Surface Chemistry of Glass: 
Interfacial water and mechanochemical properties

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• This work was supported by National Science Foundation (Grant No. DMR-1207328).
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 $P_{\text{Hertzian}}$ = 360 MPa)

Optical profilometry

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

Unreliable Dynamic Interfaces have Limited the Development of Complex MEMS

mechanical lock: enabled by 24 independent A/B events

M. T. Dugger
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.

Device fails when $F_{\text{adhesion}} > F_{\text{actuation}}$

2 Minutes @100 Hz operation

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

Micro-scale lubrication with a molecular adsorbate film

United States Patent
Dugger et al.

METHOD FOR LUBRICATING CONTACTING SURFACES

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)

Patent No.: US 8,071,164 B1
Date of Patent: Dec. 6, 2011
Increased Operating Life of Gear Train with Vapor Phase Lubrication

M. T. Dugger

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

With VPL, device was stopped at $4.8 \times 10^8$ cycles without failure
  - 1000 ppm pentanol, <100 ppm H$_2$O
VPL is Effective on MEMS Devices with Thermal Actuators

M. T. Dugger

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)

Si-O-Si Rupture via Methanol

Red – O
Yellow – Si
White – H
Grey – C

CH₃OH\textsubscript{\text{gas}}

ΔE\textsubscript{a}

Stable & low density form of SiO₂

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

\[
\text{Rxn rate} \propto \exp\left(-\frac{E_a}{RT}\right)
\]

<table>
<thead>
<tr>
<th>(R_1)</th>
<th>(R_2)</th>
<th>(E_a (kJ/mol))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>114</td>
</tr>
<tr>
<td>CH₃</td>
<td>H</td>
<td>151</td>
</tr>
<tr>
<td>H</td>
<td>CH₃</td>
<td>112</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>154</td>
</tr>
<tr>
<td>propyl</td>
<td>propyl</td>
<td>224</td>
</tr>
</tbody>
</table>

“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

\[
\equiv \text{Si-O}^- \text{Na}^+ + \text{H}_2\text{O} \rightarrow \equiv \text{Si-O}^- + \text{Na}^+ + \text{OH}^-
\]

\[
\equiv \text{Si-O-Si} \equiv + \text{OH}^- \rightarrow \equiv \text{Si-OH} + \equiv \text{Si-O}^-
\]

\[
\equiv \text{Si-O}^- + \text{H}_2\text{O} \rightarrow \equiv \text{Si-OH} + \text{OH}^-
\]

\[
\equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O} \rightarrow \equiv \text{Si-OH} + \text{HO-Si} \equiv
\]

R.A. Schaut, C.G. Pantano. 2005
Influence of water vapor on crack propagation in soda lime glass

S. M. Wiederhorn

Freiman, Wiederhorn, & Mecholsky,

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...
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

Carrier gas

Gas with controlled humidity

Applied load

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

Optical profilometry images of the substrate

<table>
<thead>
<tr>
<th>Humidity</th>
<th>Total Displaced Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% RH</td>
<td>-21000 μm³</td>
</tr>
<tr>
<td>40% RH</td>
<td>-30000 μm³</td>
</tr>
<tr>
<td>90% RH</td>
<td>-32000 μm³</td>
</tr>
</tbody>
</table>
Humidity dependence of wear of *soda lime glass* surface rubbed with *pyrex ball*.

Optical profilometry images of the substrate:

- 20% RH: -13000 μm³
- 40% RH: -18500 μm³
- 90% RH: +25000 μm³
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
A small increase in humidity from dry air drastically change the surface scratch behavior of glass.

In dry N₂:

- Pyrex ball
- SLG substrate
  - Height (µm)
  - Distance (µm)
  - 8.8 µm

In 20% RH:

- Pyrex ball
- SLG substrate
  - Height (µm)
  - Distance (µm)
  - 4.3 µm

Friction Coefficient vs. Sliding cycles for 20% RH and Dry N₂.
As RH approaches saturation, the SLG surface becomes “wear-resistant”...

In 20% RH

In 40% RH

In 90% RH
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...

carrier gas (Ar or dry clean air)

heated bubbler 1

heated bubbler 2

condenser

Humid gas

vent

Silicon ATR Crystal

Penetration depth @ 3000 cm$^{-1}$ = ~ 300 nm → detect adsorbed molecules only
Water adsorption on SiO$_2$ in humid ambience

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

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/SiO₂.

Sum-Frequency-Generation (SFG) Vibration Spectroscopy

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

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

\[ I(\omega_{SFG}) \propto |\chi_{\text{eff}}^{(2)}|^2 I(\omega_{\text{VIS}})I(\omega_{\text{IR}}) \]

\[ \chi_{\text{eff}}^{(2)} \neq 0 \]

No inversion symmetry in both molecular and optical length scales

\[ \chi_{\text{eff}}^{(2)} = 0 \]

Inversion symmetry

Random

Piezoelectric crystals
Crystalline biopolymers

Centrosymmetric crystals
(such as NaCl)
Symmetrically arranged groups
(such as CH\textsubscript{2} in well-packed SAM or lipid bilayer)

Interfaces

Amorphous polymers
Bulk water & vapor

Glass
Co-adsorption of water & alcohol on SiO$_2$

A. L. Barnette and S. H. Kim,


**ATR-IR spectra**

Propanol mole fraction in the vapor mixture of propanol & water

- $y=1.00$
- $y=0.88$
- $y=0.60$
- $y=0.40$
- $y=0.36$
- $y=0.35$
- $y=0.24$
- $y=0.00$

**SFG spectra**

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- $y=0.00$
Co-adsorption of water & alcohol on SiO$_2$

Water adsorption on Glass as a function of RH
(glass cleaning = ethanol rinsed, and then soaked/aged in water for 3 hr)

**Fused quartz glass**

L. Bradley, Z. Dilworth, C. G. Pantano, & S. H. Kim
“Hydronium Ions in Soda-lime Silicate Glass Surfaces”
(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.
\[ \text{Na}^+ = 0.1\text{nm} \]
\[ \text{K}^+ = 0.14\text{nm} \]
\[ \text{H}_3\text{O}^+ = 0.14\text{nm} \]
Water ingress into glass

Hydrolysis & network corrosion

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

Pristine Na-silicate glass

In water or near-saturation humidity

$Na^+$ leach during aging in liquid water

Equilibrium with adsorbed water layer

L. C. Bradley et al. JACERS 2013
Formation of $\text{H}^3\text{O}^+$ formation in the $\text{Na}^+$-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

Dry $N_2$ 90%RH

40%RH

20%RH
HTC cellphone glass

Dry N\textsubscript{2}

\begin{itemize}
  \item 2.2 \textmu m
\end{itemize}

20\%RH

\begin{itemize}
  \item 3 \textmu m
\end{itemize}

40\%RH

\begin{itemize}
  \item 3.7 \textmu m
\end{itemize}

90\%RH

\begin{itemize}
  \item 4.8 \textmu m
\end{itemize}
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 $P_{\text{contact}} < \text{Hardness}$ $\rightarrow$ hillock (surface protrusion)
When $P_{\text{contact}} > \text{Hardness}$ $\rightarrow$ wear (material removal)

**SiO$_2$ ball** (diameter=1000nm)
$P_{\text{contact}} \ll \text{Hardness}$

Substrate = Si wafer with native SiO$_2$

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

Hardness:

<table>
<thead>
<tr>
<th>Ball</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$ = 20GPa</td>
<td>Soda lime glass = 5.9GPa</td>
</tr>
<tr>
<td>$\text{Si}_3\text{N}_4$ = 14.5GPa</td>
<td>vs.</td>
</tr>
<tr>
<td>$\text{SiO}_2$ = 6.0GPa</td>
<td></td>
</tr>
<tr>
<td>pyrex = 4.3GPa</td>
<td></td>
</tr>
</tbody>
</table>
No surprise in dry $N_2$ environment...

**$SiO_2$ ball**

**$Si_3N_4$ ball**

**$Al_2O_3$ ball**

Soda lime glass
In 90% RH, SiO$_2$ ball wears and the scratch in soda lime glass is negligible.
In all humidity, the “hard” $\text{Si}_3\text{N}_4$ ball wears and the “soft” soda lime glass is almost intact.

![Graphs showing friction coefficients and wear over sliding cycles for different humidities: 20%, 40%, and 90% RH, with corresponding wear depths at each humidity level.](image-url)
In intermediate humidity, \textit{Al}_2\textit{O}_3 ball wears and the scratch into \textit{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 adsorbtion.

Pyrex ball

SLG substrate

Dry N₂

90% RH

n-pentanol vapor

n-propanol vapor

Frictional coefficient

Sliding cycles (N)

Dry N₂

90%RH

n-propanol vapor

n-pentanol vapor

Height (µm)

Distance (µm)

Dry N₂

90%RH

n-pentanol vapor

n-propanol vapor
Mechanical property of surface region of glass
Nanoindentation test

Indentation load–displacement curve

- **Hardness**
  \[ H = \frac{F_{\text{max}}}{A_p} \]

- **Contact stiffness**
  \[ S = \frac{dF}{dh} \]

- **Reduced elastic modulus**
  \[ Er = \frac{S \sqrt{\pi}}{2 \sqrt{A_p}} \]
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?

\[ y = 99.83x^{-0.045} \]

\[ y = 102.25x^{-0.056} \]

Or is it just a measurement artifact?

Conclusions

• Water activity at glass surface
  – equilibrium with the gas phase water
  – Quite different from that at SiO$_2$ surface
  – At high RH, H$_3$O$^+$ 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)

<table>
<thead>
<tr>
<th>H_f (nm)</th>
<th>E_r (GPa)</th>
<th>H (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>59.3 ± 0.5</td>
<td>5.6 ± 0.1</td>
</tr>
<tr>
<td>90</td>
<td>58.6 ± 0.6</td>
<td>5.6 ± 0.1</td>
</tr>
<tr>
<td>50</td>
<td>43.2 ± 1.1</td>
<td>4.6 ± 0.2</td>
</tr>
</tbody>
</table>