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The Role of Water on the Tribological Properties of Molybdenum Disulphide Films

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Sandia National Laboratories

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UF | UNIVERSITY of FLORIDA TRIBOLOGY LABORATORY

Education

PhD, University of Florida, Mechanical Engineering, 2012

M.S., University of Florida, Mechanical Engineering, 2009

B.S., University of Florida, Mechanical Engineering, 2007

Professional Experience

Graduate student intern at Sandia National Laboratories, Albuquerque, NM July 2011 - present

Research Activities

Polymer composites: Developed novel polymeric composites to test under both terrestrial and space conditions.

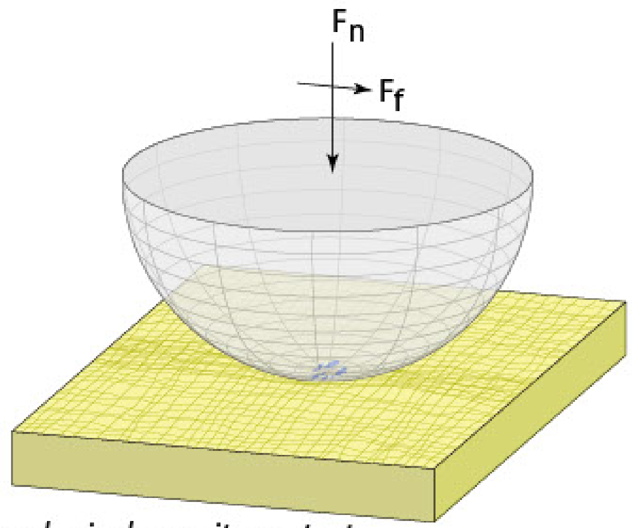
High temperature materials: Worked with a coating company to help in the development process for novel high temperature thin films. I also worked on developing high temperature composite bulk matermaterials to test in cyclic environments.

Instrumentation design: Redesigned 2 vacuum tribometers and designed/built an ambient environment tribometer.

Solid lubricant coatings: Peformed environmental testing on numerous solid lubricant coatings, focusing mainly on molybdenum disulphide. Temperature, relative humidity, vacuum, and background gas affects were studied.

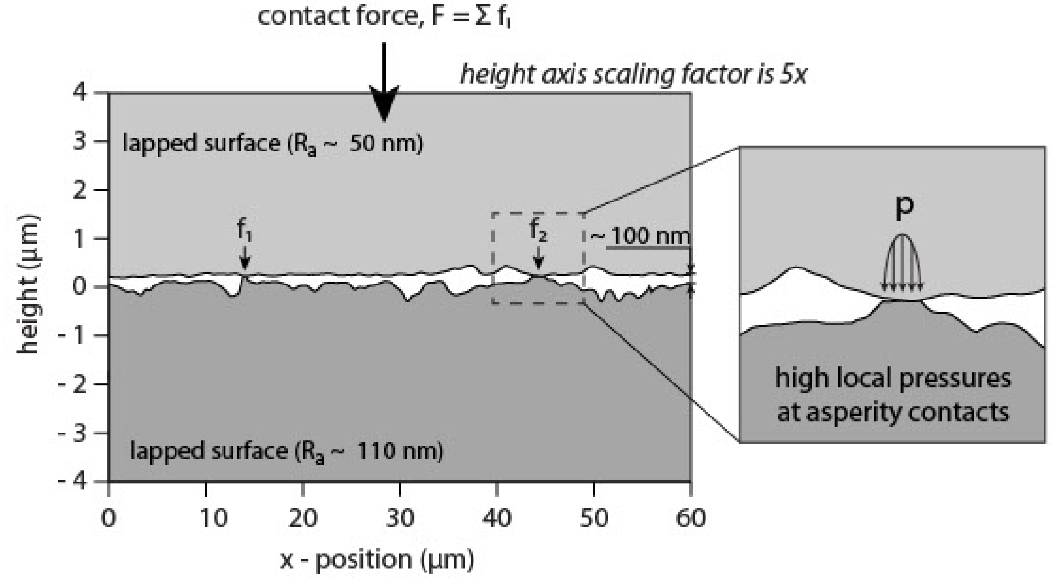
What is Materials Tribology?

Macroscopic Tribology Testing

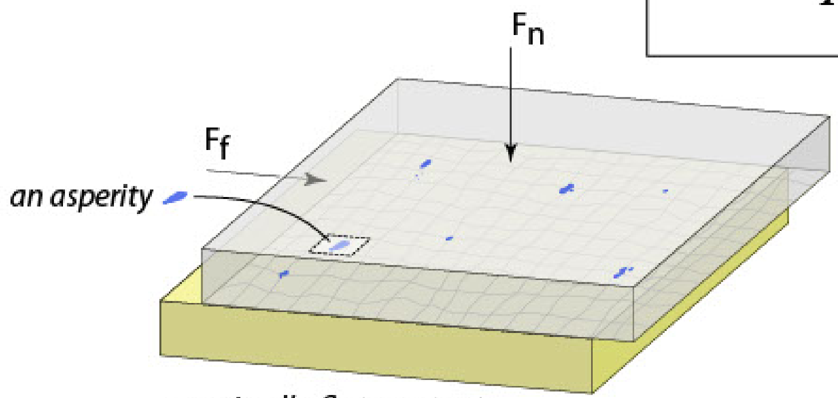


spherical asperity contact

Surface Roughness

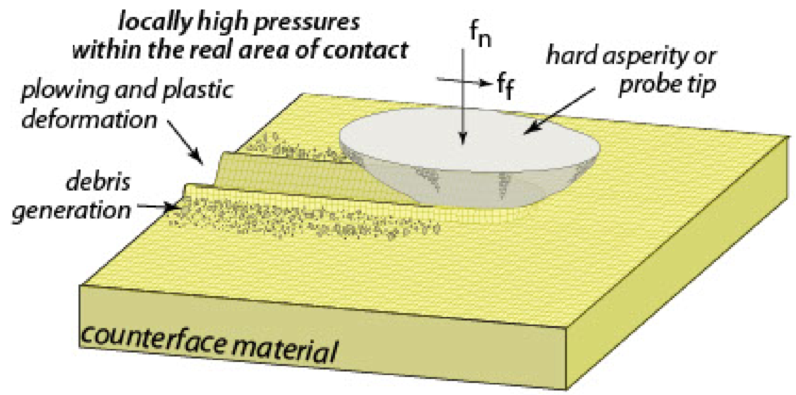


friction coefficient	wear rate
$\mu \cong \frac{F_f}{F_n}$	$k \cong \frac{V}{F_n d}$



nominally flat contact

Tribological Deformations

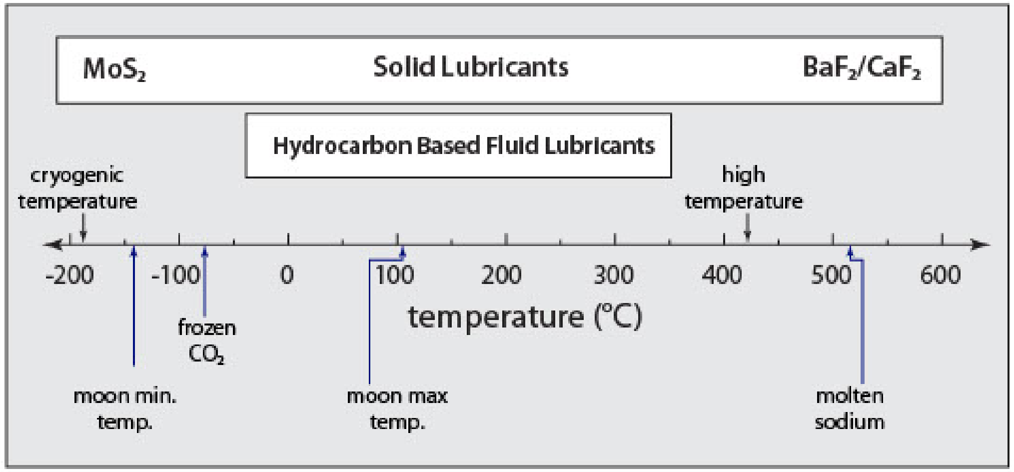


Hydrocarbon Based Fluid Lubricants

1. Benefits:
   - low friction coefficients
   - excellent wear protection

2. Drawbacks:
   - narrow temperature range
   - recirculation and filtration
   - environmental concerns

3. Example: 5P4E (maximum temperature 350°C)



Solid Lubricants

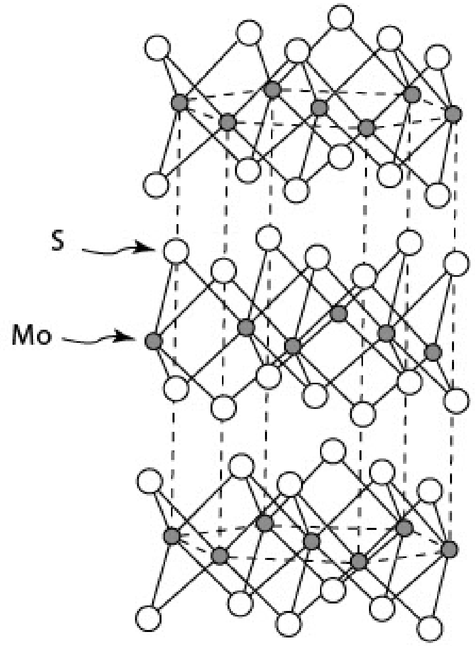
1. Benefits:
   - broad temperature range
   - lubricant remains in the contact
   - friction coefficient is less sensitive to speed variations
   - can be applied as a coating
   - can be used in vacuum
   - low friction coefficients ($0.001 < \mu < 0.1$)

2. Drawbacks:
   - finite lifetimes due to wear
   - generation of wear debris

3. Examples:
   a) low shear strength materials
      i silver
      ii calcium/barium fluoride
   b) lamellar solids
      i graphite
      ii **molybdenum disulphide**
      iii hexagonal boron nitride
   c) polymers
      i polytetrafluoroethylene (PTFE - Teflon)

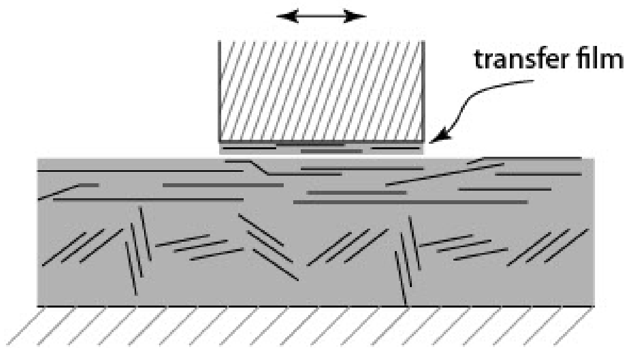
molybdenum disulphide has:

- hexagonal, layer-lattice structure
- covalent bonding between the S-Mo-S and van der Waals attraction between each tri-layer

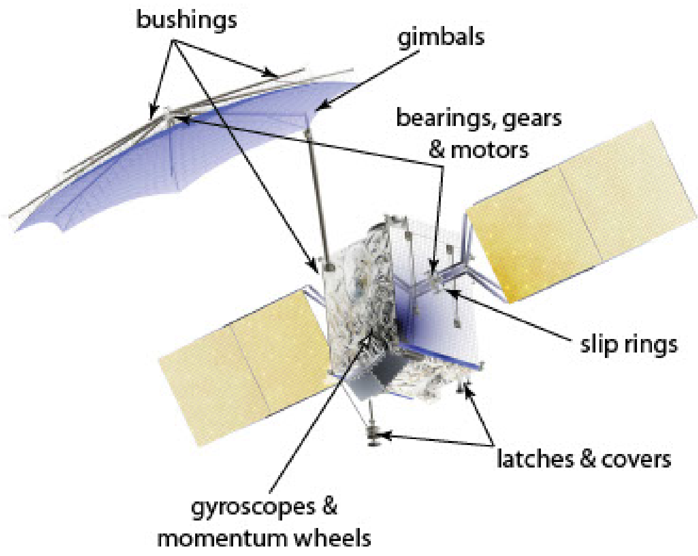


The layer-lattice structure and van der Waals forces allows for easy slip between the tri-layers which provides the low friction properties.

Amorphous MoS_2 coatings are known to form crystalline layers which orient themselves upon sliding leading to the low friction characteristics.



Satellites



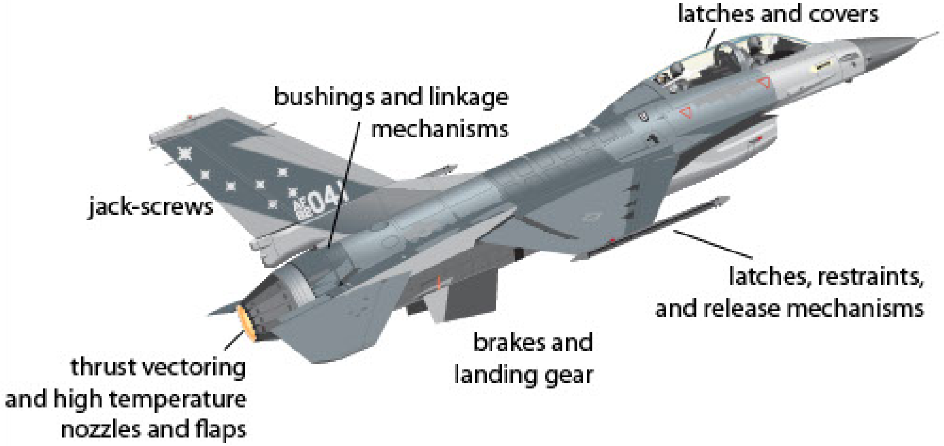
Operating Environments

Environmental Extremes:

- extraterrestrial deployment (UH vacuum, -150°C to 100°C)
- terrestrial testing (ambient lab air)

Packaged antennas must survive extended cycled deployment in ambient humid conditions prior to deployment in space.

Aircraft Actuators



Operating Environments

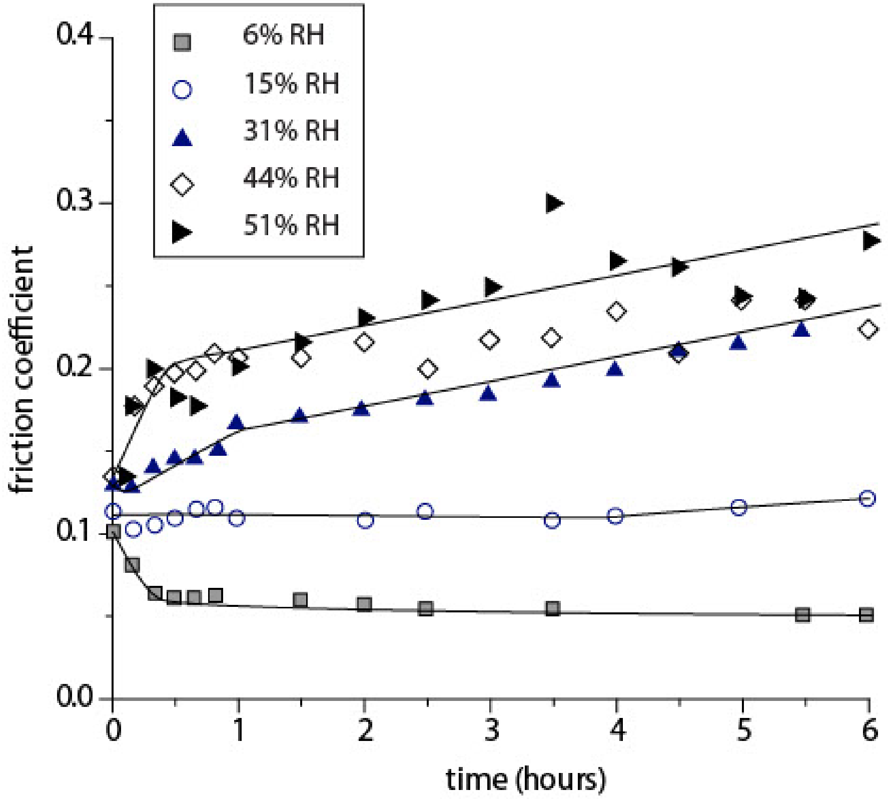
Environmental Extremes:

- high altitude dog fights (-50°C, low humidity)
- equatorial carrier operations (>35°C, >90% humidity)

Devices must function for 1000's of cycles between environmental extremes.

Since 1951 over 1,000 papers have been published on the topic of MoS_2 Tribology.

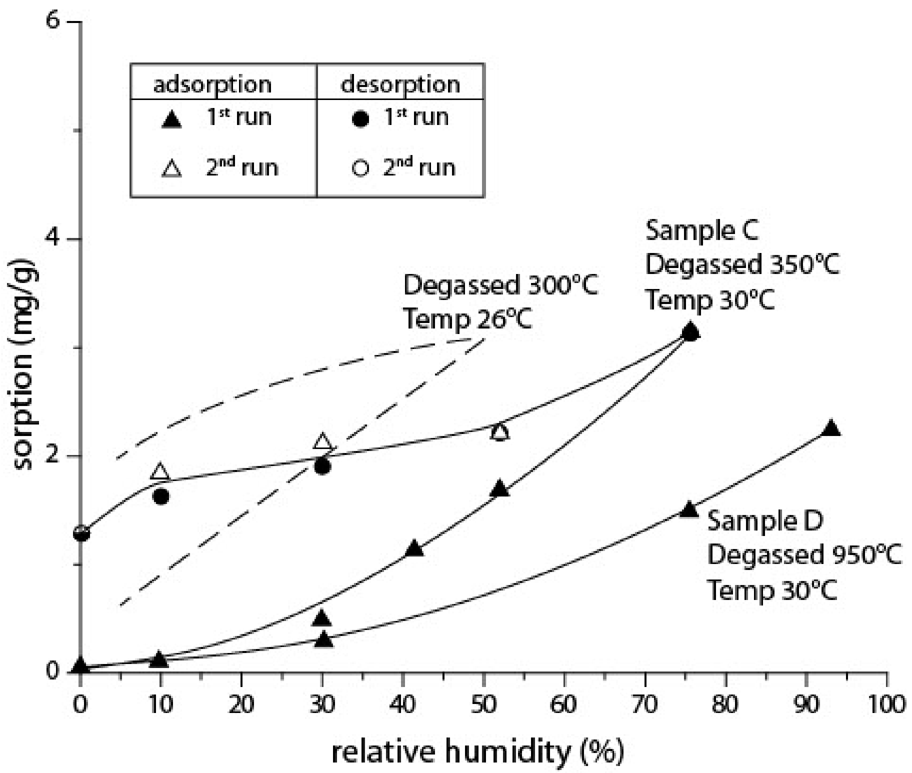
The first report on the effect of relative humidity on the friction and wear of MoS_2 is from at NACA publication in 1953 by M. B. PETERSON & R. L. JOHNSON.



The steady state friction coefficient values decrease with decreasing relative humidity in the environment.

Data adapted from Peterson, M.B. and Johnson, R.L., Friction and wear investigation of molybdenum disulfide I - effect of moisture, NACA, 1953

The reversible sorption and desportion of water vapor on MoS_2 after various degassing methods.



There are both reversible and irreversible portions of water sorption in MoS_2 powder samples.

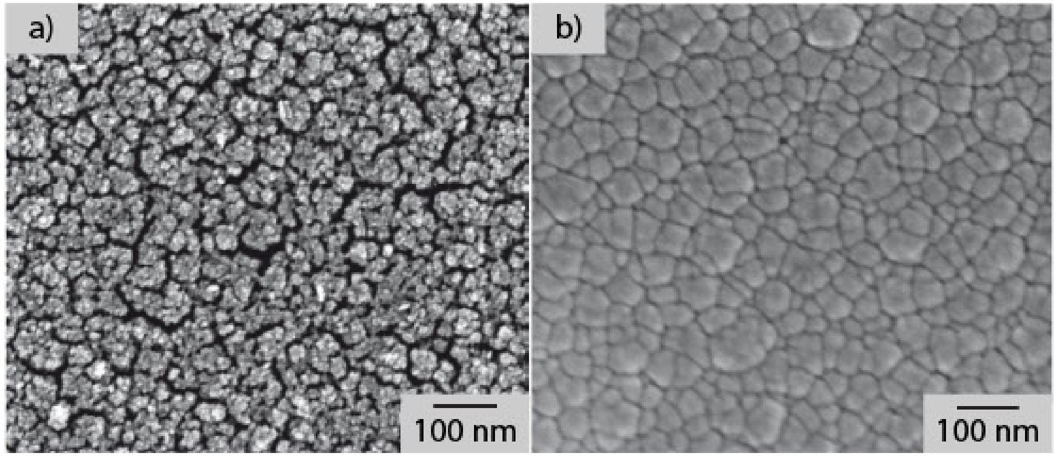
Johnston, R.R.M. and Moore, A.J.W., Water adsorption on molybdenum disulfide containing surface contaminants, Journal of Physical Chemistry, 1964, 68(11)

Composites of MoS_2

Pure MoS_2 has shown differences between its tribological behavior in dry and moist environments. A necessity for improvements of the performance in moist environments led to the development of composite MoS_2 coatings through various deposition processes. The addition of dopants was made to improve the friction, wear, and environmental stability of the coatings.

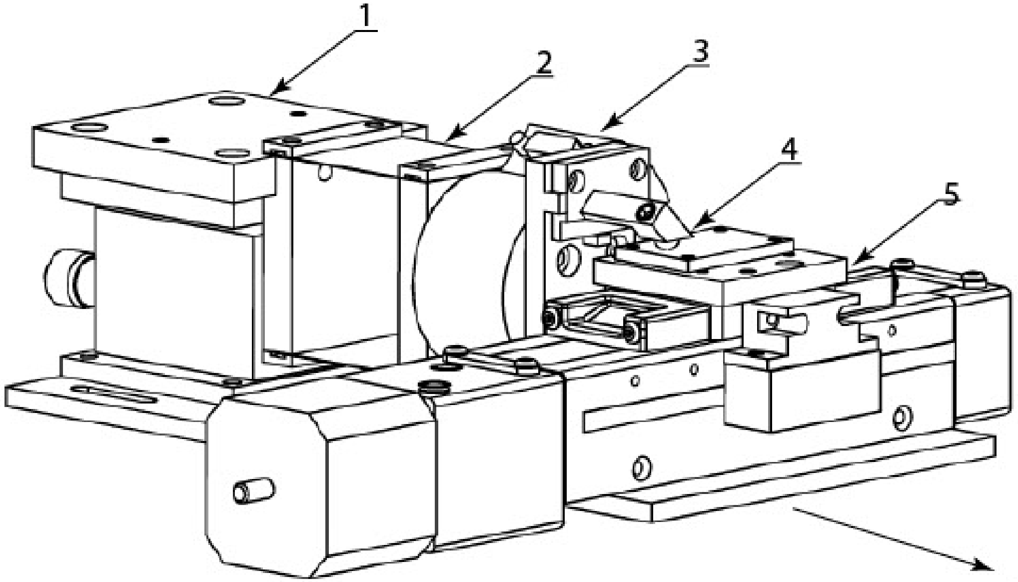
Examples of composite MoS_2 coatings in use today:

- MoS_2
- MoS_2 + Ni
- MoS_2 + Ti
- MoS_2 + Sb_2O_3
- MoS_2 + Sb_2O_3 + Graphite
- MoS_2 + Sb_2O_3 + Au

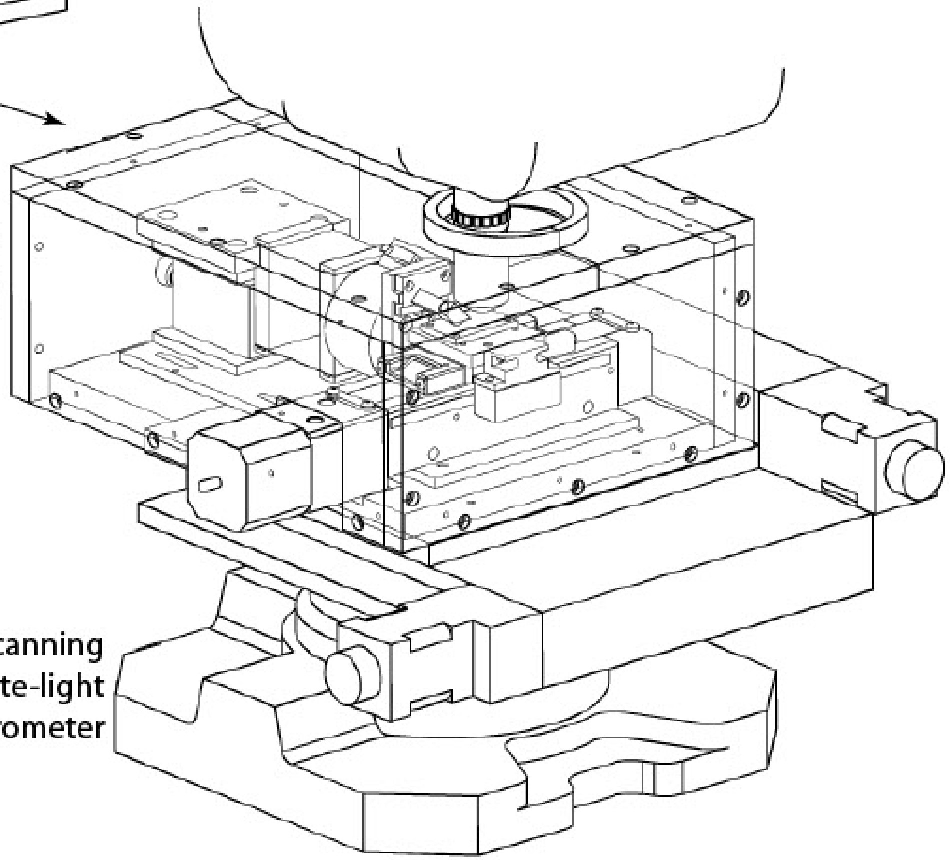


a) sputter deposited MoS_2 film on Si
b) sputter deposited MoS_2/Sb_2O_3/Au film on Si

Images a) and b) adapted from Scharf, T. *et al.*, Acta Materialia, 2010, 58: p. 4100-4109



1. vertical stage
2. parallel leaf flexure
3. six-channel load cell
4. pin and counterface
5. reciprocating table



environmentally controlled chamber

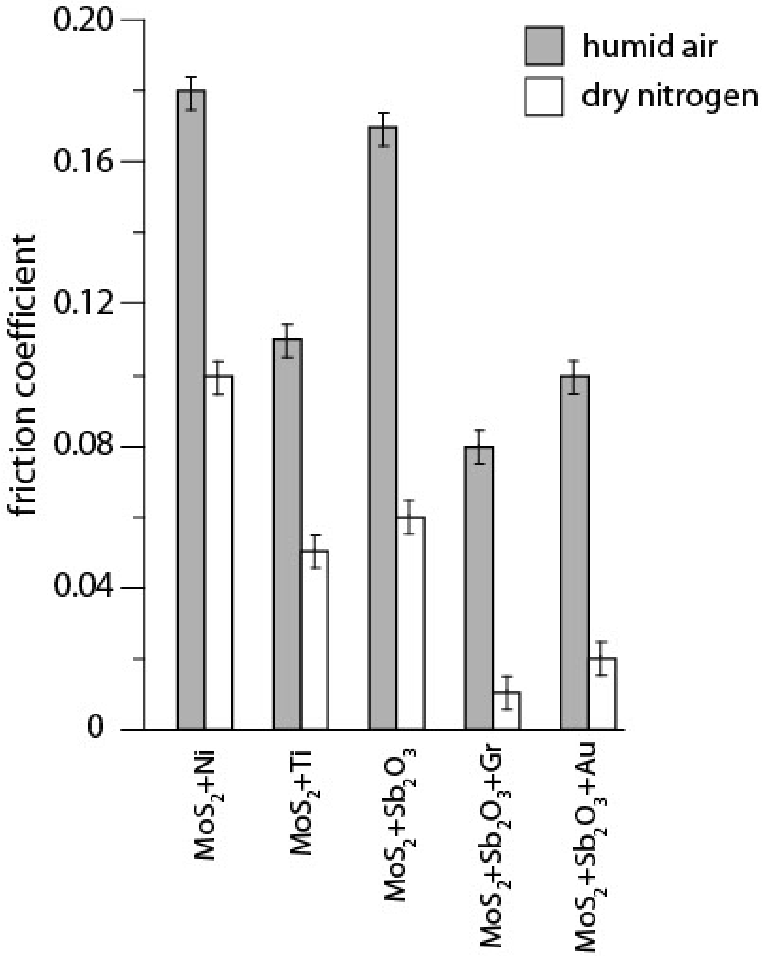
scanning white-light interferometer

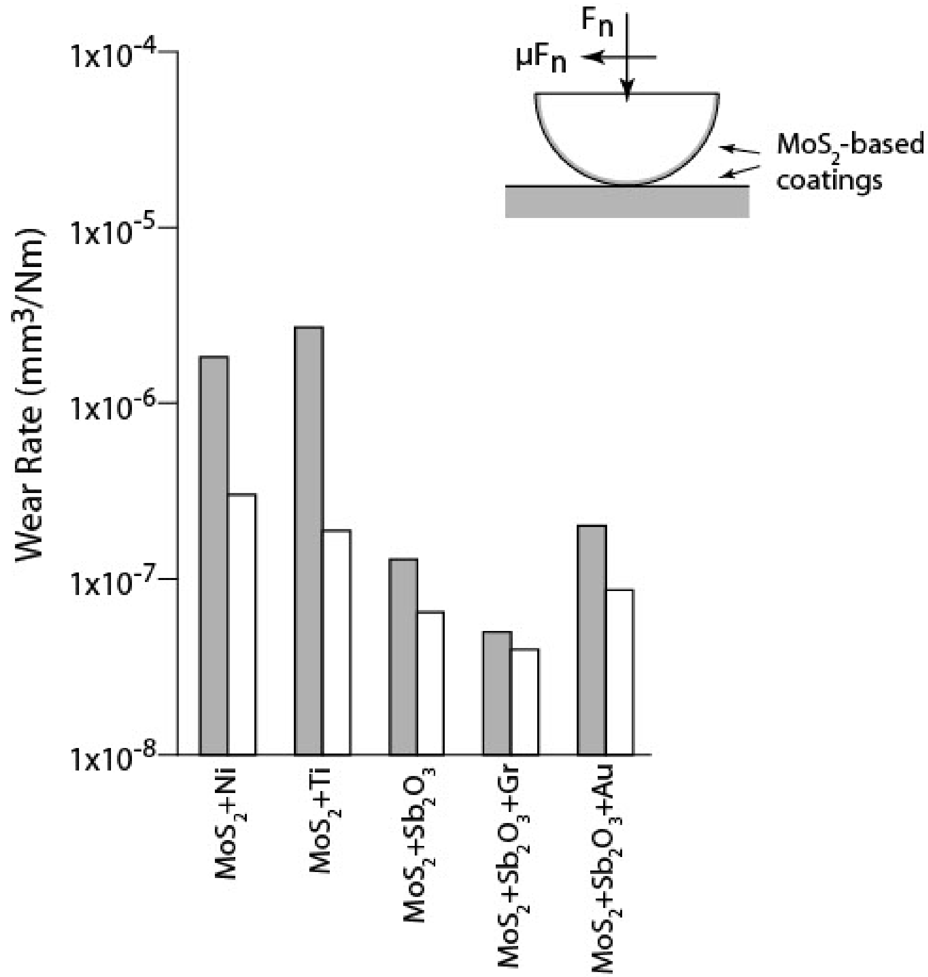
Capabilities of the Tribometer:

- in situ measurements of friction
- environmental control
- in situ measurements of wear using a scanning white-light interferometer

Review of Experiments

All tests were run at 1.3 GPa contact pressure, 10 mm/s sliding speed, for 10,000 cycles; the total sliding distance was 100m. The error bars for the friction coefficient are the associated standard deviation of the data. The wear rate error bars are the associated uncertainty in the measurements as they were point measurements and the standard deviation cannot be derived. They are smaller than the data points and thus are not shown.





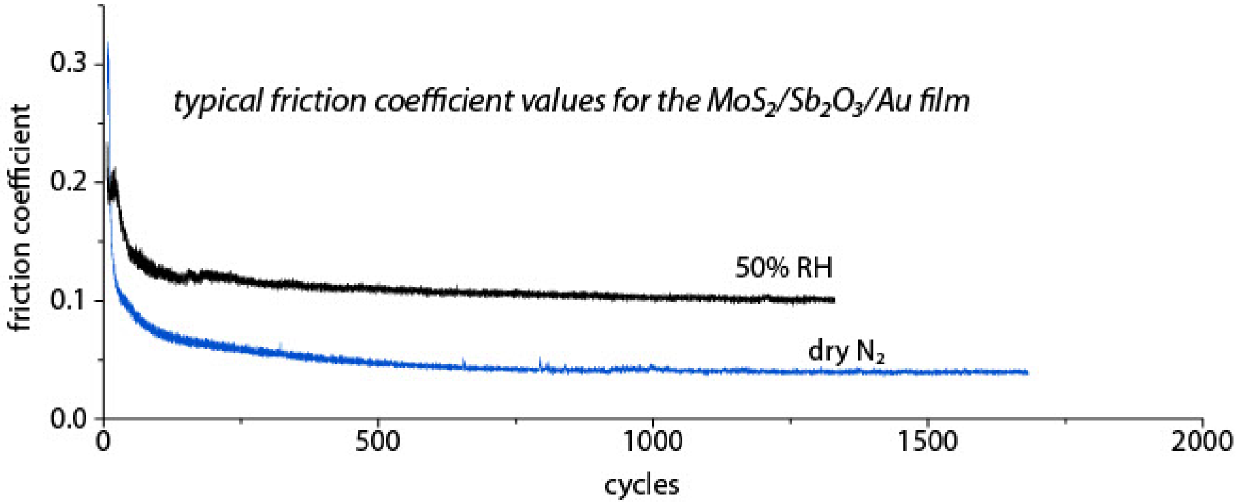
Friction increases with increasing relative humidity, wear does not follow as strong of a trend.

Summary of Trends

Friction coefficient decreases with a decrease in water content

Static friction coefficient values increase with an increase in water content

The water sorption on MoS_2 powder is a reversible process once a portion of water is irreversibily sorbed



Questions to be Addressed

Does a film of MoS_2 exhibit similar sorption properties as those shown by the powder sample?

What is the amount of water being absorbed into the films?

Is the water sorption affected by the density/porosity and thus surface area/volume ratio of the films?

Does thickness of the coating play a role on the water uptake?

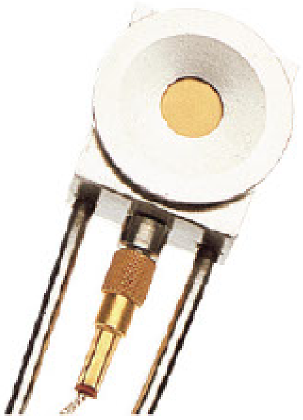


Image courtesy of Inficon

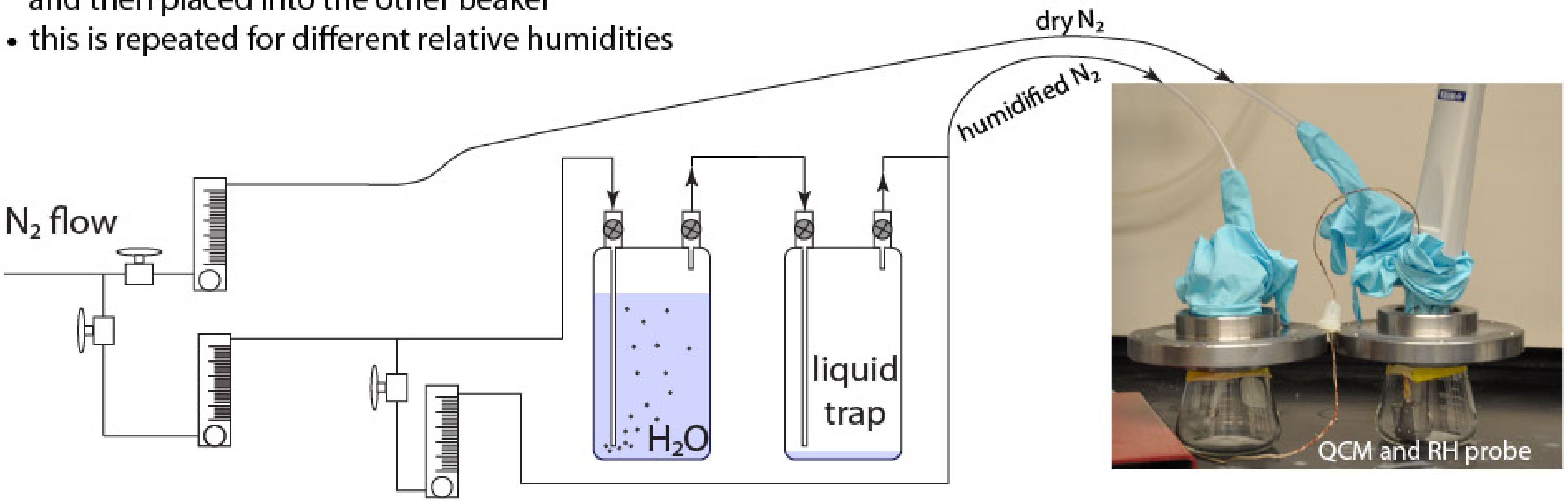
Quartz Crystal Microbalance's (QCM) work using the piezoelectric effect from the quartz crystal. Alternating currents are applied to the crystal which creates a standing shear wave. The frequency of oscillation of the quartz crystal is dependent upon the mass of the crystal, thus if a change of mass occurs, the frequency will change correspondingly.

The Sauerbrey's Equation is used to calculate mass change per unit area:

$$\frac{\Delta m}{A} = -\frac{\Delta f}{2 f_0^2}\sqrt{\mu_q \rho_q}$$

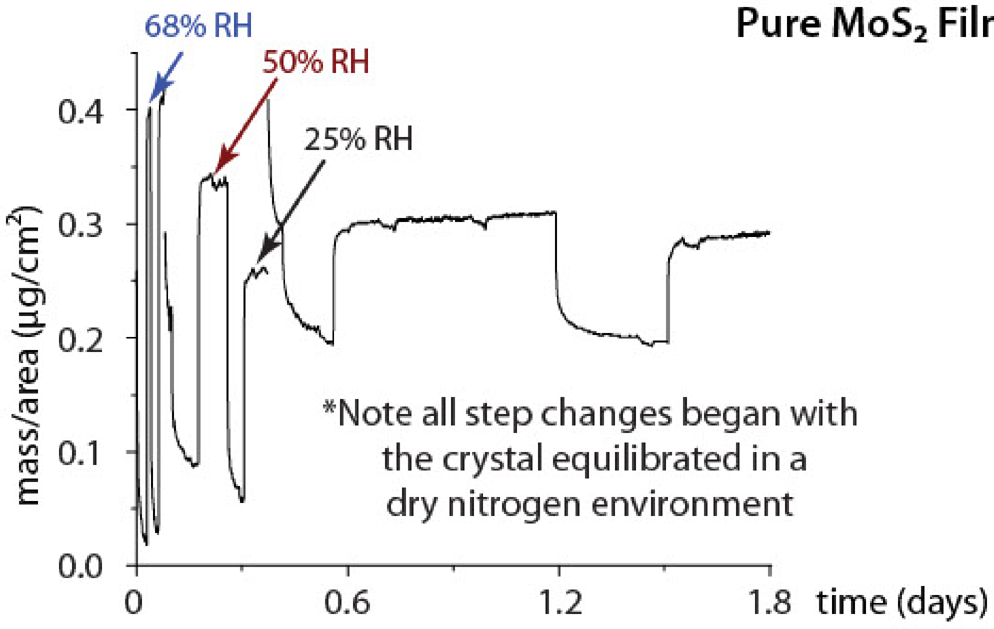
Relative Humidity Step Changes Set Up

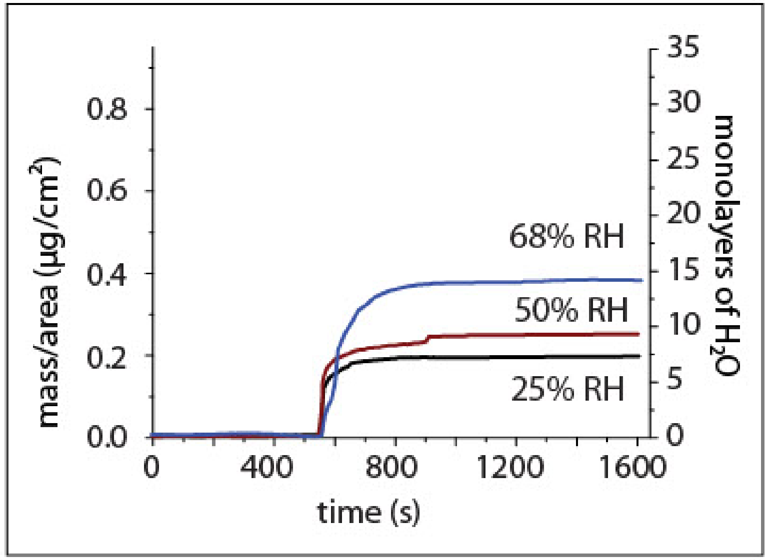
- 2 beakers, one with dry N_2 and one with humidified N_2 flowing at ~5 LPM
- QCM and RH probe are placed into one beaker, allowed to reach steady-state, and then placed into the other beaker
- this is repeated for different relative humidities



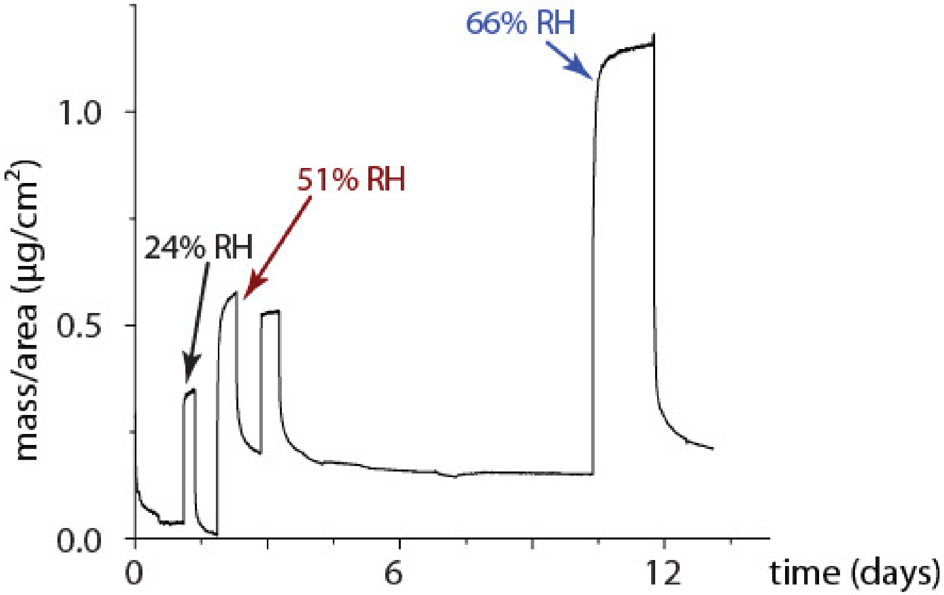
Step Change in Relative Humidity Experiments

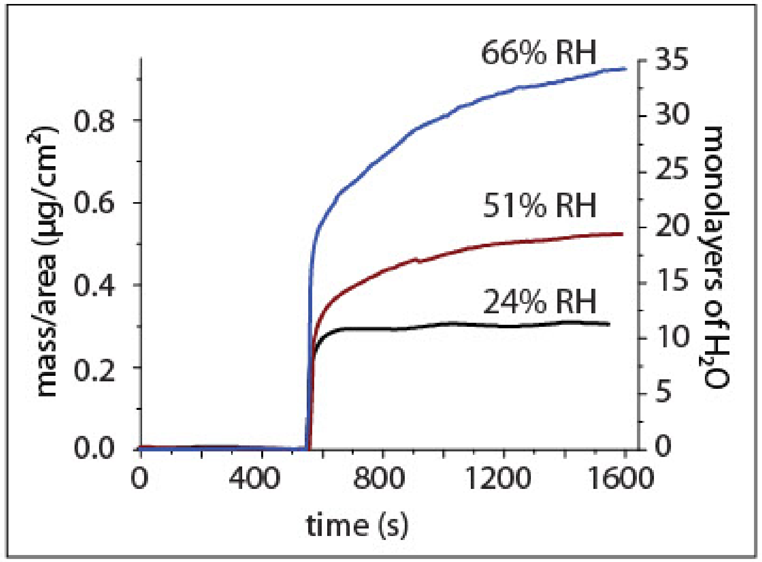
Pure MoS_2 Film





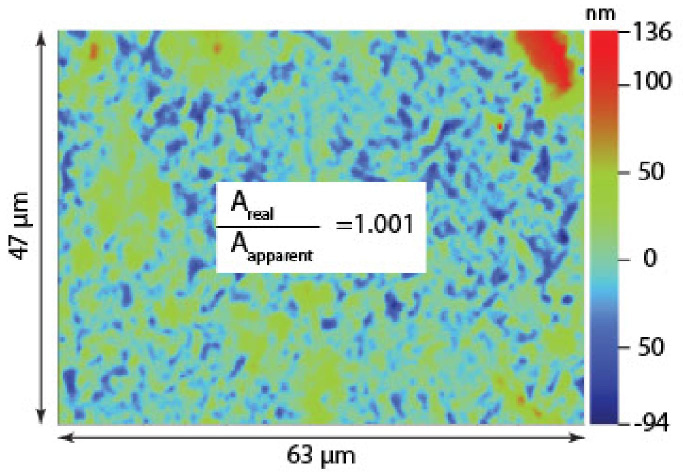
$MoS_2/Sb_2O_3/Au$ Film

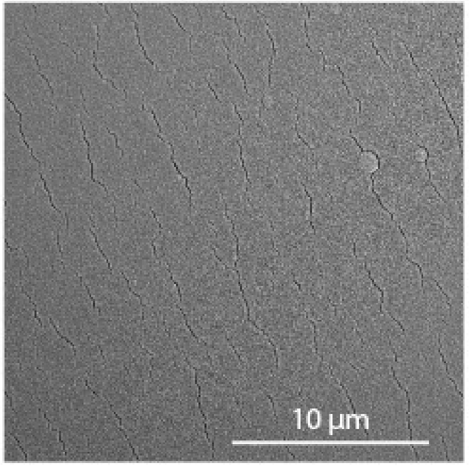




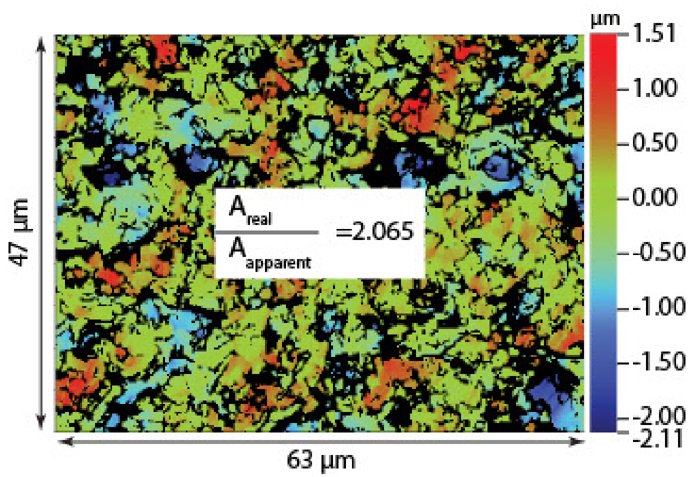
Surface Area Differences in MoS_2 Films

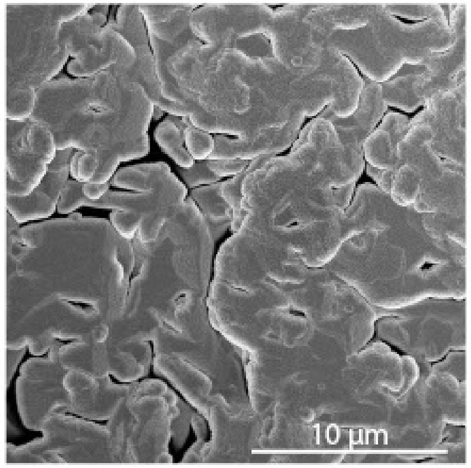
Pure MoS_2 deposited on a surface with Ra~8 nm



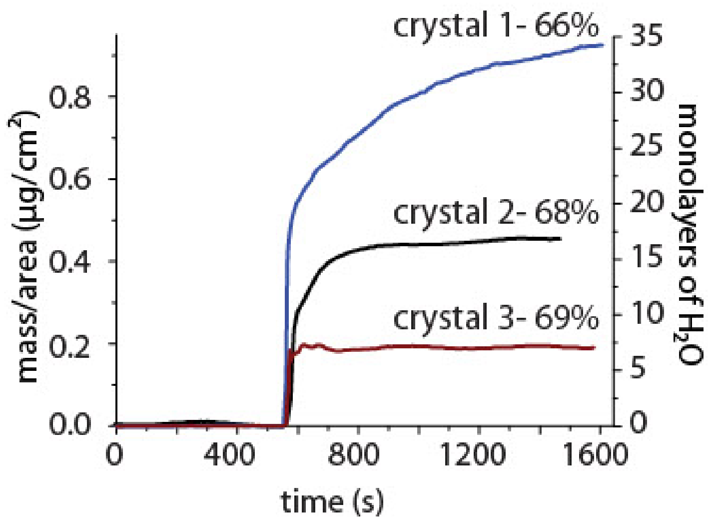


Pure MoS_2 deposited on a surface with Ra~350 nm



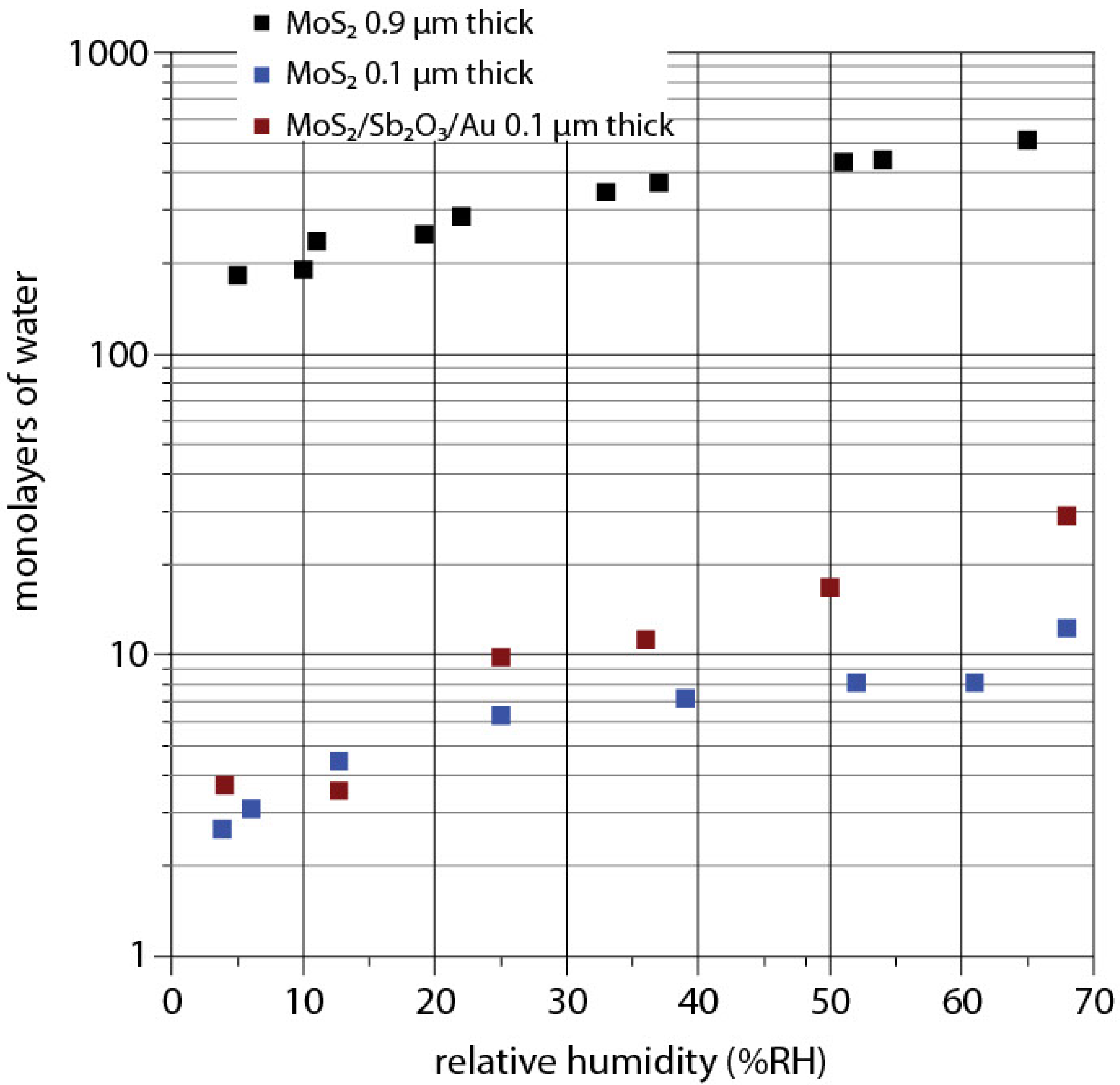


A variability between different coated QCM crystals is seen. There is the potential that this is directly related to a variation of the real surface area.



One QCM crystal for each coating is chosen to make comparative measurements.

* Note: SEM images were provided by Richard Grant



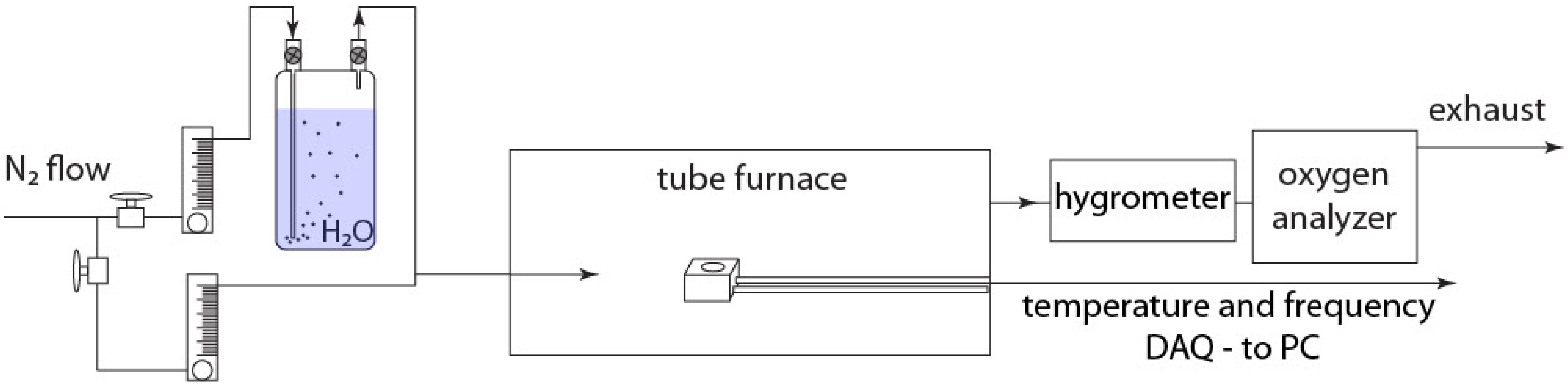
An increase in the thickness of the sample increases the quantity of reversible water uptake.

14 - thickness step change data.ai

Due to the potential for irreversibly sorbed water content in the films, heating of the coated QCM crystal in an inert environment was explored.

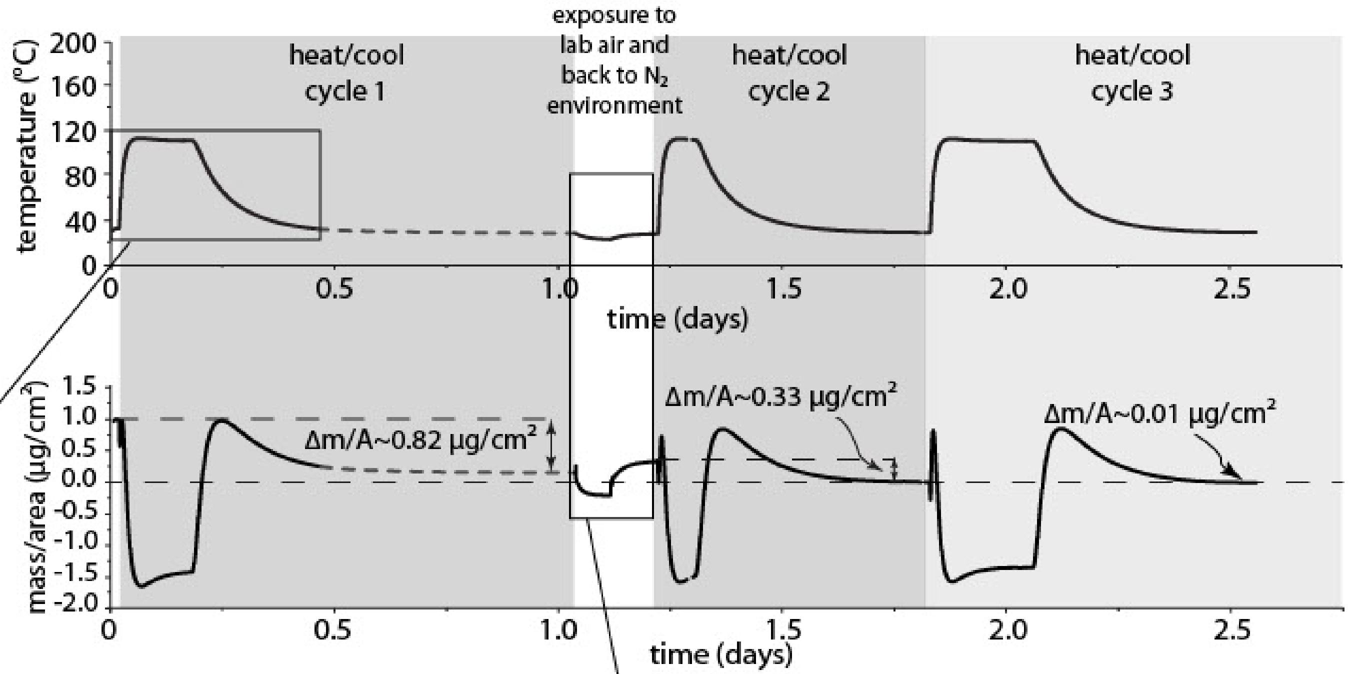
Furnace Experimental Set Up

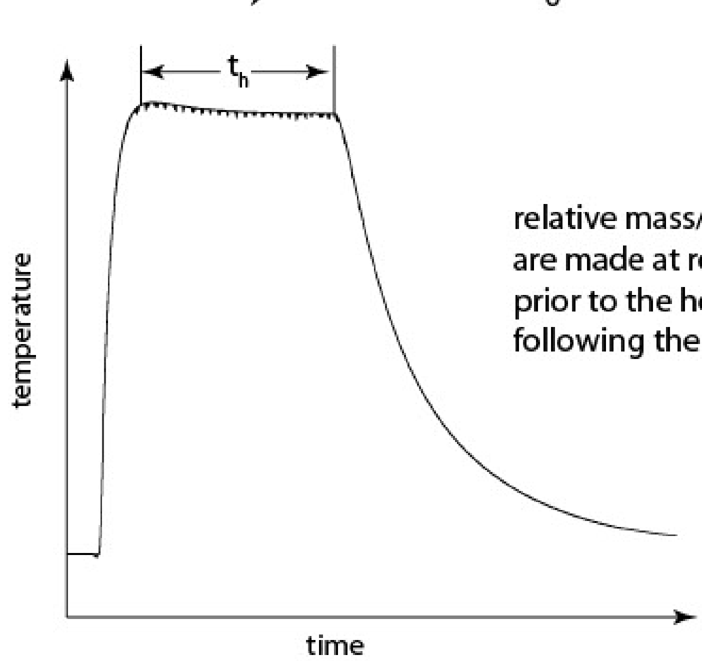
- Thermo Electron Corporation Lindberg/Blue M tube furnace was used to heat the crystal
- a nitrogen flow through system was established through the furnace in which gas analysis was performed on the exhaust flow
- a bubble humidification system was added to allow for relative humidity changes to the environment
- temperature is measured via a thermocouple attached directly to the quartz crystal holder
- all experiments were run under conditions of <10 ppm of O_2



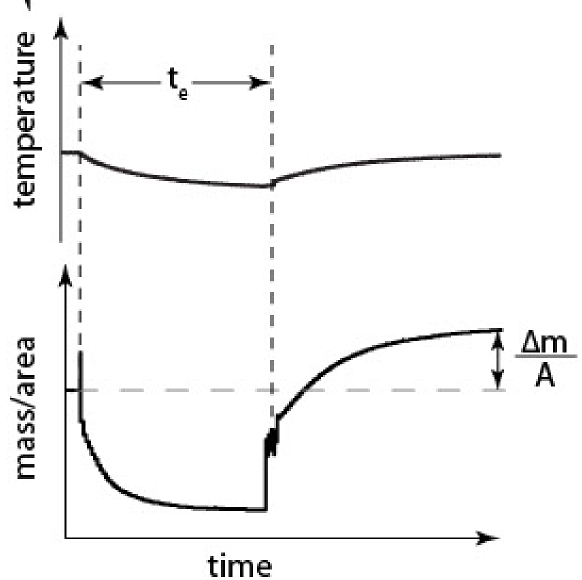
15- QCM furnace setup.ai

The heat/cool cycles are all achieved in a dry N_2 environment with O2<5 ppm.





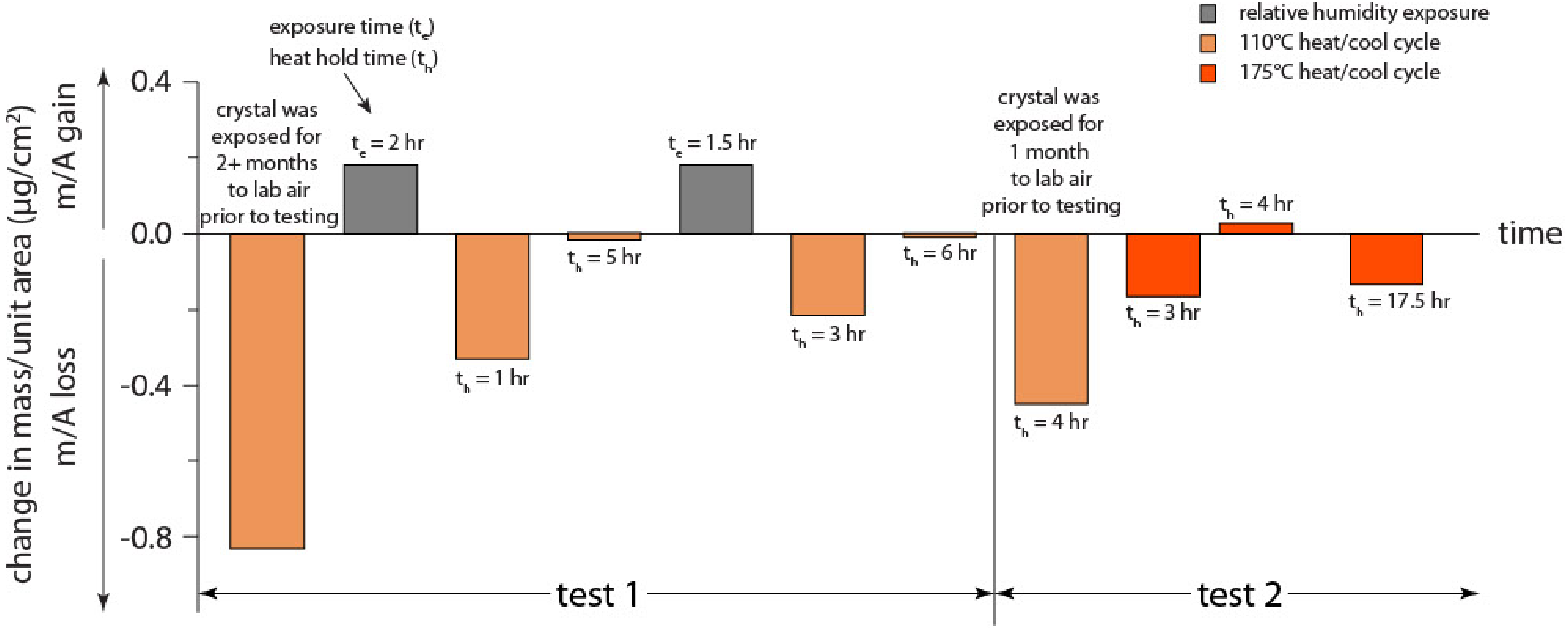
relative mass/area measurements are made at room temperature prior to the heat/cool cycles and following the heat/cool cycle



16- heat n cool cycle description.ai

Inert Environment Heating Experiments on Pure MoS_2 Film

Relative changes in the mass per unit area are shown. All data was measured with the same coated quartz crystal. The crystal was initially exposed to numerous relative humidity cycled changes and then this experiment was commenced.

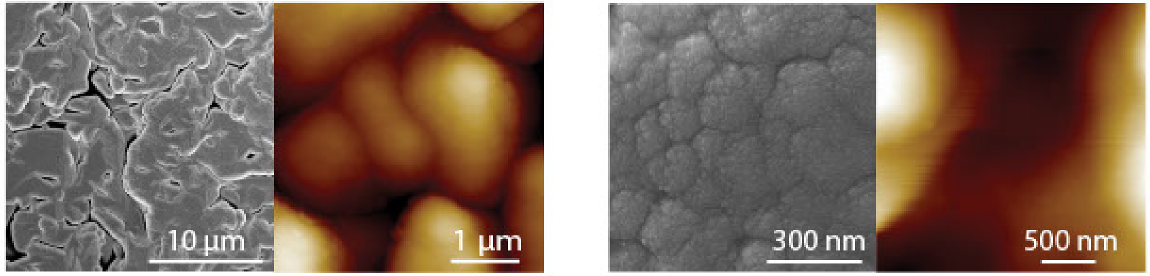


A large mass per unit area loss was observed after the first 110°C heat/cool cycle, but was minimal upon additional 110°C heat/cool cycles.

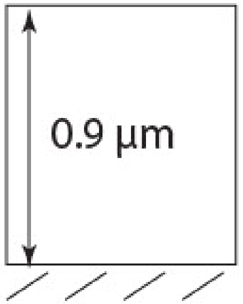
Additional quantities of mass per unit area loss were observed with the 170°C heat/cool cycles.

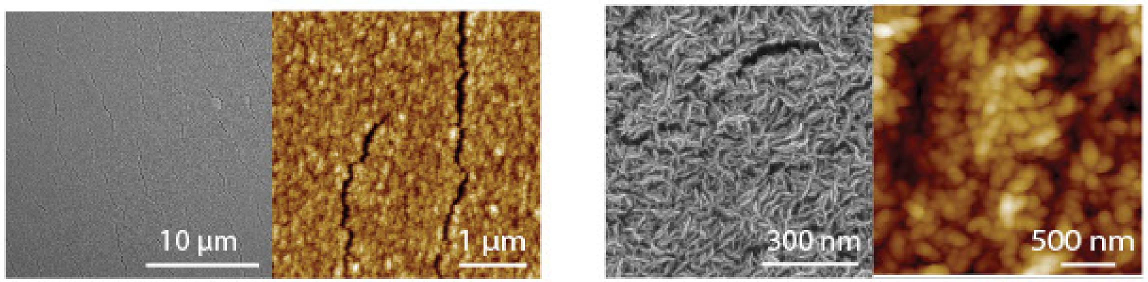
film thickness | mm to µm scale | µm to nm scale

MoS_2 film on rough crystal



MoS_2 film on polished crystal



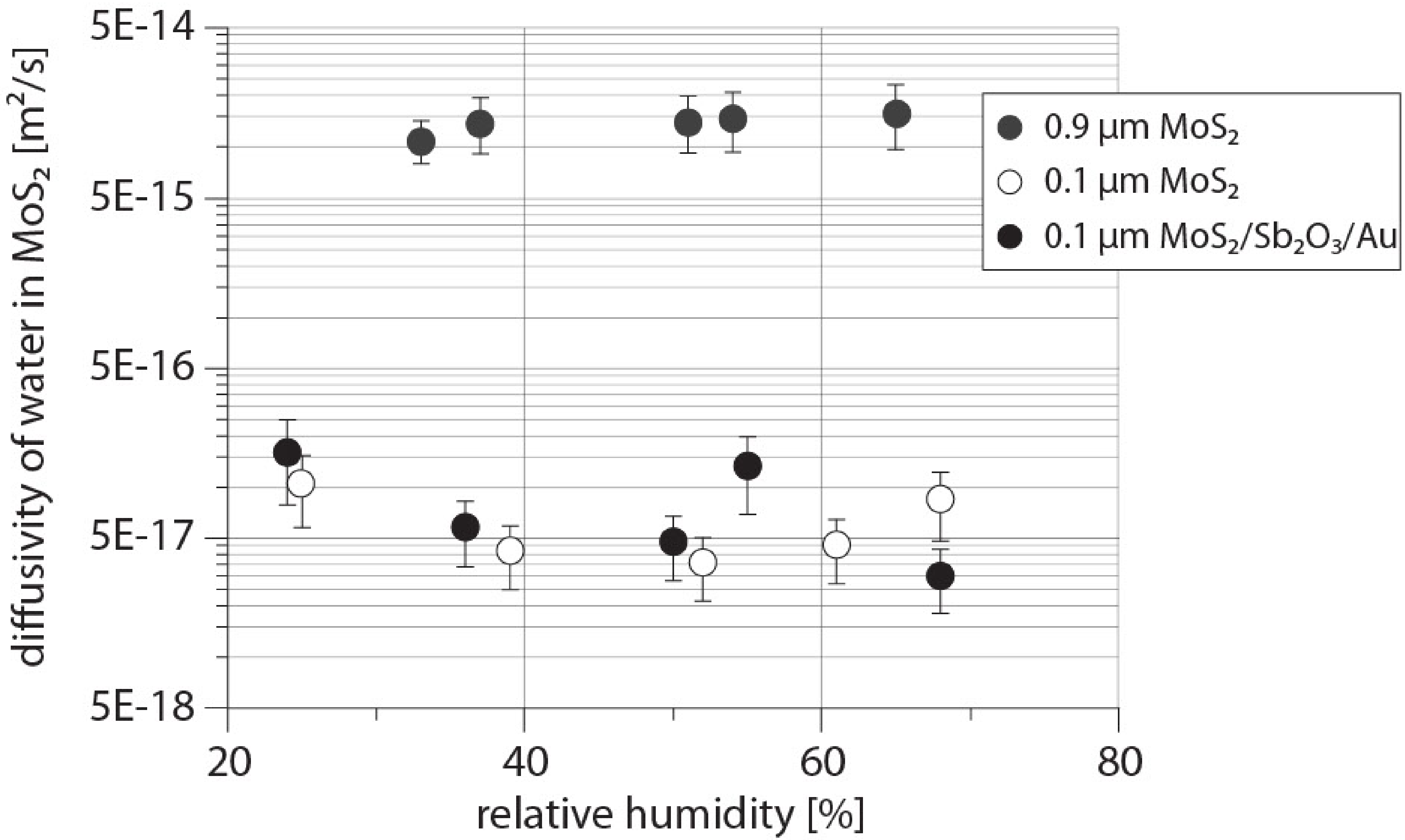


ratio of rough to polished surface areas	1:9	2:1	1:4+

The ratio of water uptake between rough/thin and polished/thick MoS_2 films was 1:40. Thus, this is not strictly a surface phenomena but rather water permeating into the film (absorption).

* Note: SEM images were provided by Richard Grant and AFM images were provided by Anna Trujillo

Diffusivity of Water into MoS_2 Films Results



Diffusivity values for the two thin films were found to be on the same order of magnitude and the thicker film was found to be 2 orders of magnitude faster.

Friction and wear both increase with an increase in relative humidity

Two diffusion processes were observed:

- water that requires a thermal input to be removed
- water that is reversibly absorbed at room temperature

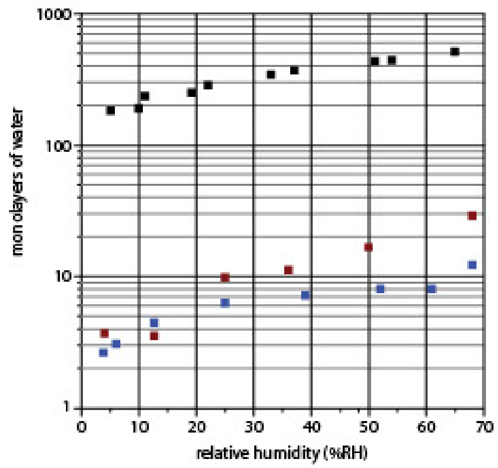
As both friction and wear are lowered by decreasing the partial pressure of water, and do not require thermal energy to lower their values, only the water sorbed at room temperature is affecting the tribological properties

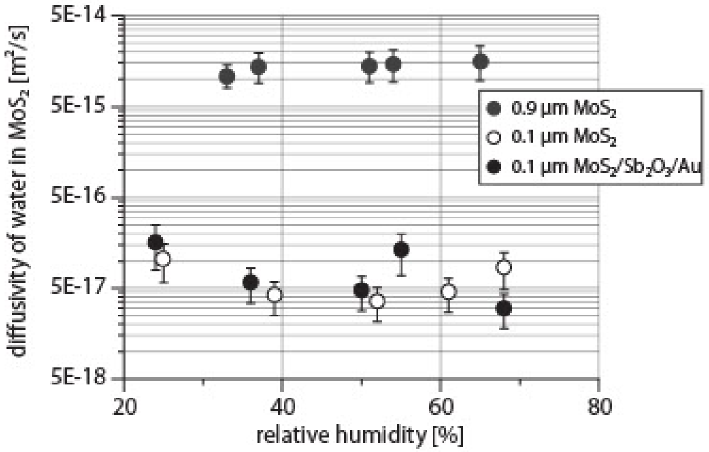
Water is shown to be absorbing into the film

- available surface area is believed to have an affect on the quantity of water sorption, but is not the major contributor
- film thickness is shown to be a larger contributor than surface phenomena

Diffusivity values were calculated for all films, with the pure and composite 0.1 µm films found to be the same order of magnitude and the pure 0.9 µm film 2 orders of magnitude faster

A direct comparison of quantity of water sorbed can not be made between the MoS_2 and $MoS_2/Sb_2O_3/Au$ due to the variability between crystals





Future Work

Explore the stoichiometric effects: MoS_2 vs. $MoS_{1.6}$

Study the effect of lamellar orientation

- amorphous, short range order vs. longer range orientation of lamellae parallel to the sliding direction

Study the effect of microstructure on the quantity of water uptake

Perform similar studies but with all films deposited on the polished quartz crystals (Ra<10 nm)

- MoS_2 film
- $MoS_2/Sb_2O_3/Au$ film

Further analyze the surface area/volume ratio for the various microstructures observed for these films

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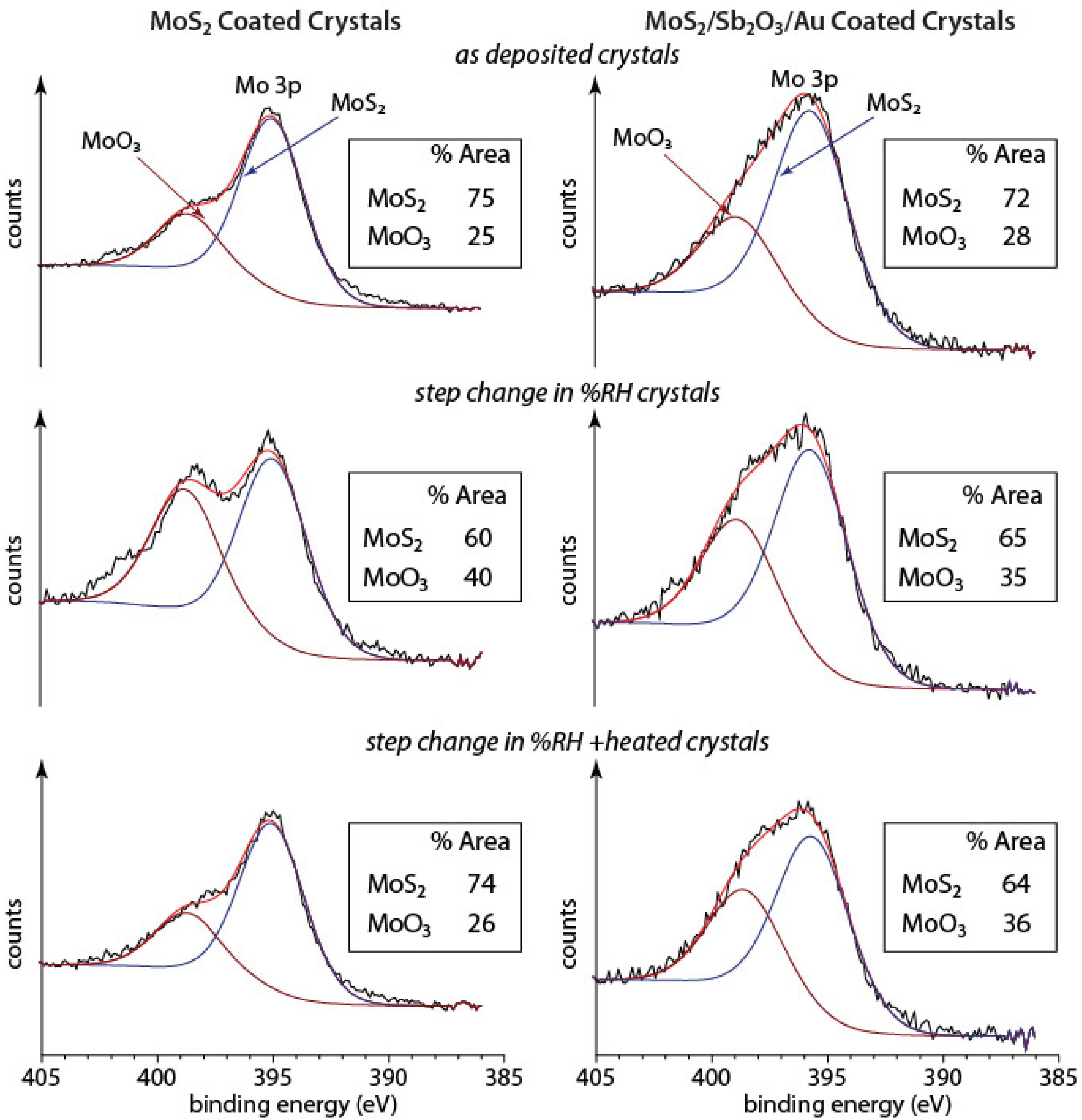
Prof. David Burris
Richard Clark
Dr. Daniel Dickrell
Alison Dunn
Dr. Matthew Hamilton
Dr. Brandon Krick
Kellon Marchman
Dr. Nathan Mauntler
Kyle Rowe
Juan Urueña
Dr. Jennifer Vail

funding provided by:

Oxidation Results from XPS on MoS_2 and $MoS_2\backslash Sb_2O_3\backslash Au$ Films



Three different crystals from each coating batch each at various stages of exposure were compared via XPS.

The as deposited crystals show the lowest amount of oxidation.

The heated crystals show similar quantities of oxidation as the crystal which was not heated.

Oxidation of the film could not be quantified with this method due to the variability in results from each crystal. Thus, the oxidation is either minimal to nonexistant but the relative quantity cannot be determined from this data.

Density and Thickness Method*

Assumptions
thickness (t) = 3.1 A
density of H_2O (ρ) = $1x10^6$ g/m^3
mass/area (m/A) = 0.0083 g/m^2

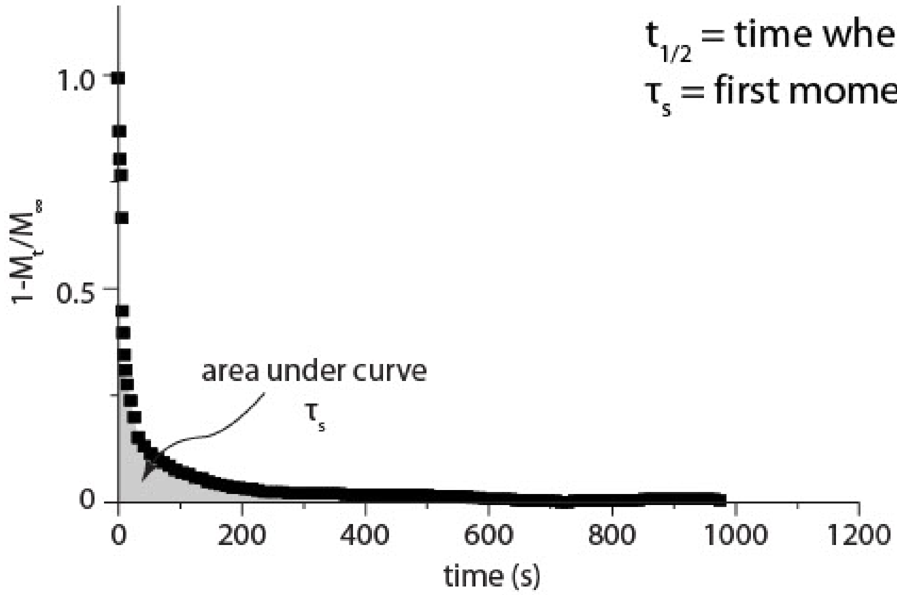
$$\frac{m/A}{\rho t} = \frac{0.0083\, g/m^2}{1x10^6\, g/m^3 \cdot 3.1x10^{-10}\, m} = 26.8 \;\; ML$$

Molecules per Area Method

Assumptions
area number density (n) = 10^{15} molecules/cm^2
molecular weight of H_2O (M)= 18 g/mol
Avogadro's number (N_A) = $6.023x10^{23}$ molecules/mol
mass/area (m/A) =0.0083 g/m^2=$8.3x10^{-7}$ g/cm^2

$$\frac{m/A}{N_A/nM} = \frac{8.3x10^{-7}\, g/cm^2}{10^{15}\, molecules/cm^2 \cdot 18g/mol \,/\, 6.023x10^{23}\, molecules/mol} = 27.8 \;\; ML$$

Moment Method



L = film thickness

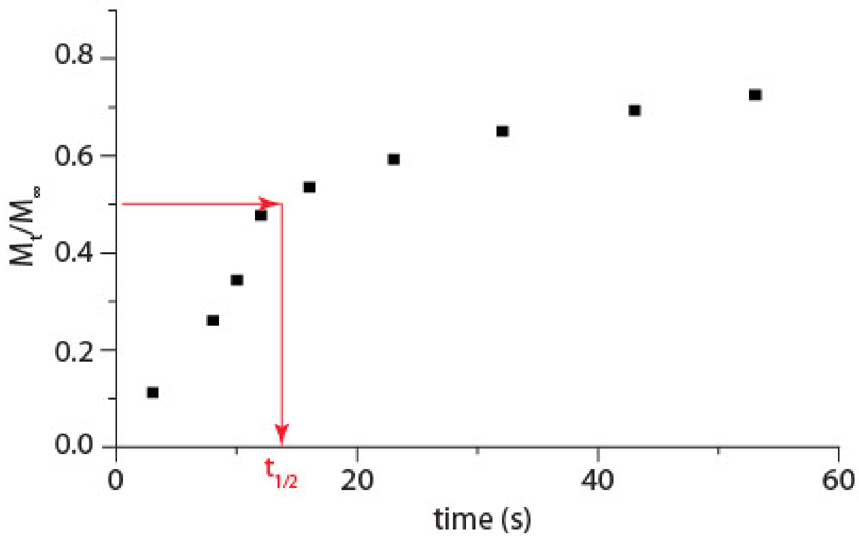
$t_{1/2}$ = time when M_t/M_∞=0.5

τ_s = first moment

$$\tau_s = \int_0^\infty \left(1 - \frac{M_t}{M_\infty}\right) dt$$

$$D \approx \frac{L^2}{3\tau_s}$$

Half-time Method



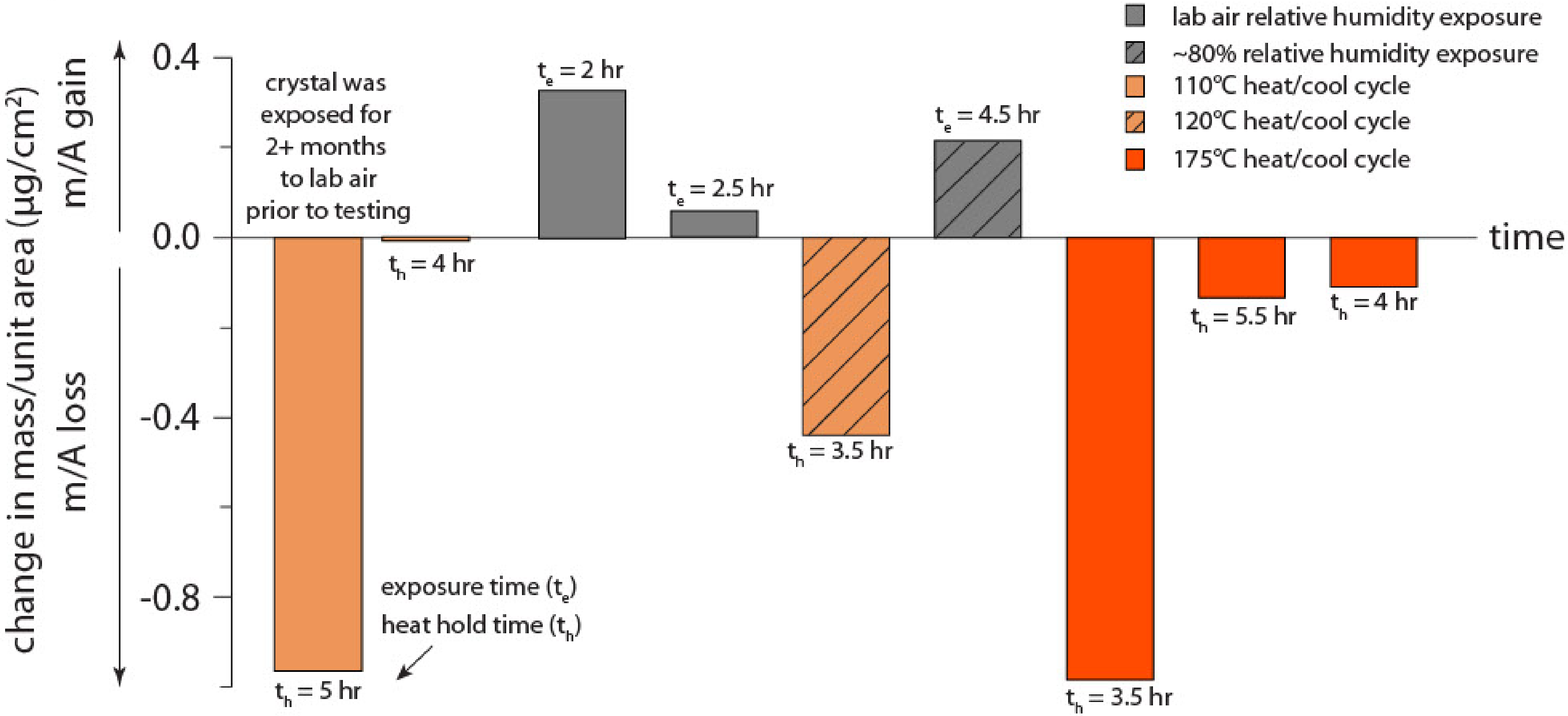
$$D = -\frac{4}{\pi^2 \left(\frac{t}{L^2}\right)_{1/2}} \ln\left[\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right]$$

$$D \approx \frac{0.049 L^2}{t_{1/2}}$$

A3-half time diffusivity method.ai

Inert Environment Heating Experiments on $MoS_2/Sb_2O_3/Au$ Film

Relative changes in the mass per unit area are shown. All data was measured with the same coated quartz crystal. The crystal was initially exposed to numerous relative humidity cycled changes and then this experiment was commenced.

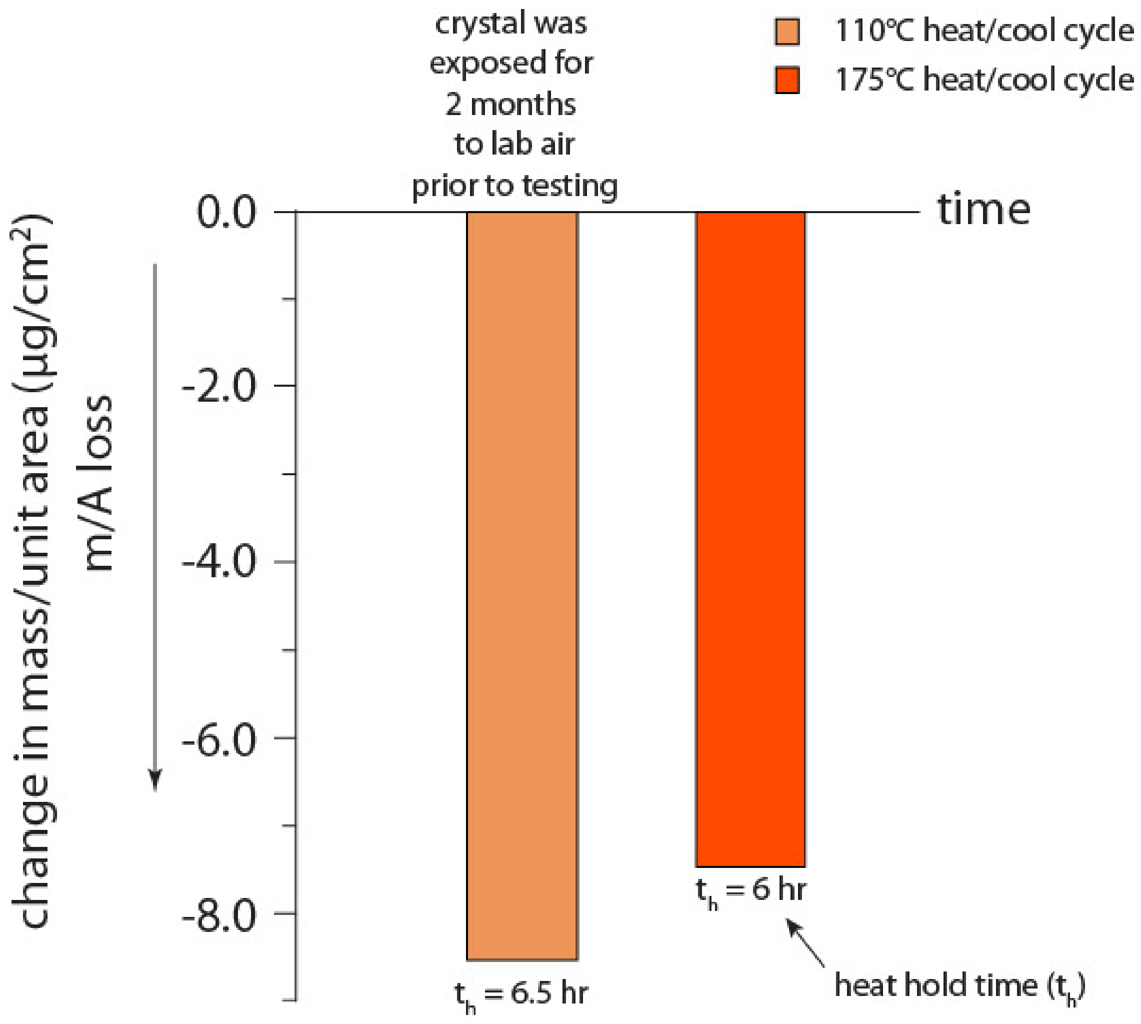


A large mass per unit area loss was observed after the first 110°C heat/cool cycle, but was minimal upon additional 110°C heat/cool cycles.

Additional quantities of mass per unit area loss were observed with the 170°C heat/cool cycles.

Inert Environment Heating Experiments on 0.9 µm Pure MoS_2 Film

Relative changes in the mass per unit area are shown. All data was measured with the same coated quartz crystal. The crystal was initially exposed to numerous relative humidity cycled changes and then this experiment was commenced.



A large mass per unit area loss was observed after the 110°C heat/cool cycle. This was an order of magnitude greater than the 0.1µm sample.

Significant additional mass per unit area loss was observed after the 170°C heat/cool cycle.

Volume Loss

Using scanning white light interferometry, a 3D surface scan of the wear track is taken.

A representative 2D slice through the wear track is taken and analyzed for the wear track cross-sectional area.

Creep of these thin film coatings is considered negligible.

The volume of material removed is then estimated by calculating the cross-sectional area of the scans. This average area is swept along the complete wear track path to calculate the volume loss.