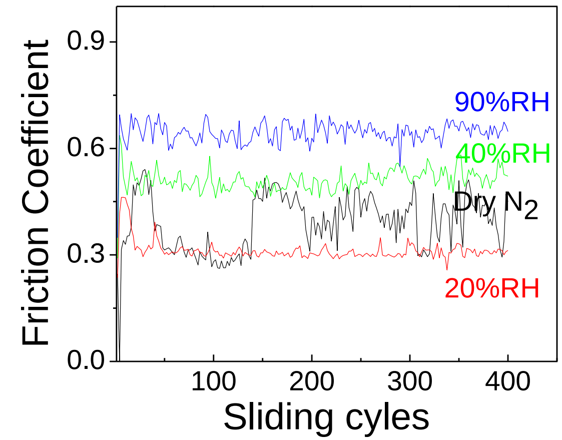


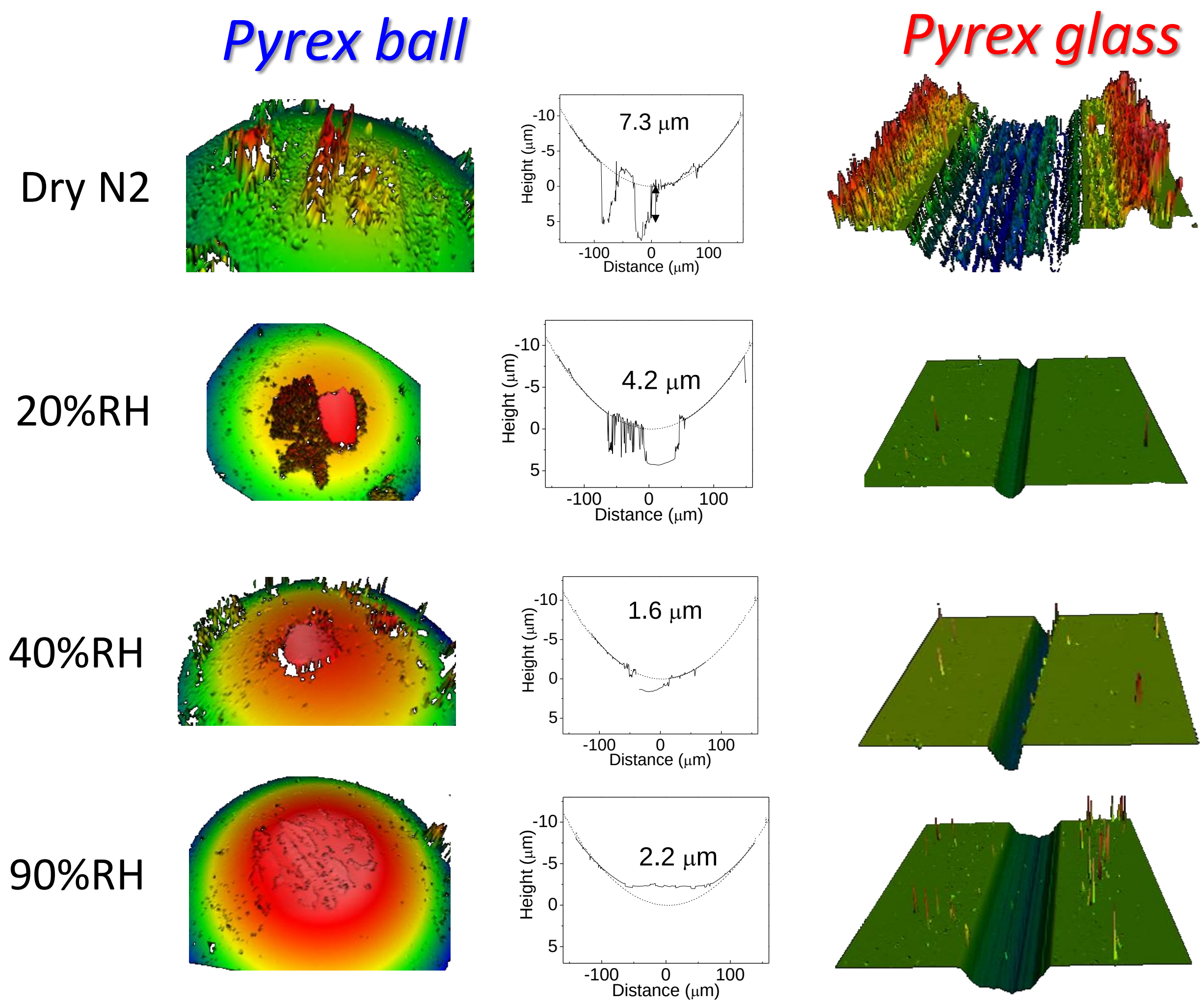
L. C. Bradley et al. JACERS 2013

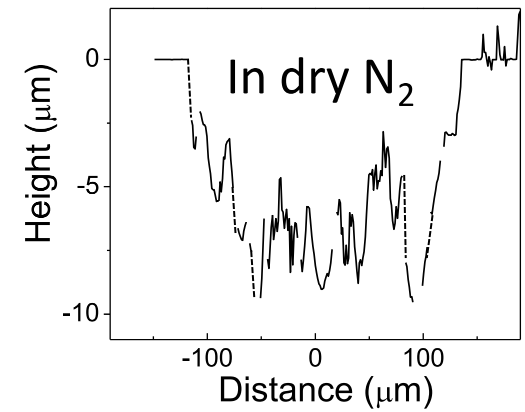
Formation of $H^{3}O+$ formation
in the Na^{+}-leached site??

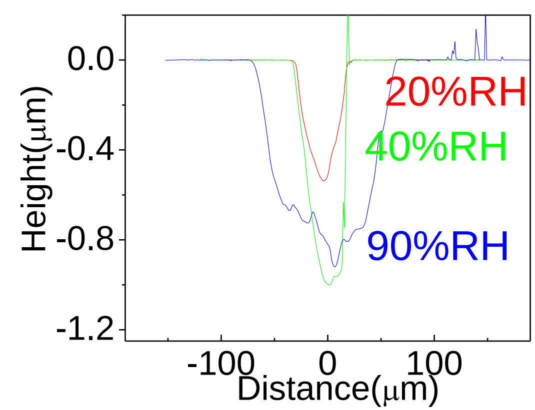
Searching for more supporting evidences..

The wear resistance at 90% RH is ***not*** observed for *pyrex glass substrate* rubbed with *pyrex glass ball*

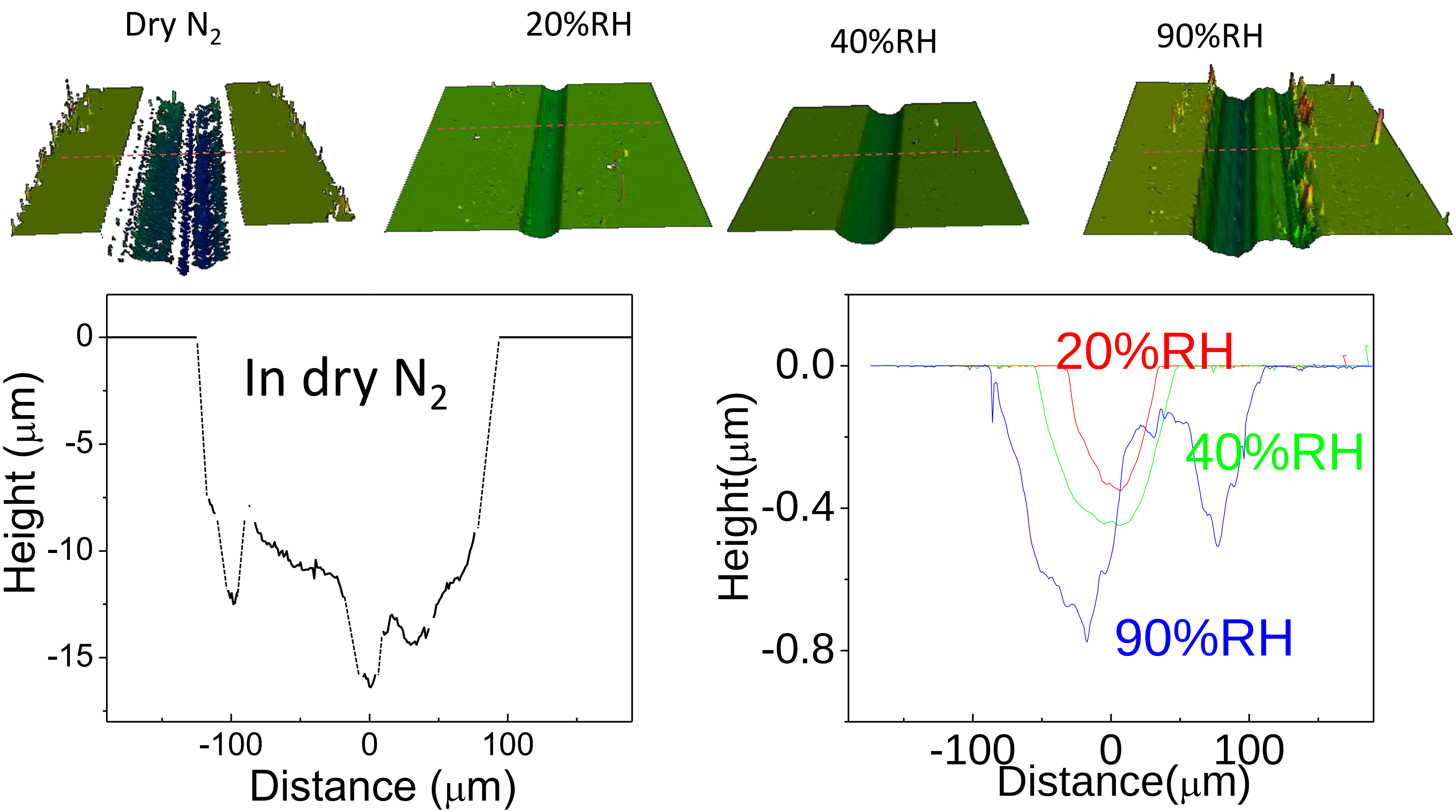








The wear resistance at 90% RH is ***not*** observed for ***AF45 alkali-free borosilicate glass*** rubbed with *pyrex glass ball*



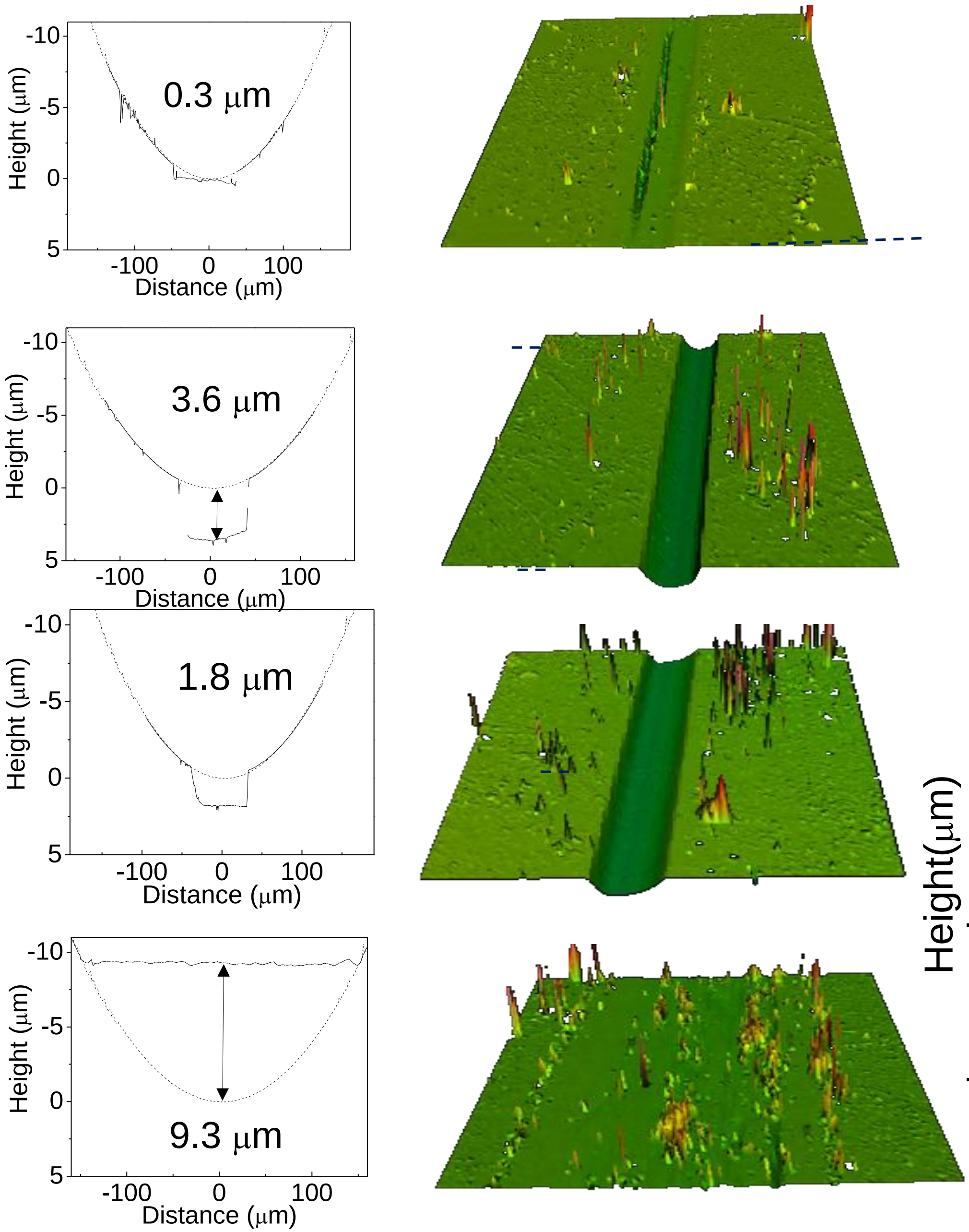
How about chemically-strengthened glasses?

Dry N_2

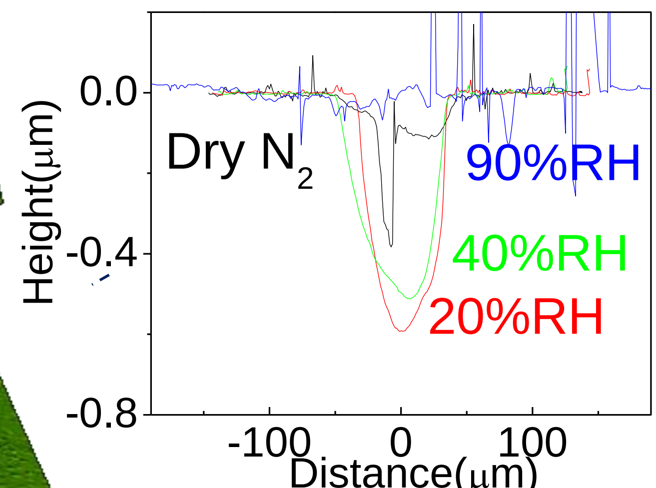
20%RH

40%RH

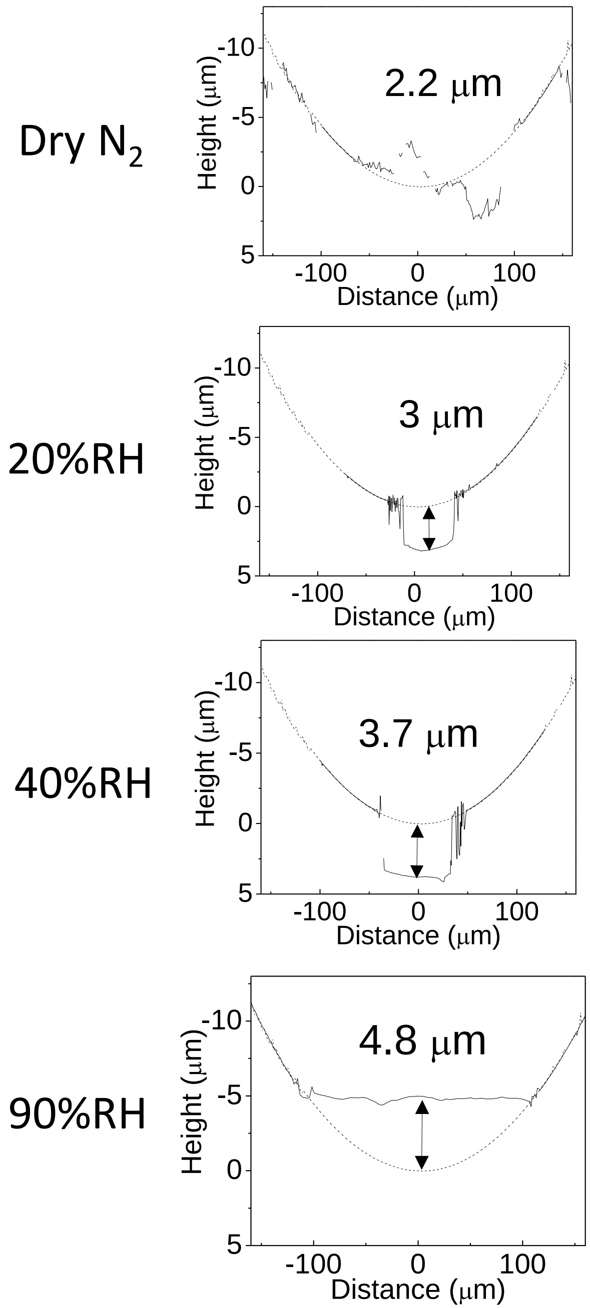
90%RH

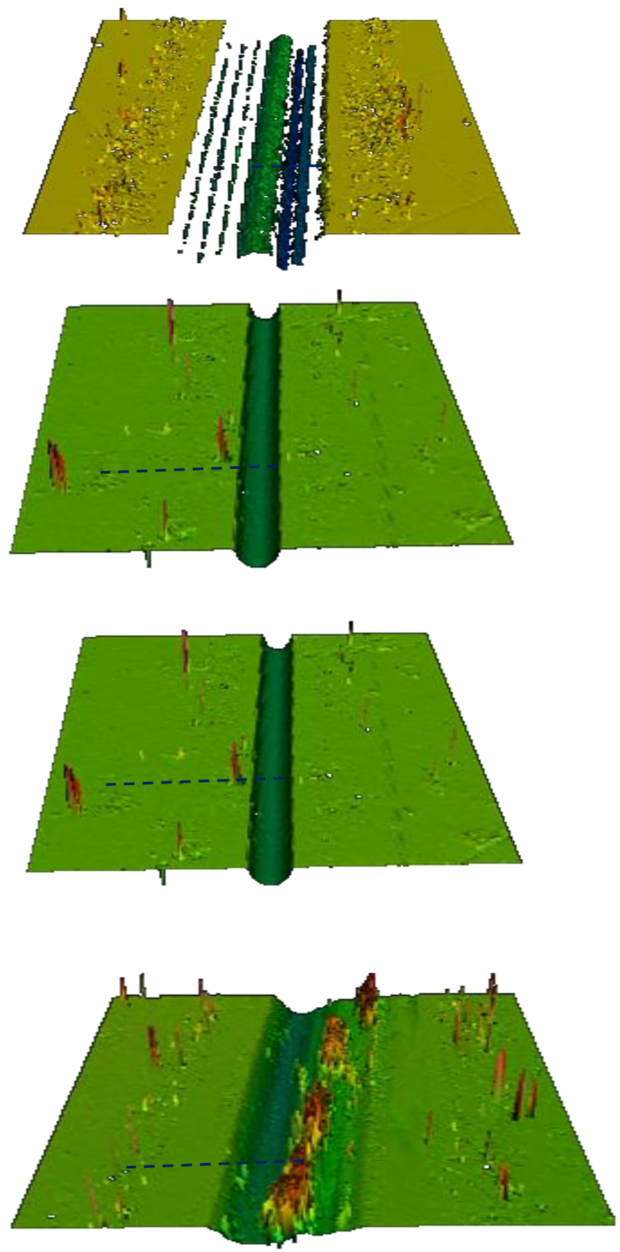


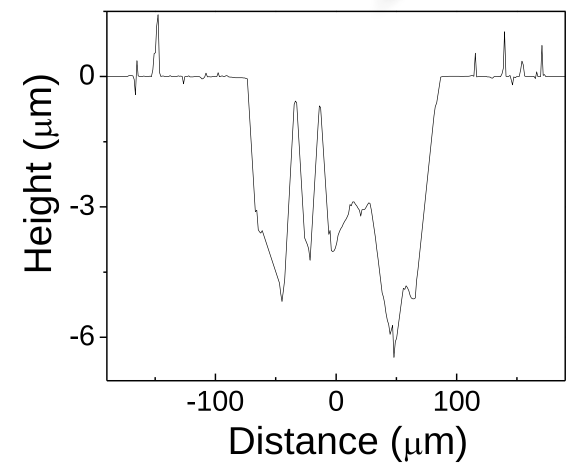
Apple iPad glass

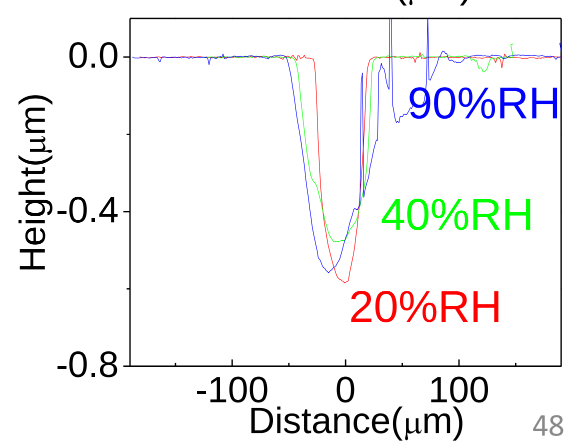


HTC cellphone glass









The surface chemistry of counter-surface sliding against glass matters…

Not only vapor environment, but also counter surface of rubbing matter…

Diamond tip (curvature=200nm)

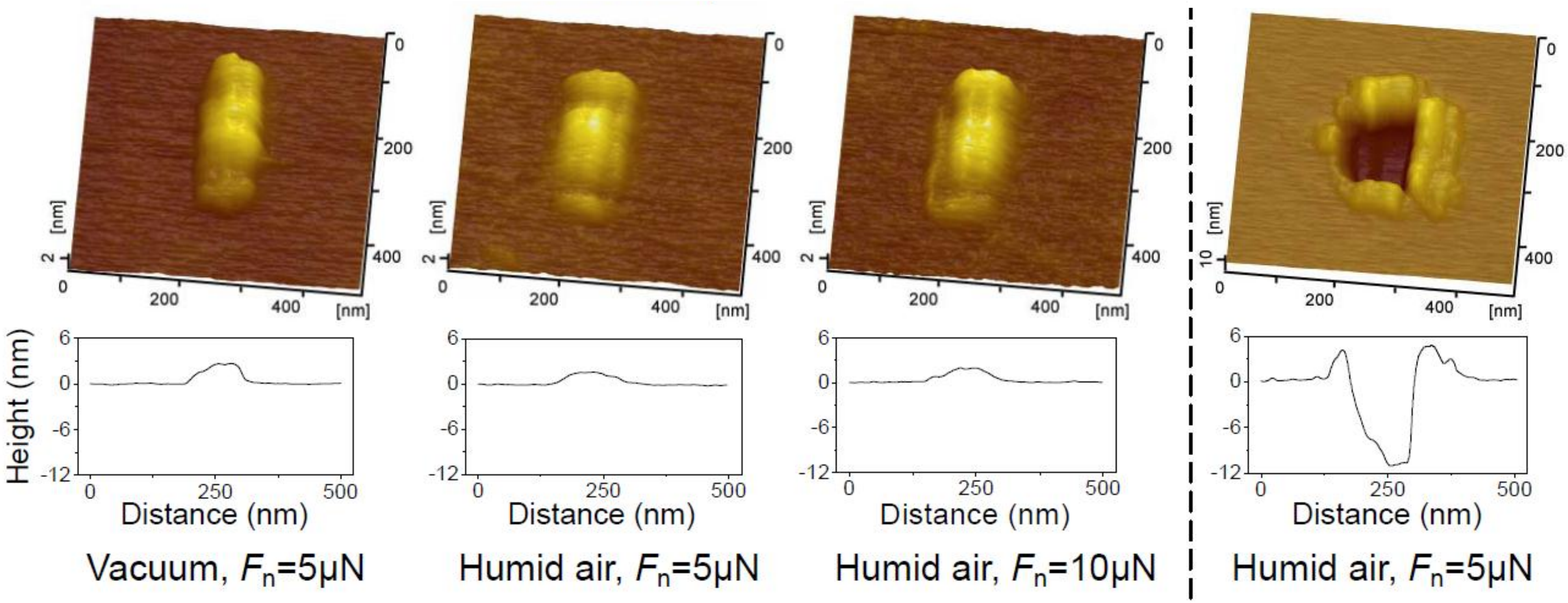
When $P_{contact}$ < Hardness → hillock (surface protrusion)

When $P_{contact}$ > Hardness → wear (material removal)

SiO_2 ball

(diameter=1000nm)

$P_{contact}$ << Hardness



Substrate = Si wafer with native SiO_2

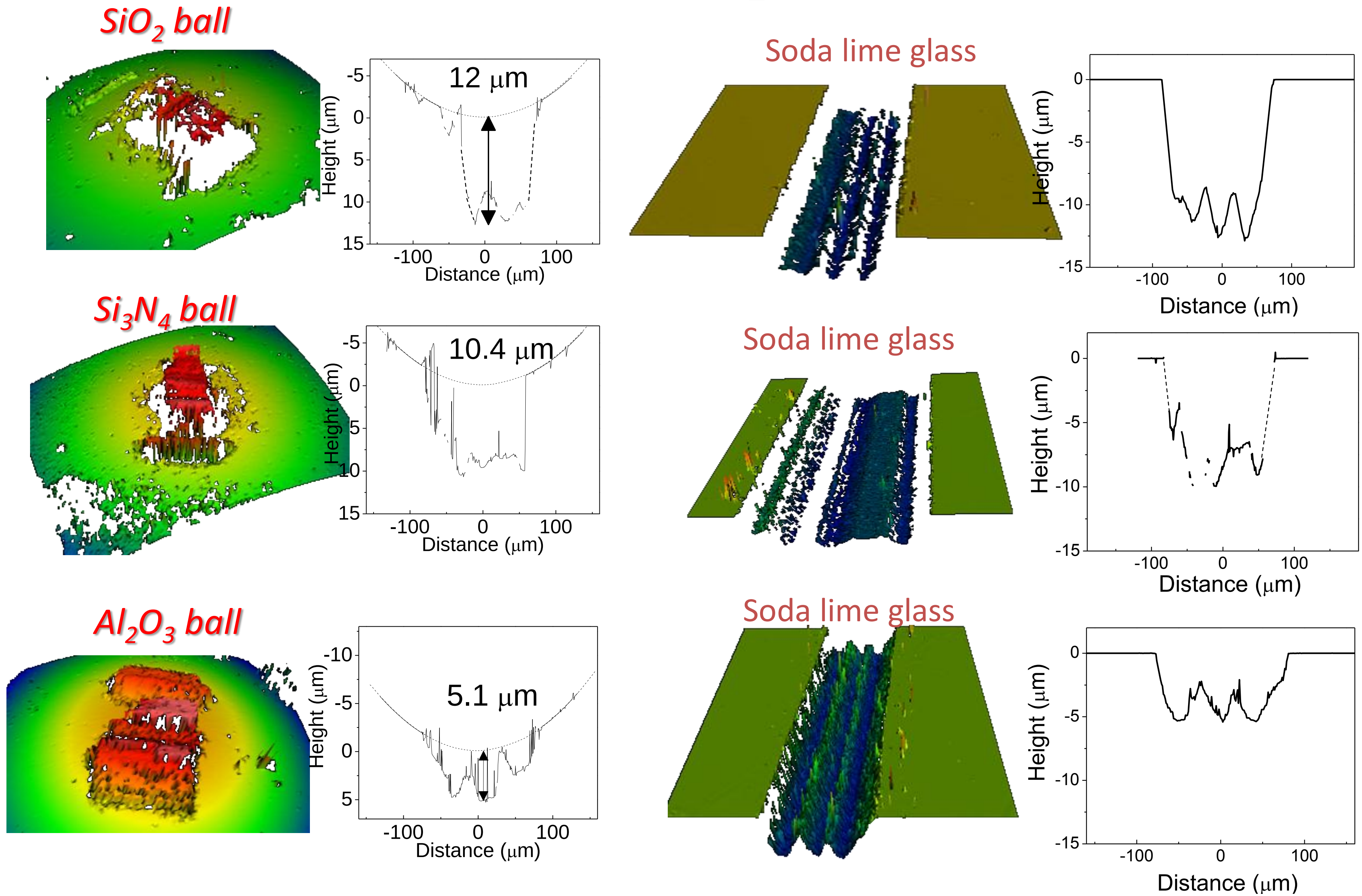
J. Yu, S. H. Kim, B. Yu, L. Qian, and Z. , *ACS Appl. Mater. Interfaces* **2012**, 4, 1585-1593.

We expect a soft material would get easily damaged when rubbed with a hard material…

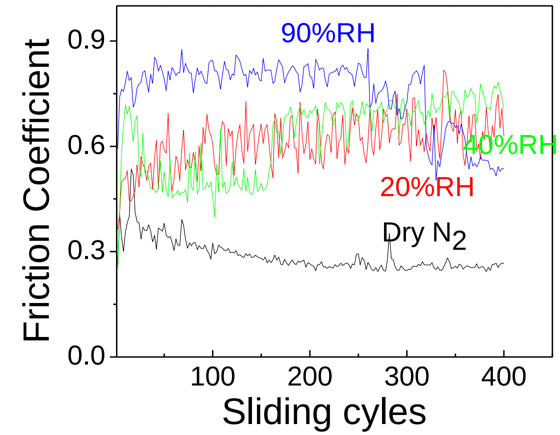
Hardness:

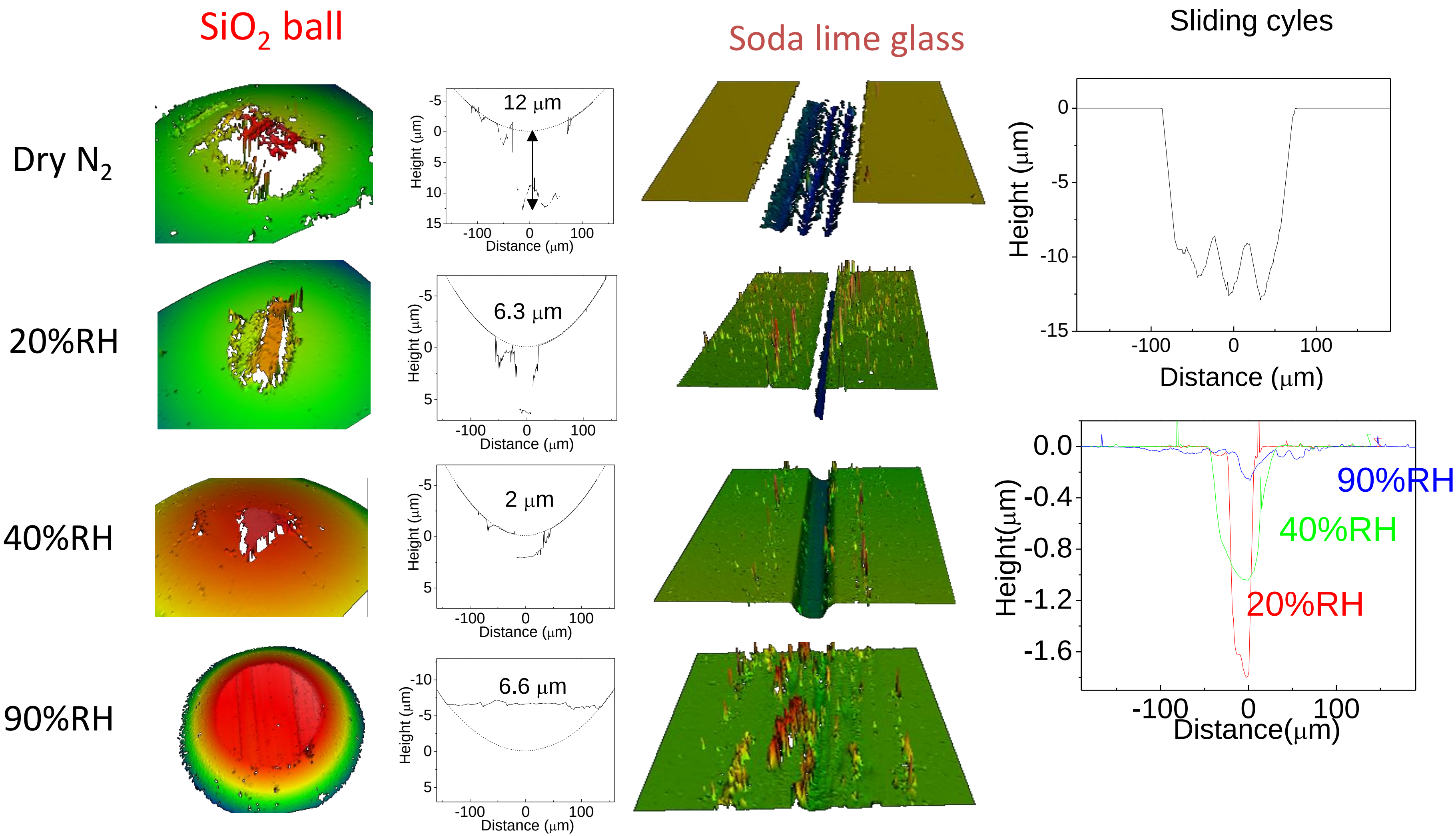
Ball		Substrate
Al_2O_3 = 20GPa		
Si_3N_4 = 14.5GPa	vs.	Soda lime glass = 5.9GPa
SiO_2 = 6.0GPa		
pyrex = 4.3GPa		

No surprise in dry N_2 environment…

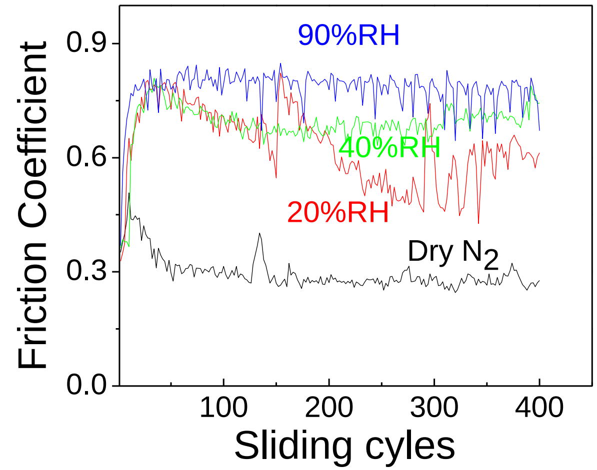


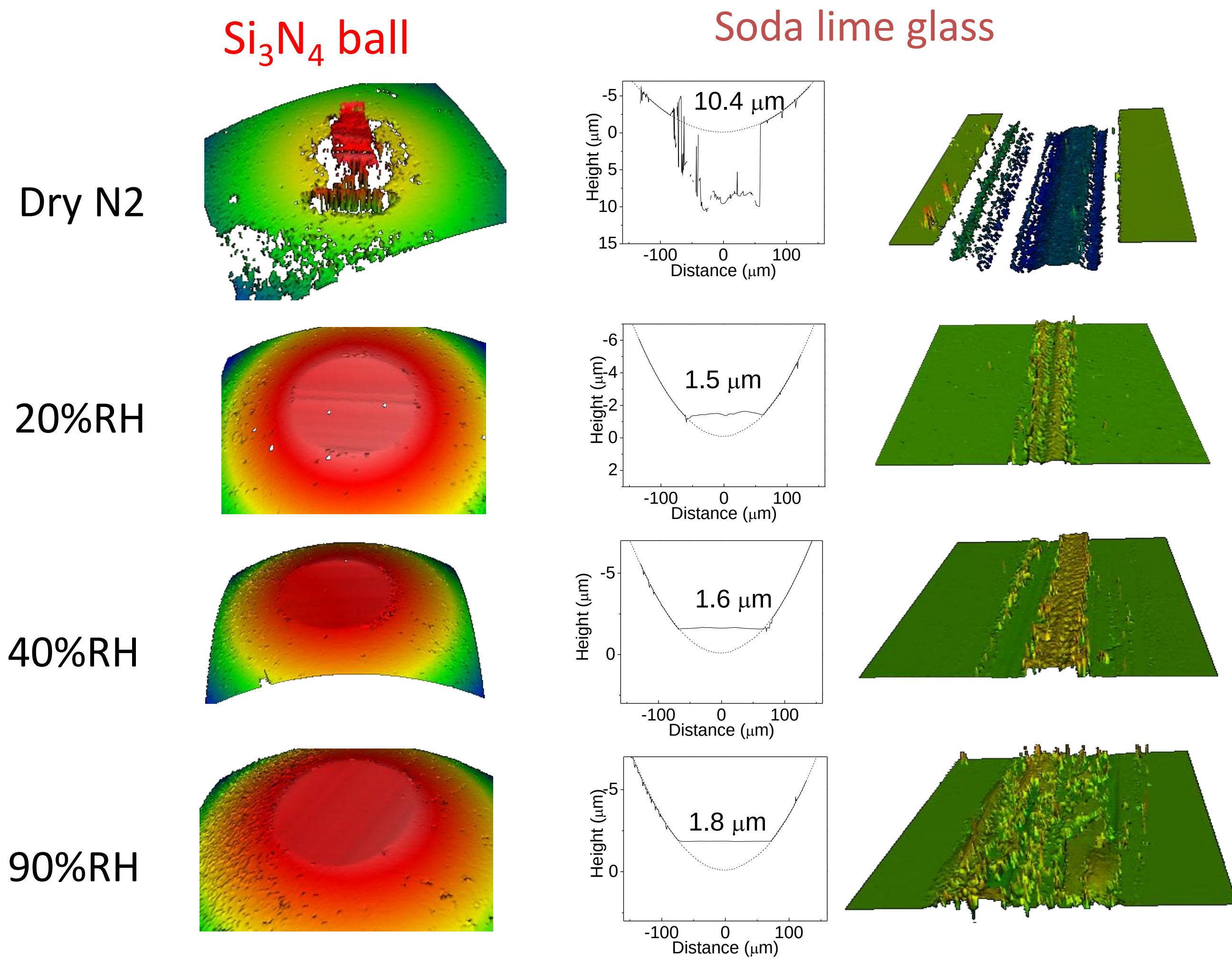
In 90% RH, *SiO_2 ball* wears and the scratch in *soda lime glass* is negligible.

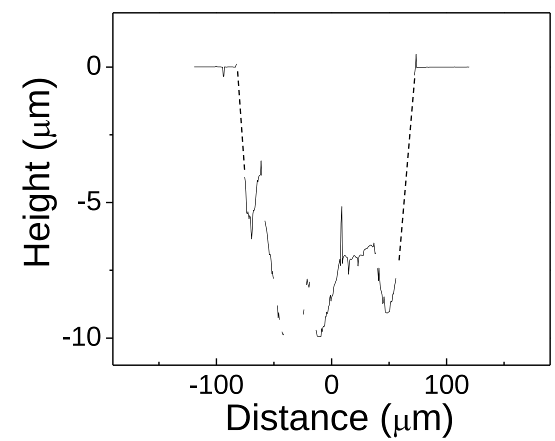


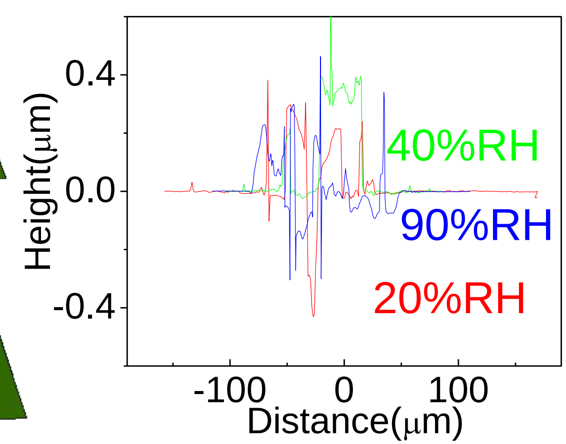


In all humidity, the “hard” ***Si_3N_4 ball*** wears and the “soft” ***soda lime glass*** is almost intact.

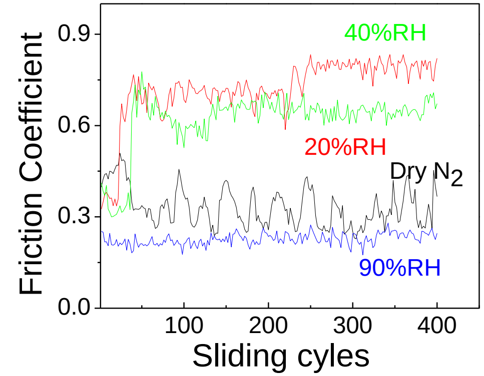


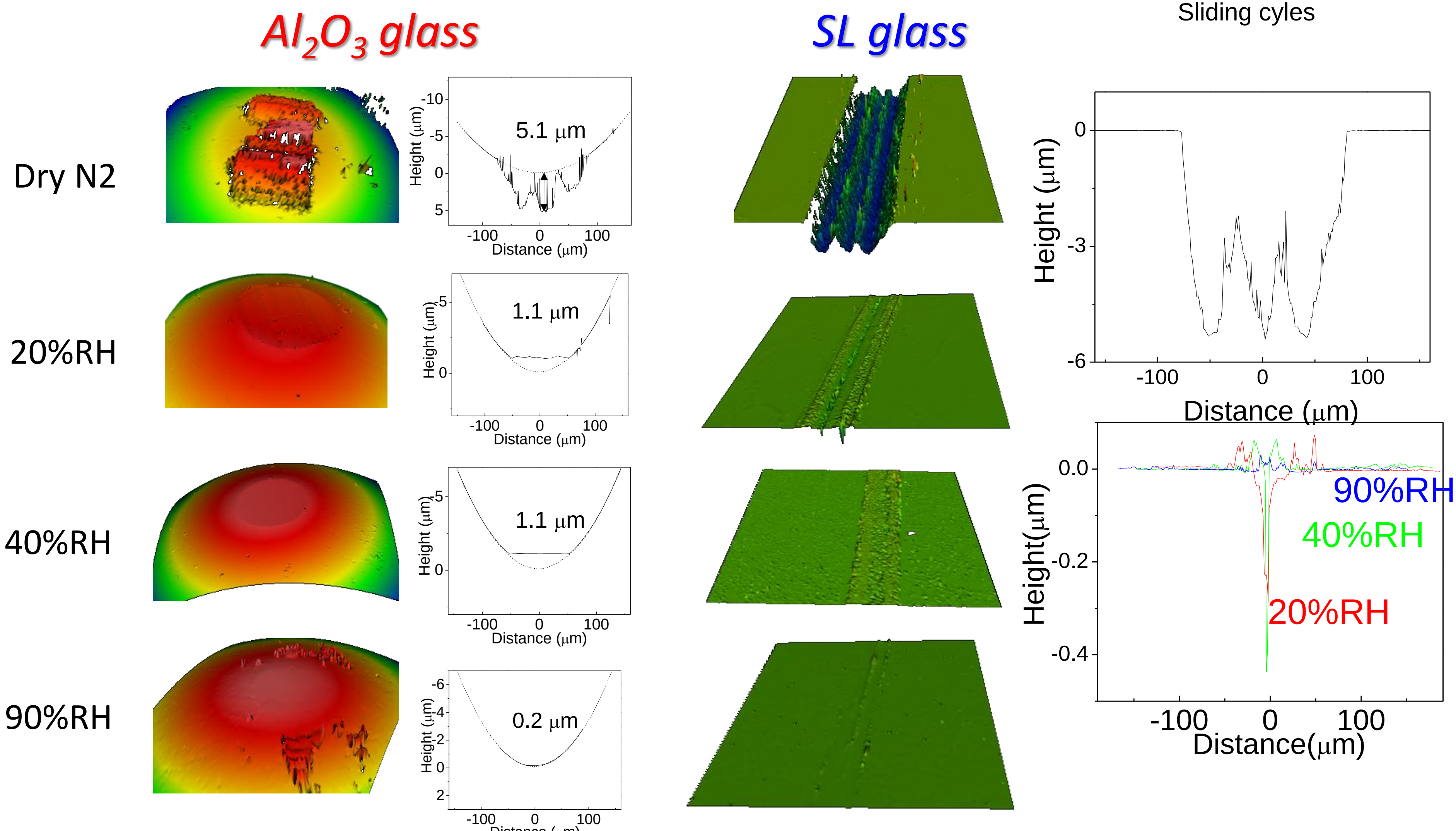






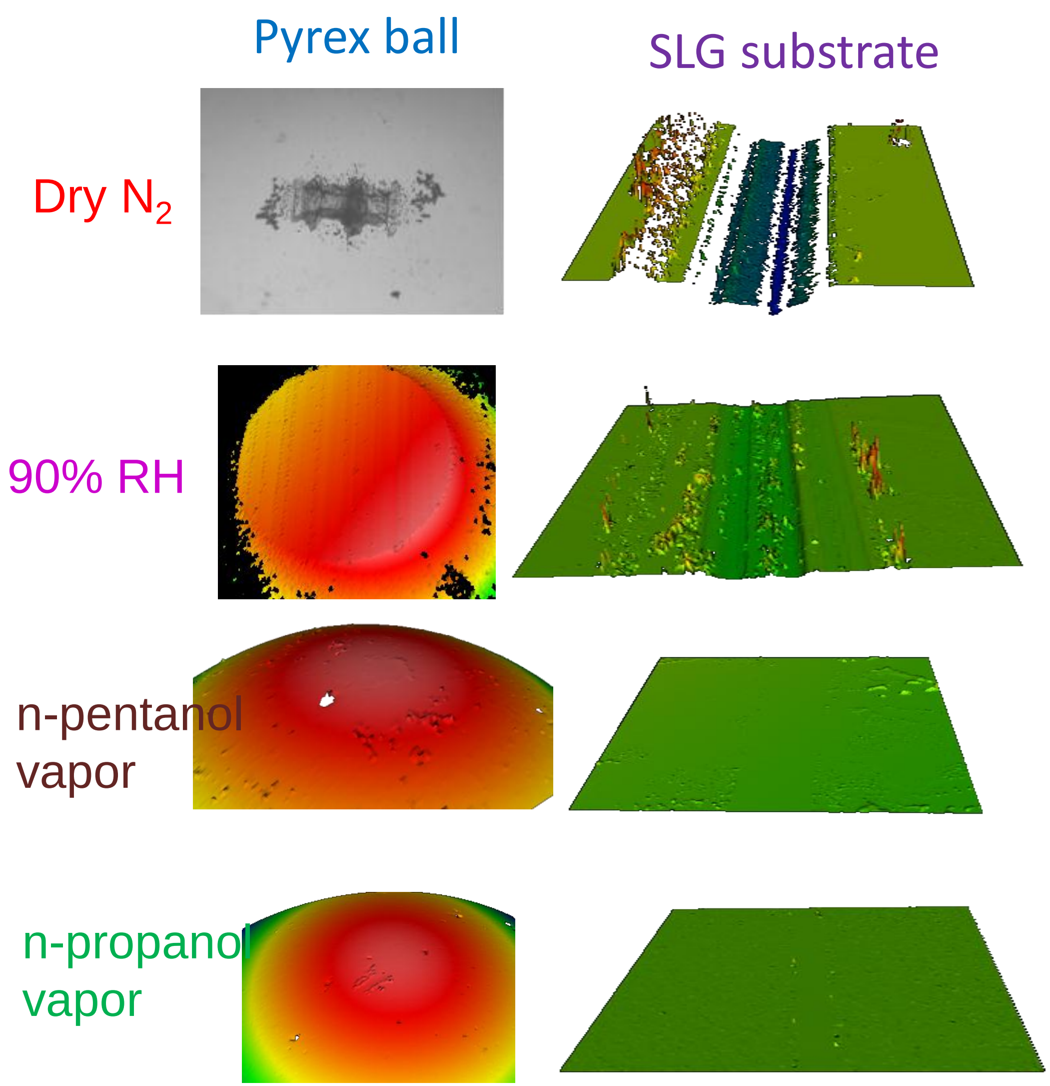
In intermediate humidity, *Al_2O_3 ball* wears and the scratch into ***soda lime glass*** by is very small.

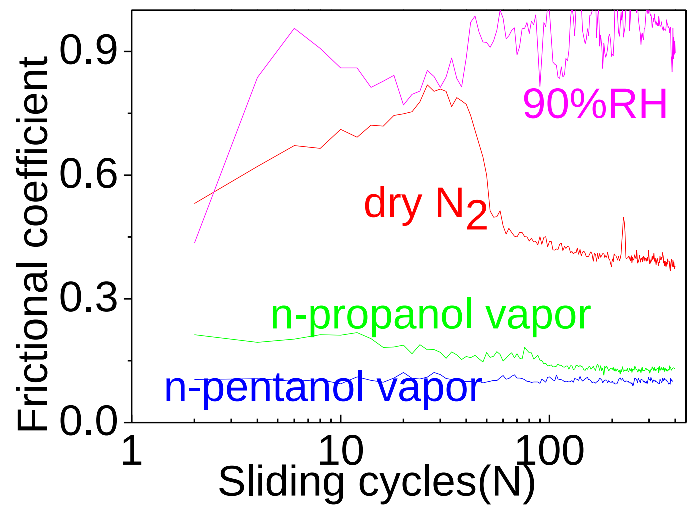


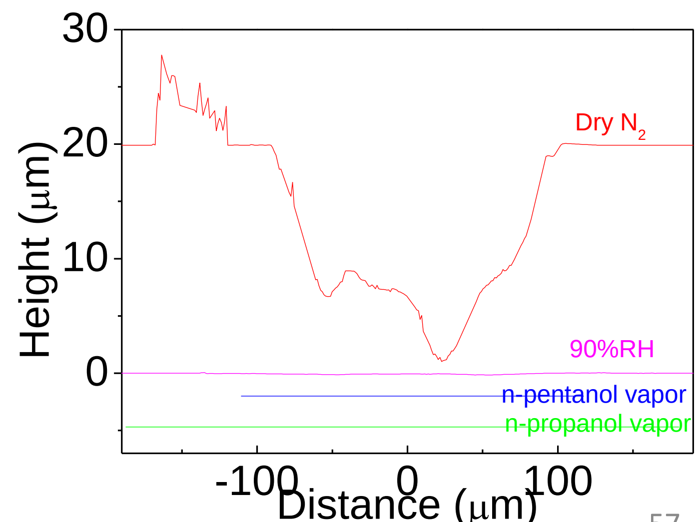


Protecting glass from being scratched using “simple” alcohol adsorption

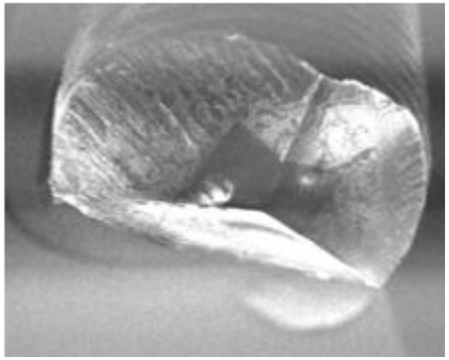
The wear of SLG / pyrex glass interface can be shut off by one monolayer-thic alcohol adsorption



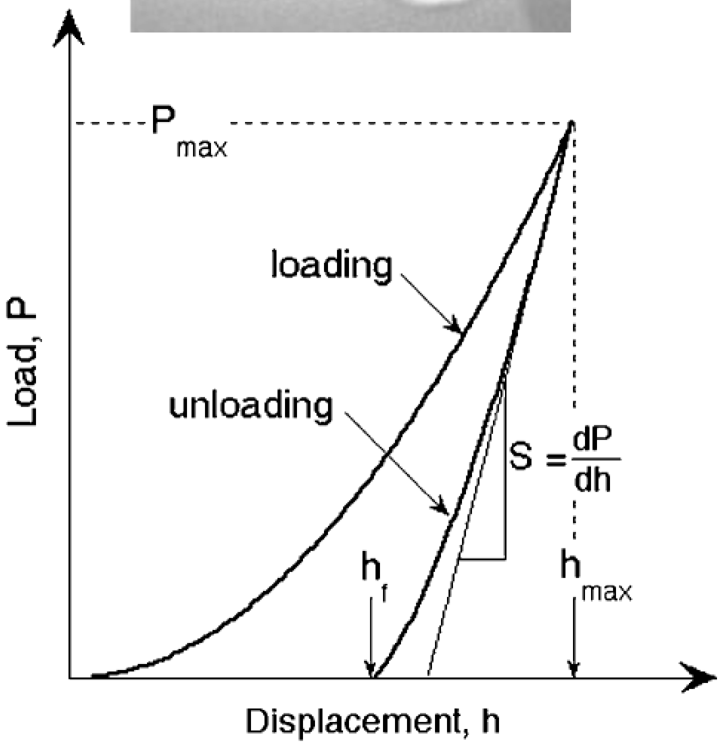




Mechanical property of surface region of glass ???



Nanoindentation test



Indentation load–displacement curve

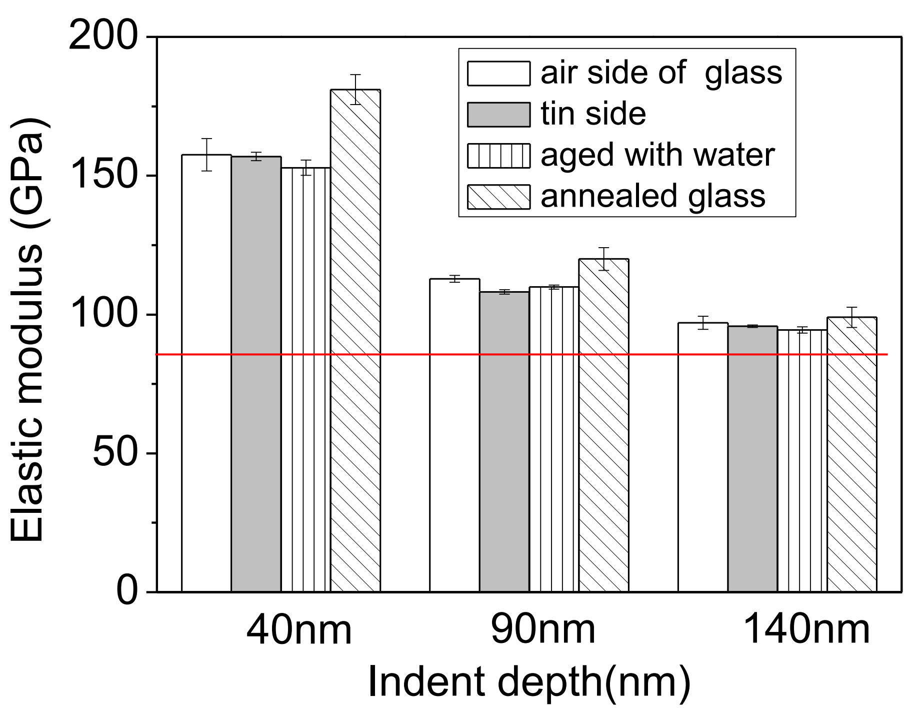
Hardness $H = \dfrac{F_{\max}}{A_p}$

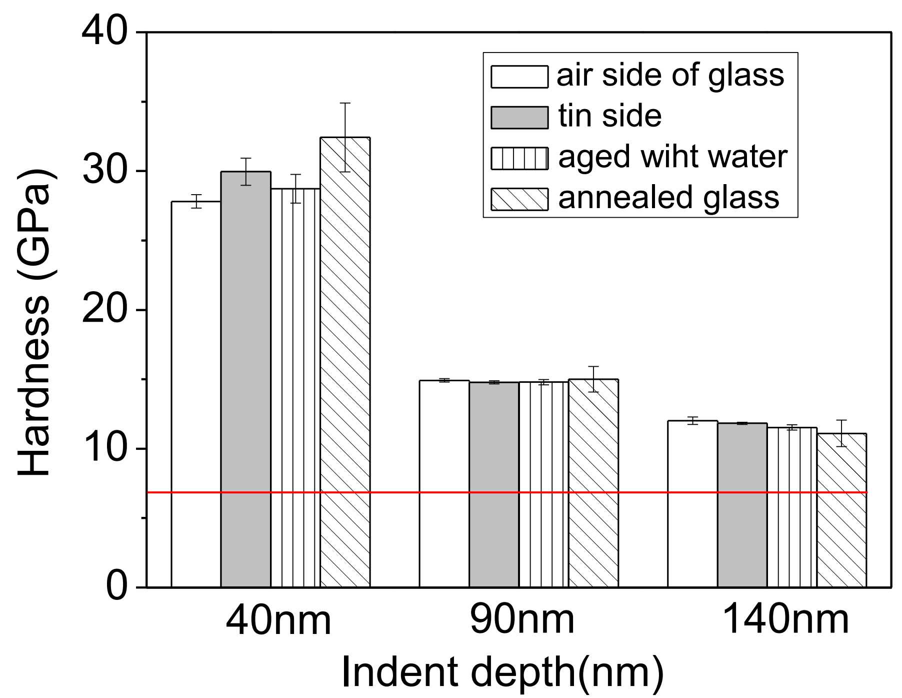
Contact stiffness $S = \dfrac{dF}{dh}$

Reduced elastic modulus $Er = \dfrac{S\sqrt{\pi}}{2\sqrt{A_p}}$

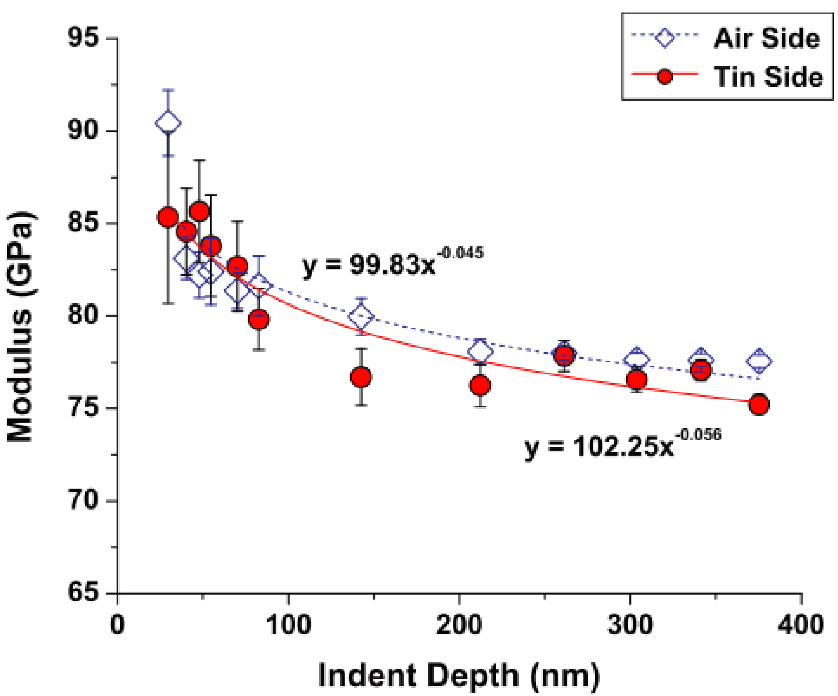
Indentation depth dependence of elastic modulus and harness of Asahi soda-lime glass surface

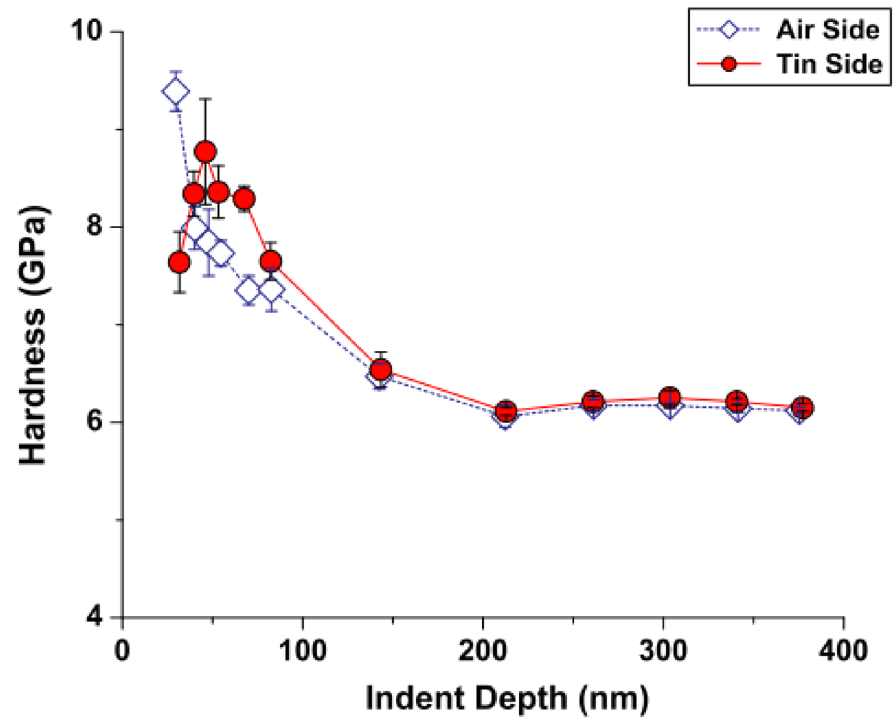
Humidity = 40 – 60%





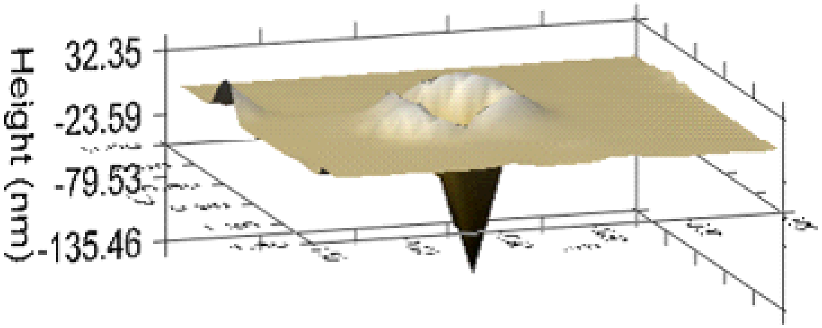
Does the surface have better mechanical strength than the bulk?

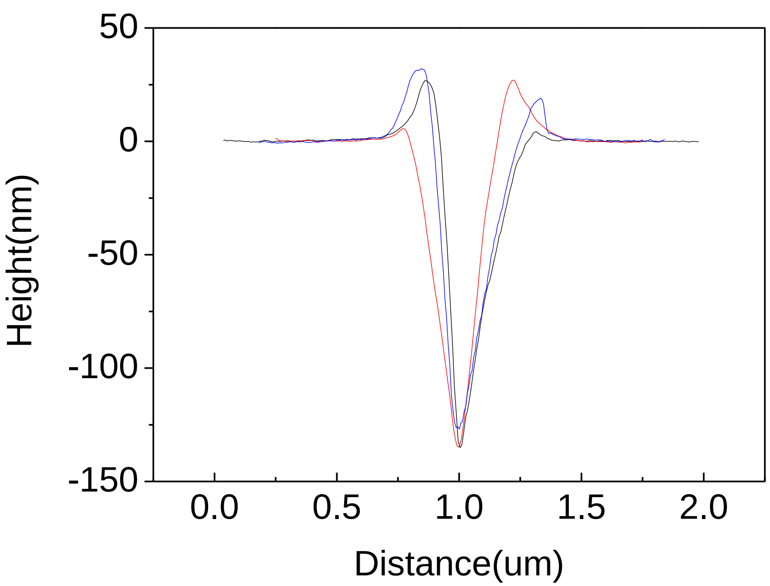


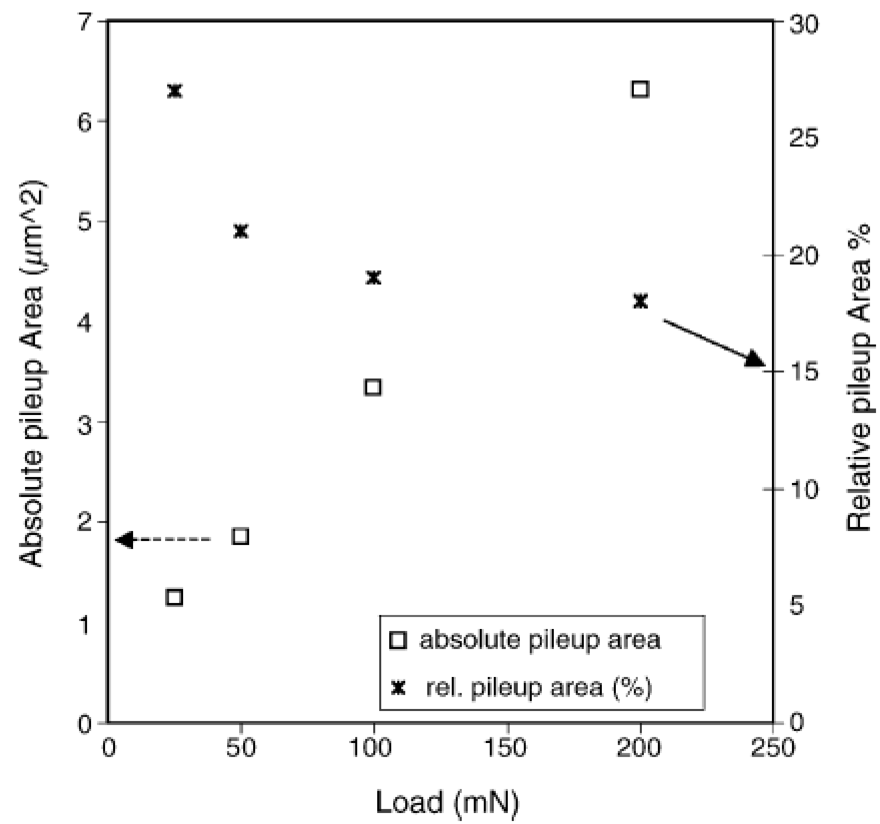


J.A. Howell et al. J. Non-Cryst. Solids, 354 (2008) 1891–1899

Or is it just a measurement artifact?





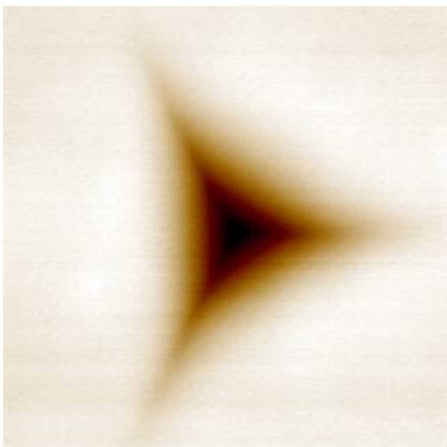


A. Bolshakov, G.M. Pharr, J. Mater. Res. 13 (1998) 1049.
K. O. kese, Z. C. Li, & B. Bergman, Mater. Sci. Eng. A 204 (2005) 1.

Conclusions

- Water activity at glass surface
  - equilibrium with the gas phase water
  - Quite different from that at SiO_2 surface
  - At high RH, H_3O^+ ions seem to be formed in the interfacial region
- Scratch resistance under shear
  - Mechanochemical effects; not just mechanical.
  - Different from stress corrosion or crack propagation
  - Functions of vapor condition and counter-surface chemistry

Nano-indentation of Diamond-like carbon (DLC)



H_f (nm)	E_r (GPa)	H (GPa)
120	59.3 ± 0.5	5.6 ± 0.1
90	58.6 ± 0.6	5.6 ± 0.1
50	43.2 ± 1.1	4.6 ± 0.2