Use of Self-Assembled Monolayers and Light to Tailor Adhesion on Surfaces for Nanomanufacturing Applications

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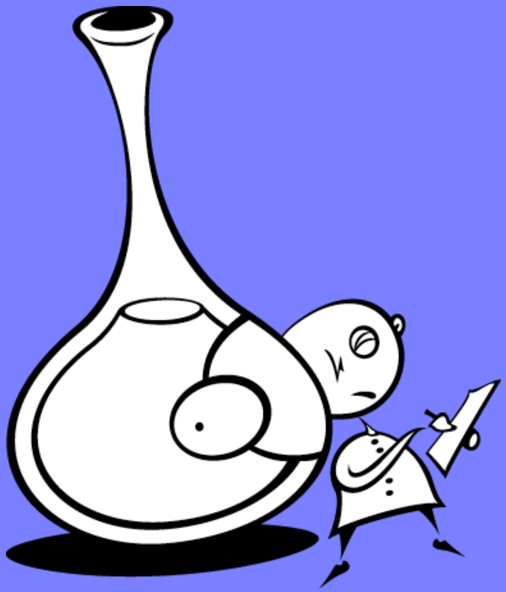
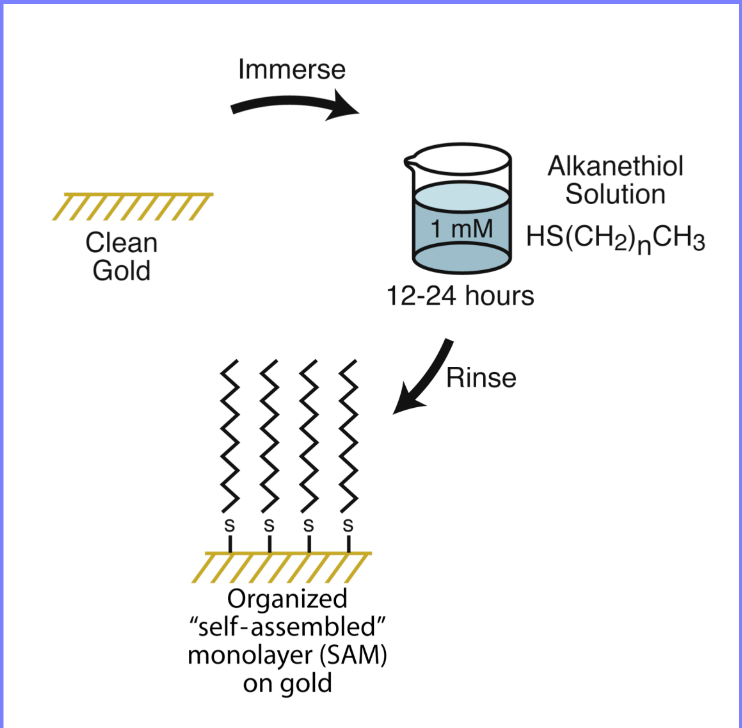
The Whitten Group

- ❖Electronic Structure of Conjugated Polymer Films
- ❖Organic-Metal Interfaces
- ❖Organic Dye-Inorganic Semiconductor Interfaces
- ❖Nanopatterning of Materials and Transfer
- ❖Measurement of Forces between Surfaces
- ❖Chemical Sensors Based on Gold Nanoparticles
- ❖Metal Oxide Surface Chemistry
- ❖Development of Low-Cost Spectroscopy Experiments for Chemical Education - Blue Diode Lasers and Light-Emitting Diodes



Self-Assembled Monolayers

Applications: Corrosion protection, biomimicry, tailoring of wetting properties of surfaces, chemical sensors, modification of electrodes for organic electronics, molecular electronics, nanotemplating/nanomanufacturing.



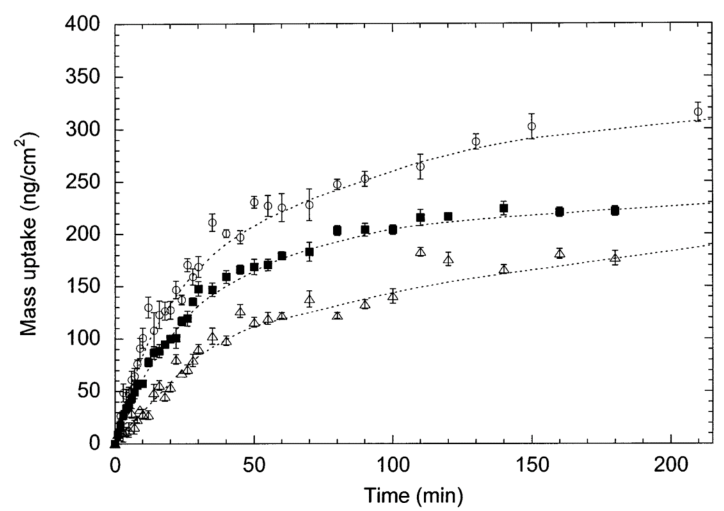
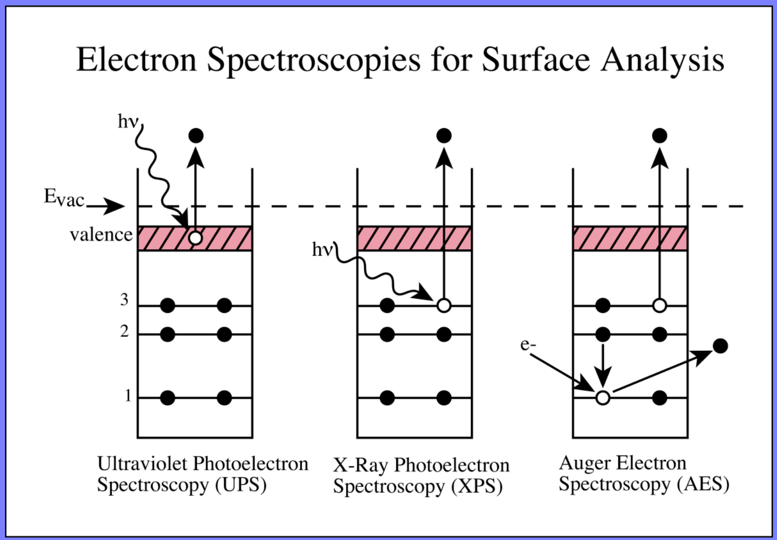
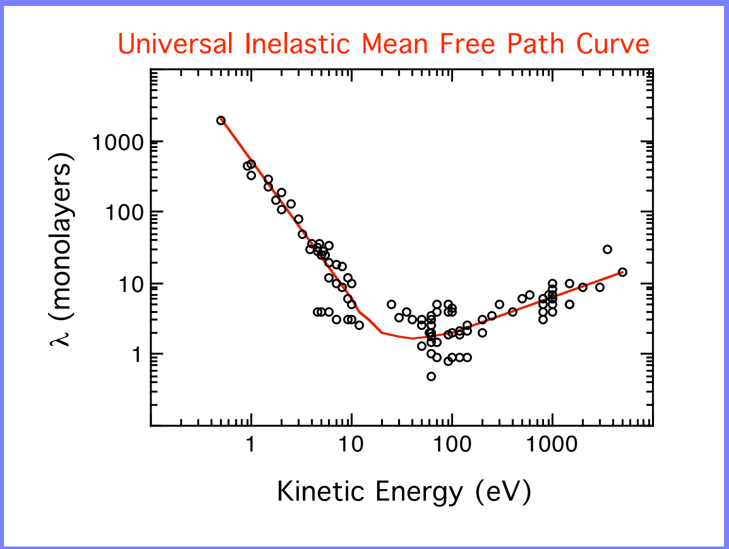


Figure 8. Mass uptake change as a function of immersion time of a quartz crystal microbalance in 1 mM 2-(3-thienyl)-ethanethiol (△), 6-(3-thienyl)hexanethiol (■), and 12-(3-thienyl)-dodecanethiol (○) solutions. The lines through the data are included to guide the eye. Note that the measurements were performed ex situ, as discussed in the text.

H. Ahn, M. Kim, D.J. Sandman, J.E. Whitten, *Langmuir*, 2003, *19*, 5303

Electron Spectroscopies





The photoelectron intensity (I) emitted at an angle θ relative to the surface plane, from depths less than d, is given by:

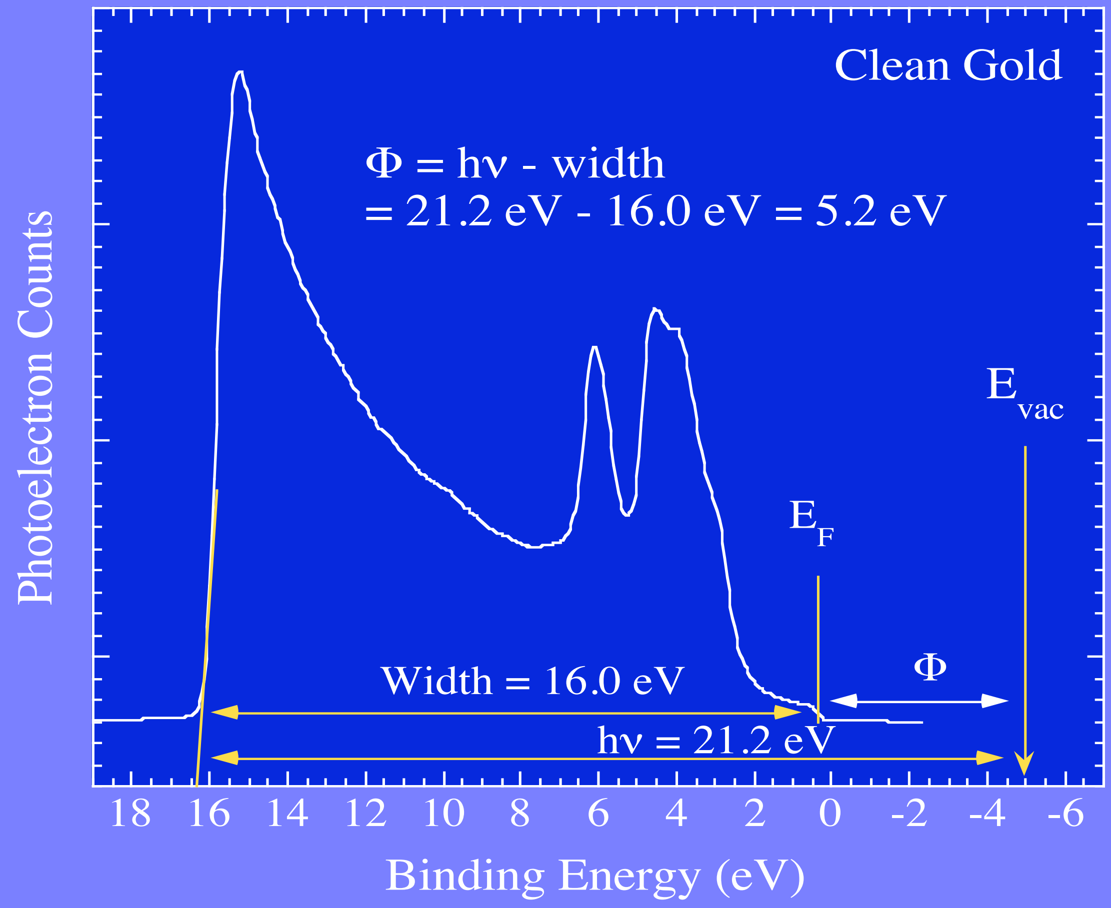
$$I = I_o \exp\{-d/(\lambda \cos(90 - \theta))\}$$

where I_o is the intensity from an infinitely thick, uniform substrate and λ is the mean free path.

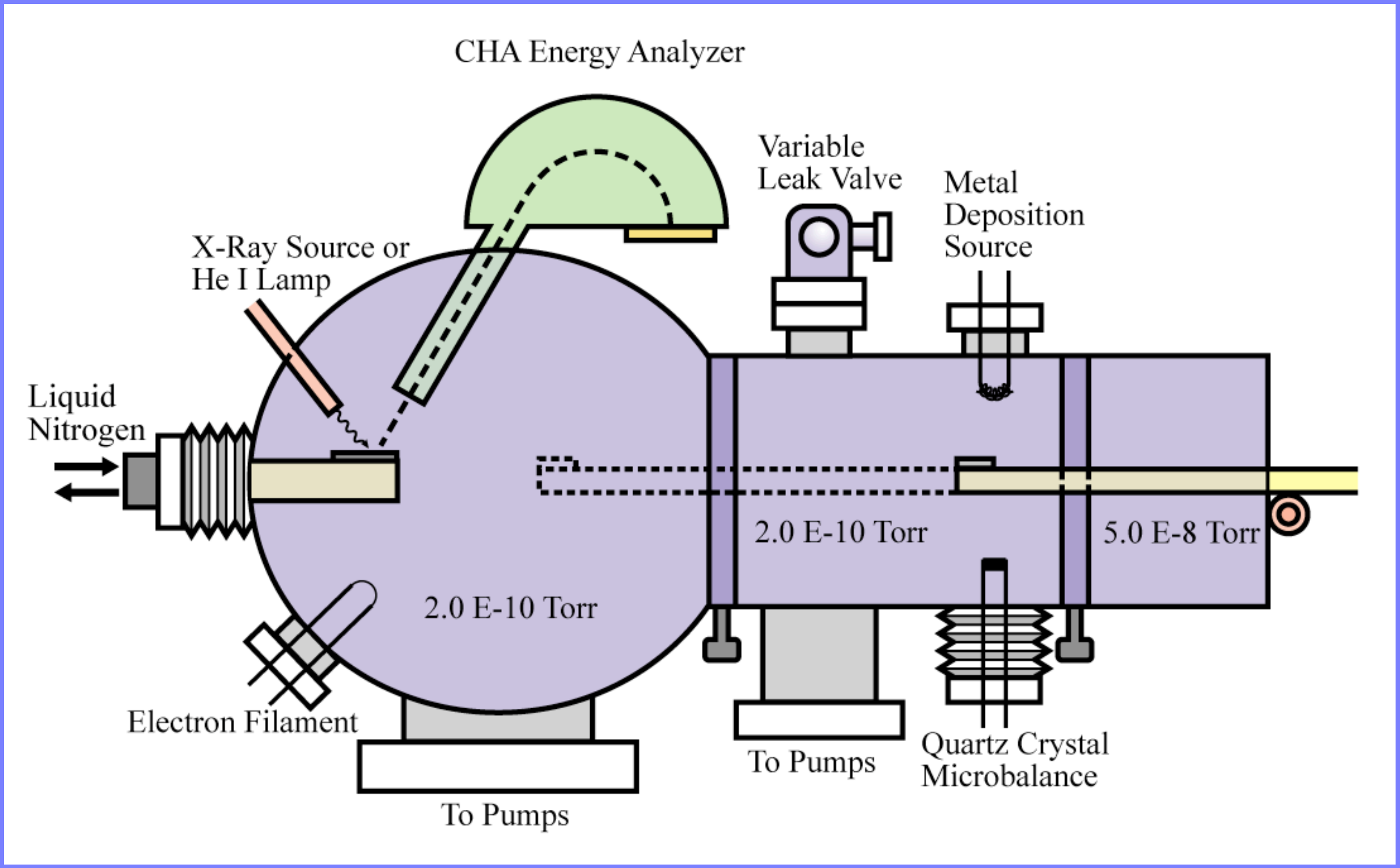
95% of the signal originates from a depth less than 3λ.

Ultraviolet Photoelectron Spectroscopy

The Work Function of a Sample Can be Calculated
from the Width of the UPS Spectrum



Experimental Apparatus



Topics to be Discussed

- Using thiol SAMs to pattern polymers, biomaterials, and conjugated oligomers.
- Comparison of thermal stability of thiol and silane monolayers.
- Sandwich structures using a mercaptosilane.
- Light-switchable functionalization for nanomanufacturing.

Template-Directed Patterning of Materials

❖The goal is to use self-assembly of alkanethiols as templates for materials that are not easily patterned by other means.

❖Microcontact printing and dip-pen nanolithography are used to form patterned arrays of alkanethiol monolayers on gold surfaces.

❖The arrays of patterned alkanethiols affect the wetting properties of the surface so that spin-coated material selectively wets or de-wets the alkanethiol patterns.

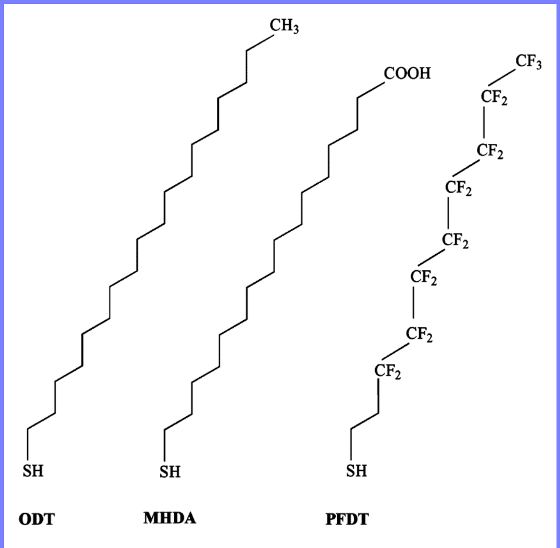


Table 1. Properties of Alkanethiol-Covered Gold Surfaces and These Surfaces after Spin-Coating PE-*b*-PEO Block Copolymers onto Them (Without Annealing)

alkanethiol	θ (adv) water	θ (rec) water	C/Au atomic ratio for 80/20 PEO/PE block[a]	C/Au atomic ratio for 20/80 PEO/PE block[b]
ODT	113 ± 1	97 ± 3	0.92	infinite
PFDT	109 ± 3	85 ± 1	12	49
MHDA	74 ± 3	40 ± 2	infinite	19

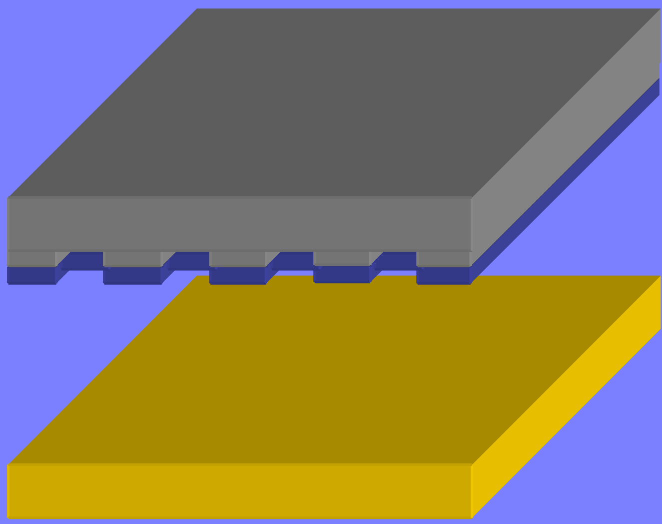
[a] The polymer was spin-coated using a 0.5 wt % solution in chloroform. [b] The polymer was spin-coated using a 0.4 wt % solution in toluene (warm solution).

A. Chandekar, S.K. Sengupta, C.M.F. Barry, J.L. Mead, J.E. Whitten, *Langmuir*, 2006, *22*, 8071

Microcontact Printing

A technique that generates patterned self-assembled monolayers of alkanethiolates on metal surfaces (gold, silver and copper).

•An "ink" of alkanethiols is spread on a patterned PDMS stamp.
•The stamp is then brought into contact with the substrate.
•The thiol ink is transferred to the substrate where it forms a self-assembled monolayer that can act as a resist against etching.



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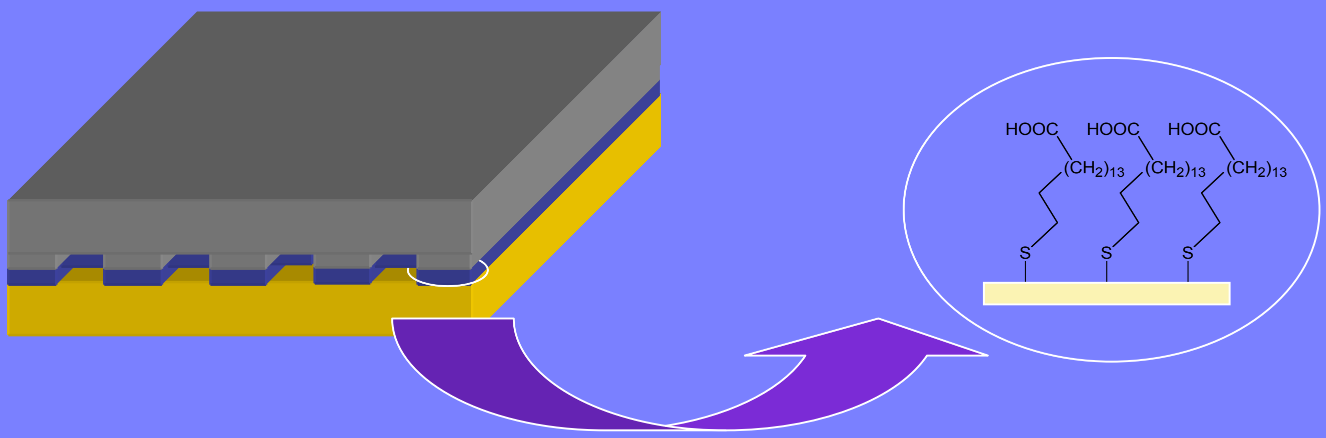
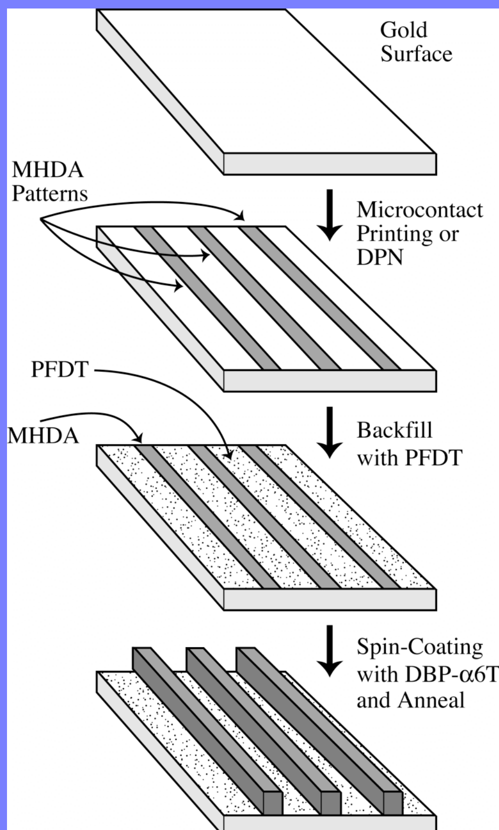
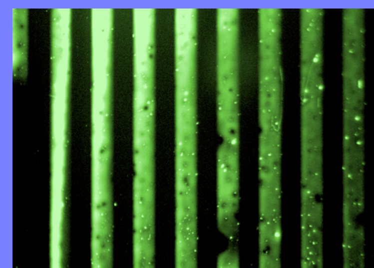
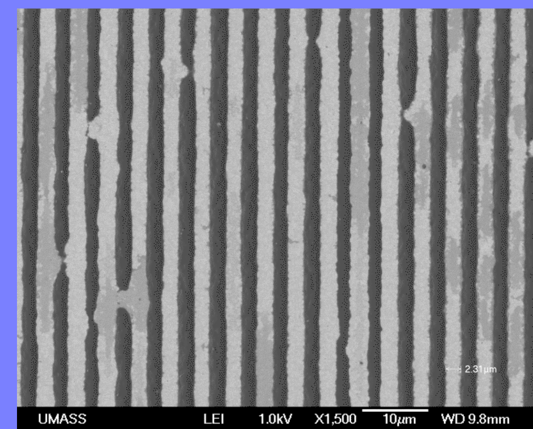


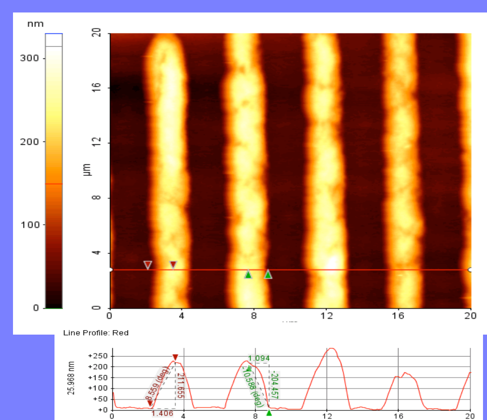
Patterning of Conjugated Polymers and Biomaterials



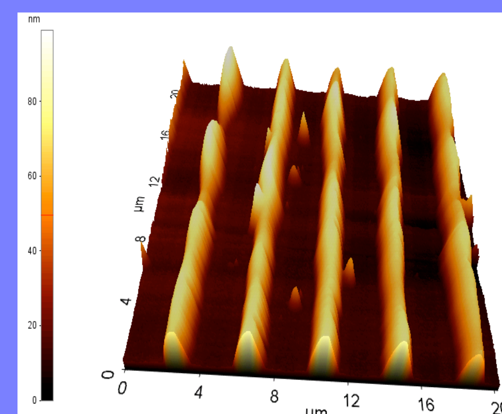


Fluorescence Microscopy of Patterned Collagen-Fluorescein



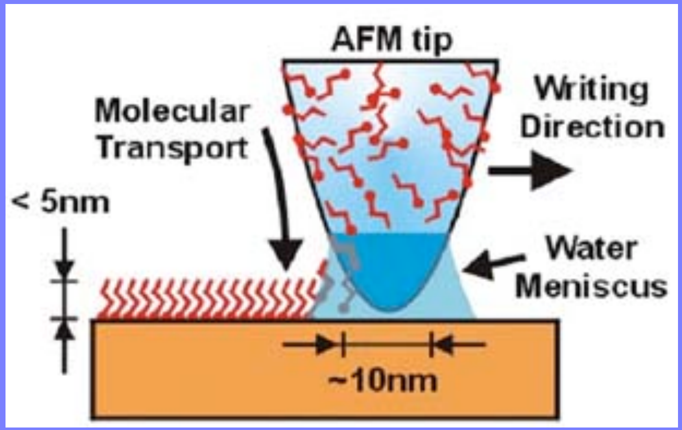


AFM of Patterned PEO-*b*-PE Polymer

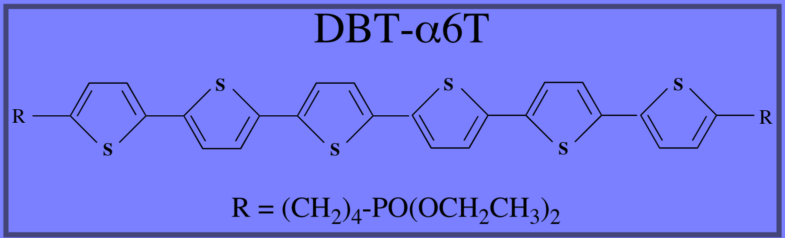


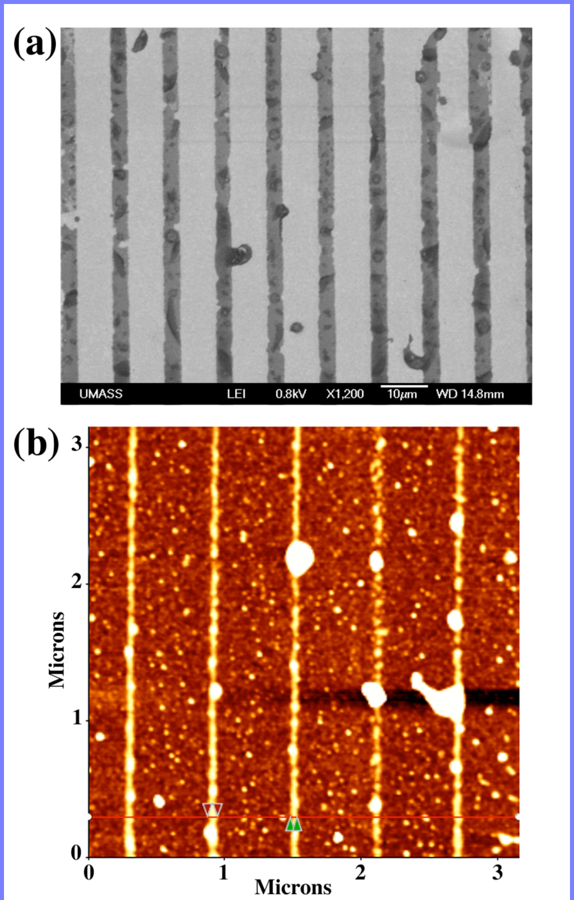
AFM and SEM Images of Patterned Poly-L-Tryptophan

Use of Dip-Pen Nanolithography to Pattern a Conjugated Oligomer



http://www.chem.northwestern.edu/~mkngrp/dpn.htm





A. Chandekar and J.E. Whitten, *Appl. Phys. Lett.*, 2007, *91*, 113103

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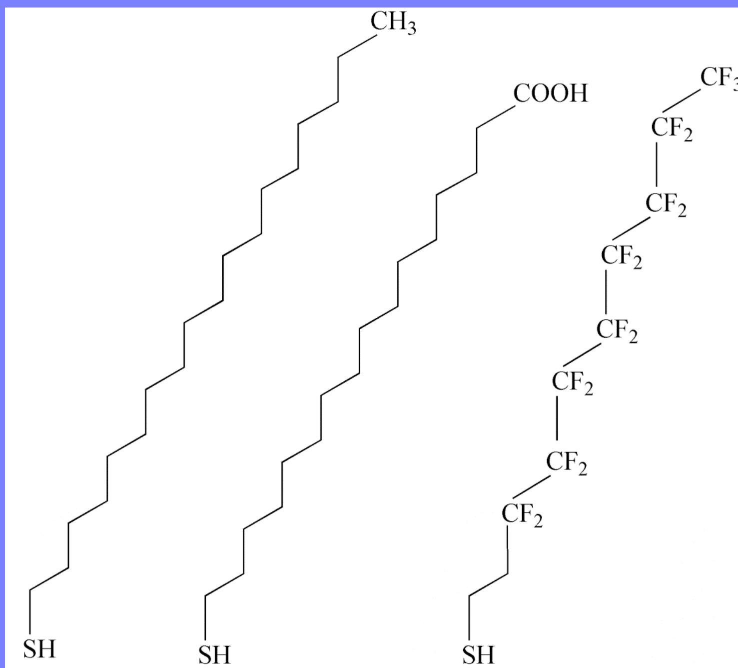
Thermal Stability of Silane SAMs on Silicon Oxide/Si(111)



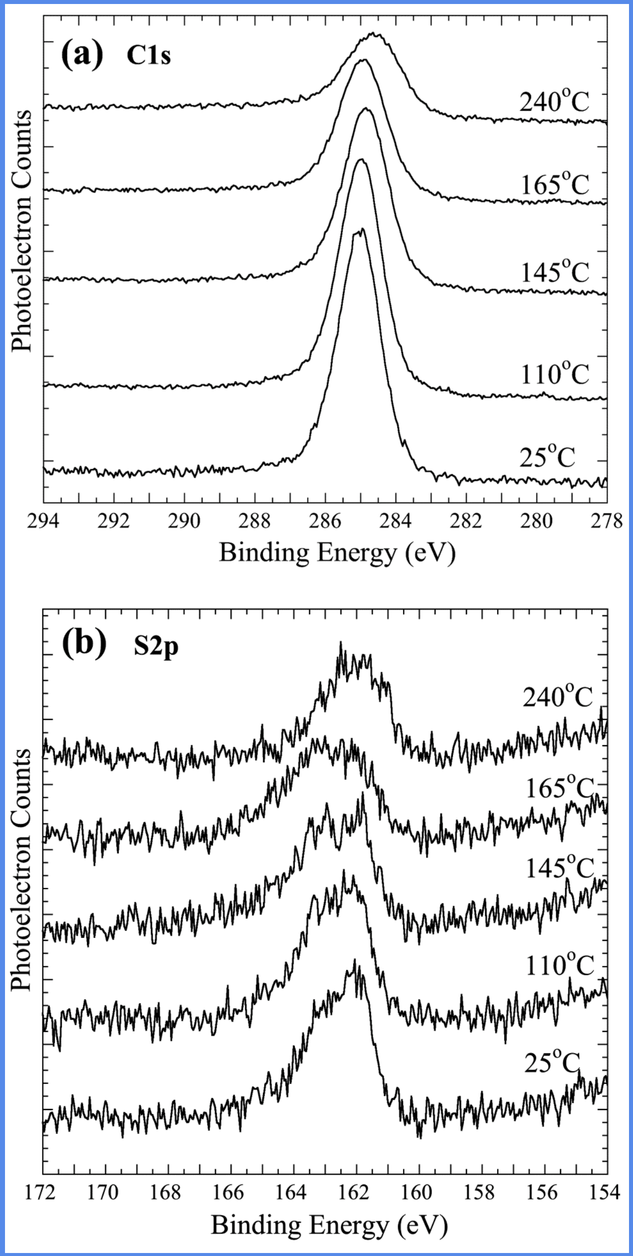
ODT **MHDA** **PFDT**

$(CH_3CH_2O)_3SiCH_2CH_2CH_2CH_2NH_2$ **ABTES**

$(CH_3CH_2O)_3SiCH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$ **PFDS**

A. Chandekar, S.K. Sengupta, J.E. Whitten, *Appl. Surf. Sci.*, 2010, *256*, 2742.

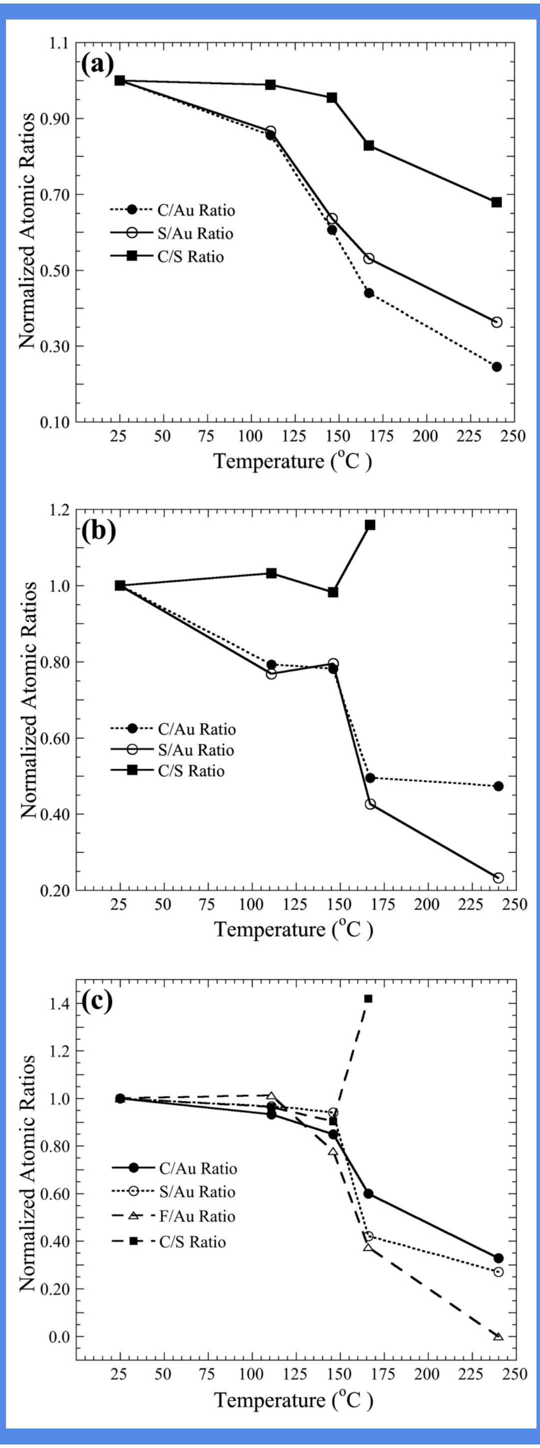
XPS of Heating of ODT/Au(111) SAM



ODT

MHDA

PFDT

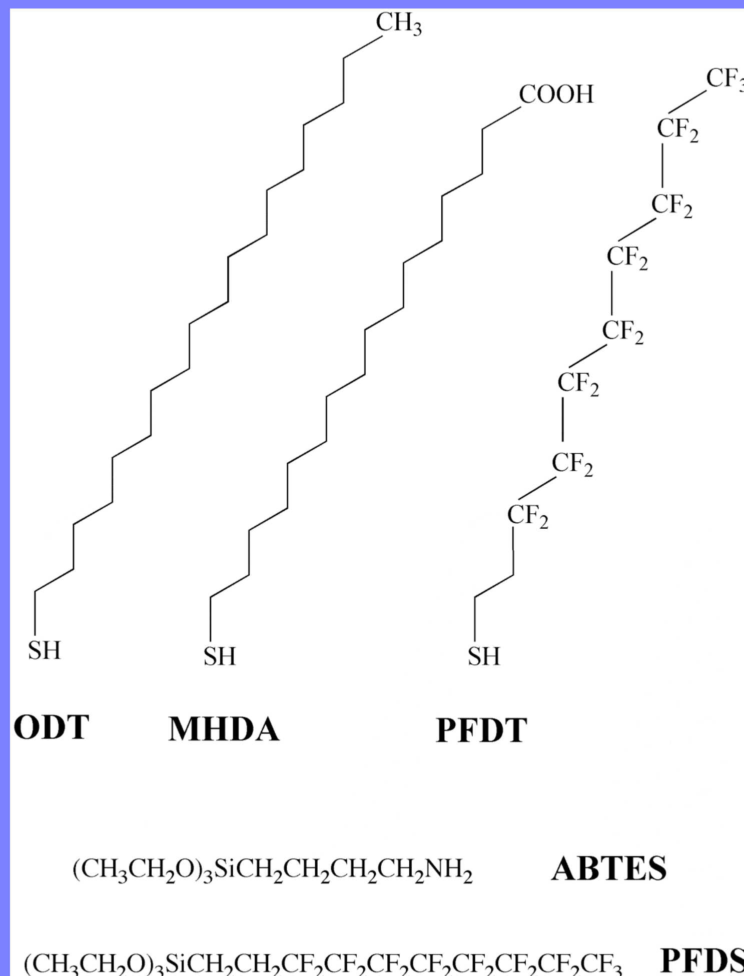


Preparation of Silane Monolayers

Si(111) substrates were:

- Ultrasonicated in methanol and acetone and then etched in pirahna solution at 80^{o}C for 30 min. This procedure removes the native oxide and grows a fresh hydroxylated surface.
- Soaked in DI water to remove residual acid.
- Exposed to UV-ozone using a Novascan PSD-UV cleaner for 20 min to produce a clean, hydroxylated surface for silanization.
- Immersed in 1 mM silane solution in anhydrous hexane for 16 hr.
- Rinsed with anhydrous hexane.

Thermal Stability of Silane SAMs on Silicon Oxide/Si(111)



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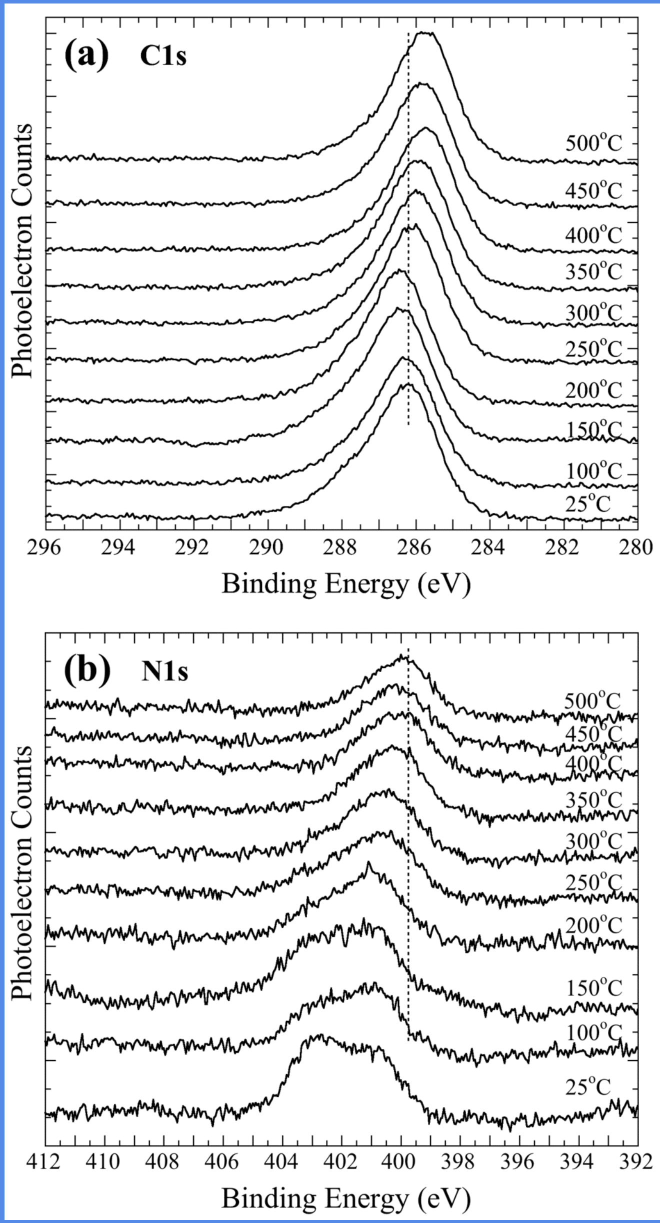
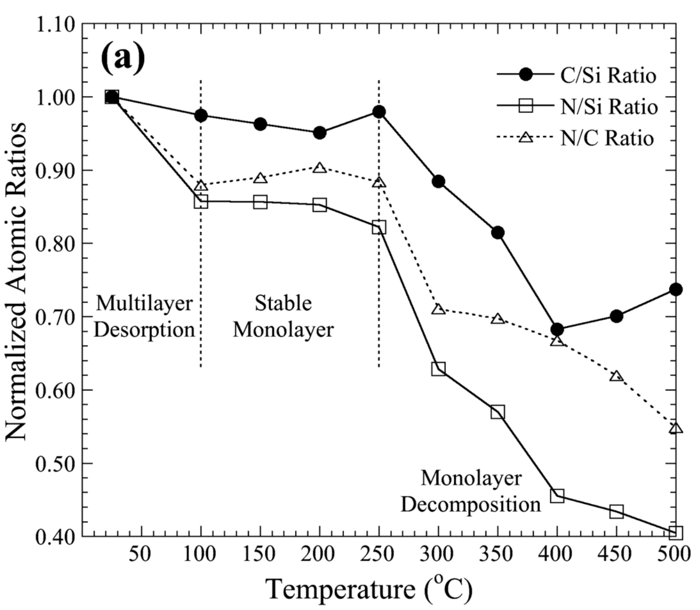
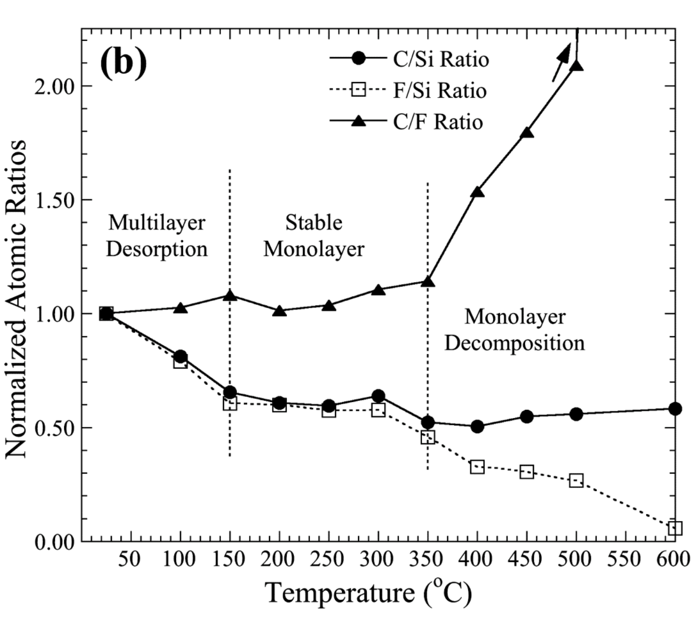
XPS of Heating of ABTES/Si(111) SAM



ABTES



PFDS



Conclusions

Monolayer/Surface	Decomposition Onset
ODT/Au	110 - 145^{o}C
MHDA/Au	145^{o}C
PFDT/Au	145-165^{o}C
ABTES/Si	250^{o}C
PFDS/Si	350^{o}C

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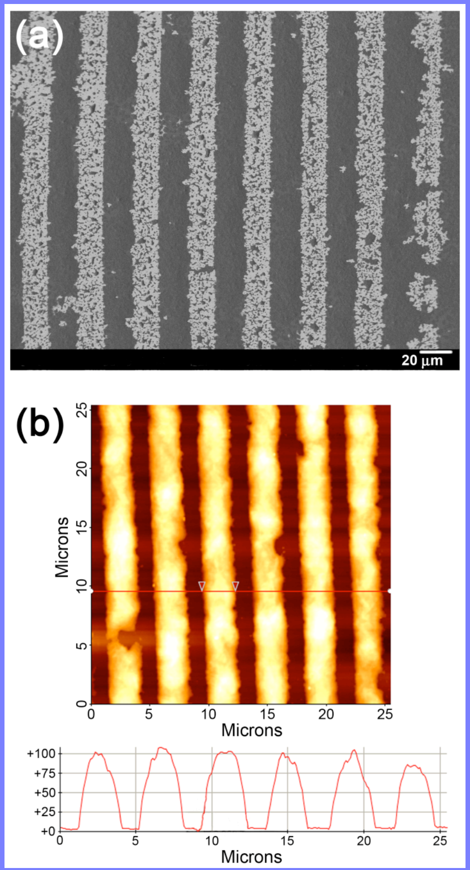
Silane-Directed Patterning



(a) FE-SEM and (b) AFM images of the surface that results when a PFDS microcontact-printed hydroxylated SiO_2 sample is spin-coated with a PEO/PE block copolymer and annealed for 2 hr at 90°C. Included with the AFM image is the cross sectional topographical height scale for the image. The units on the y-axis of the height scale are nanometers.

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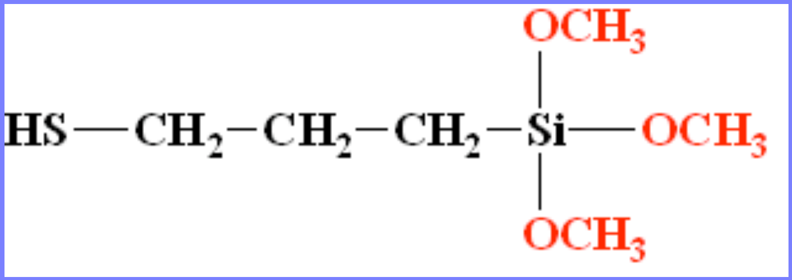
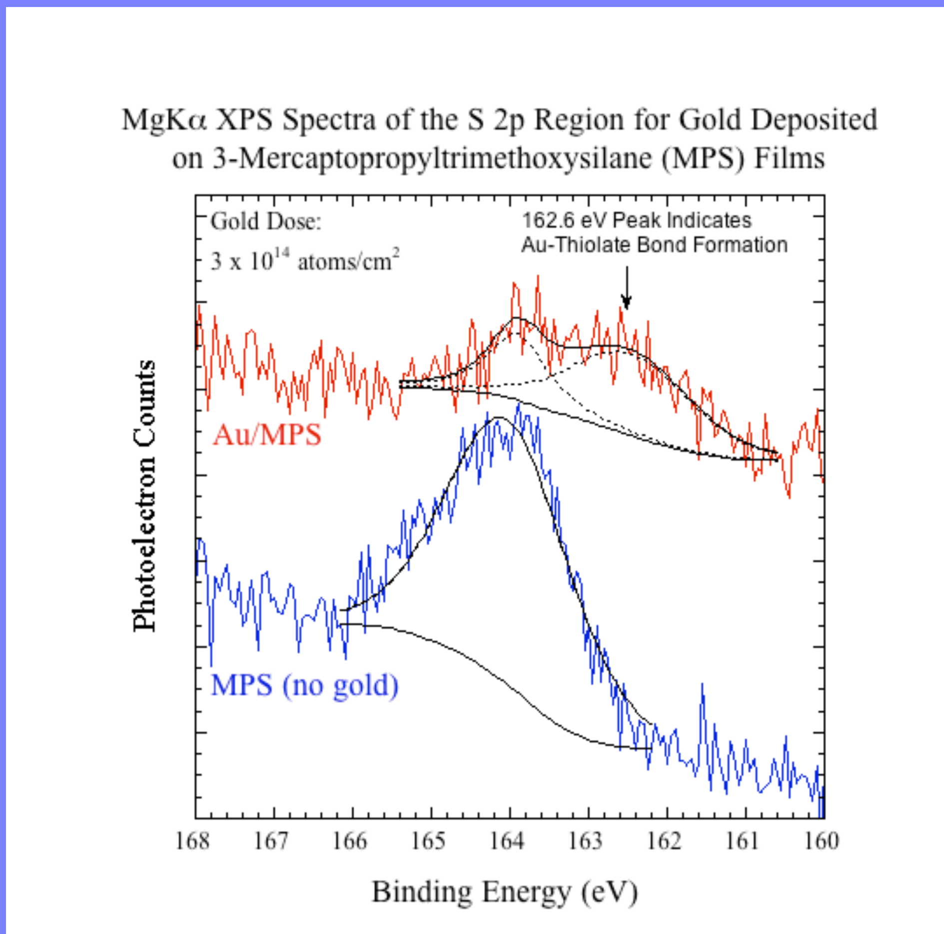
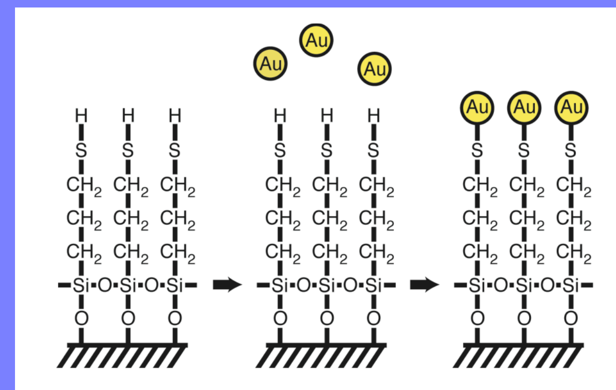
An Interesting Molecule



3-Mercaptopropyltrimethoxysilane (MPS)

XPS Confirms Bond Formation for Gold Deposited on MPS

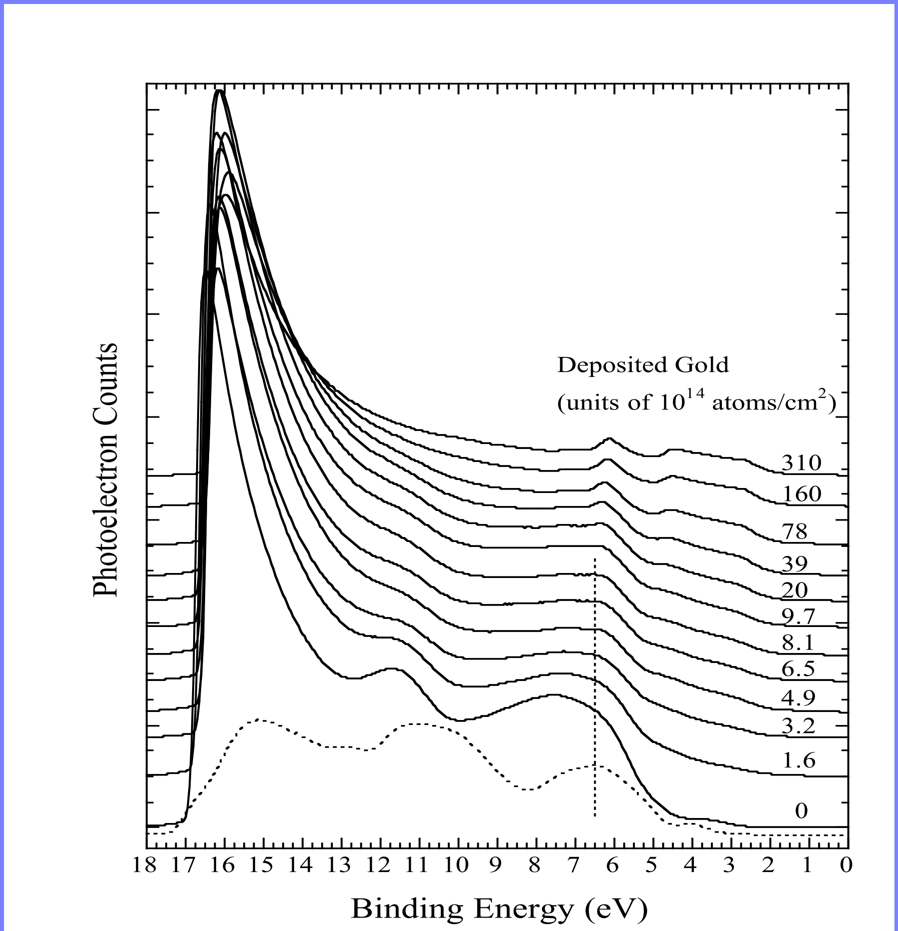




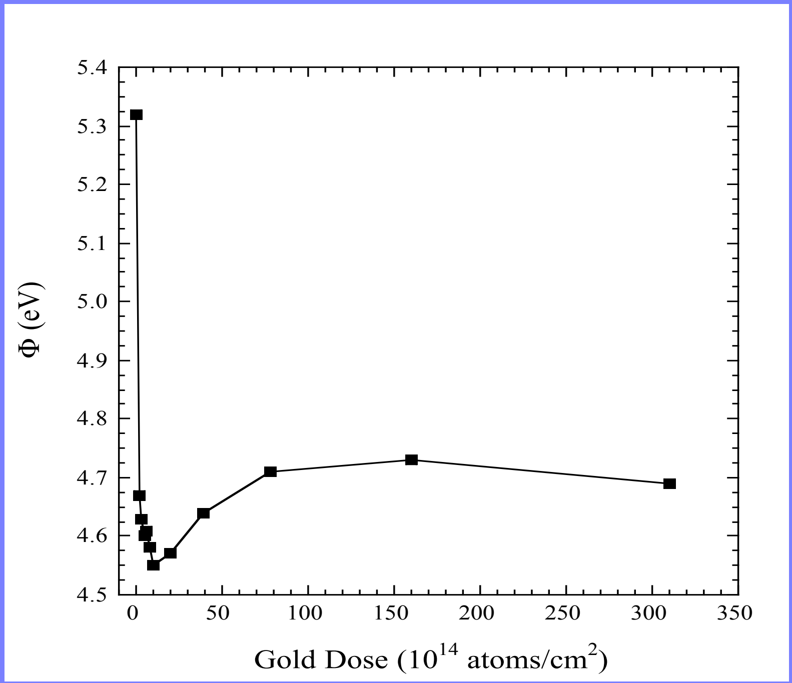
- Angle-resolved XPS shows that gold stays on top of the MPS film.
- Possibilities of molecular electronic devices (e.g., capacitors).

J. Singh, J.E. Whitten, *J. Phys. Chem. C.*, 2008, *112*, 19088.

UPS of Gold Deposition on MPS

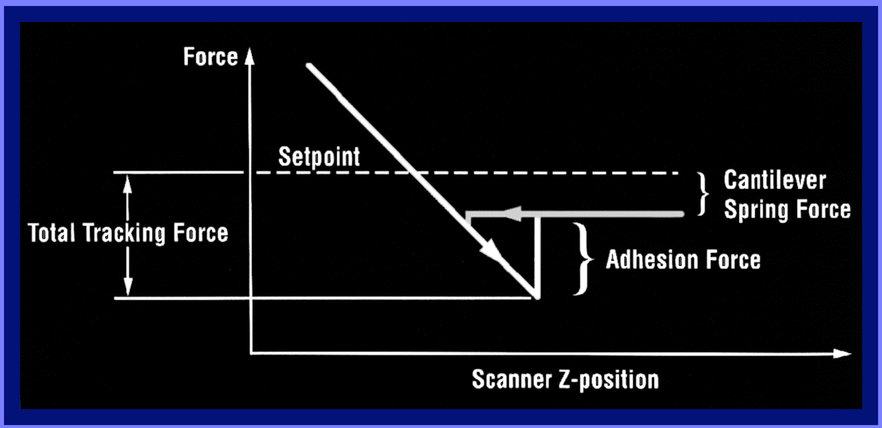


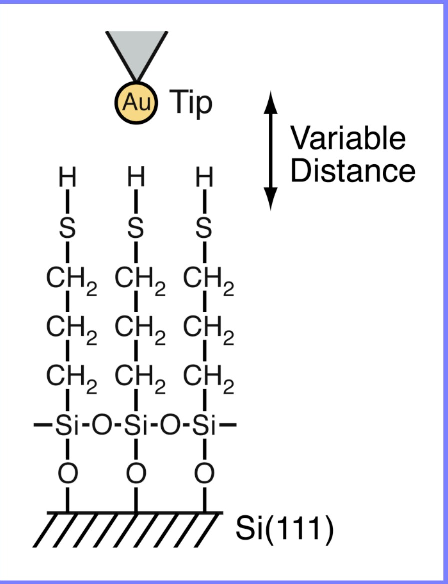
Work function vs. Gold Coverage

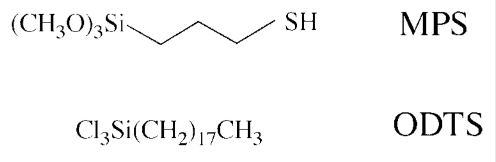


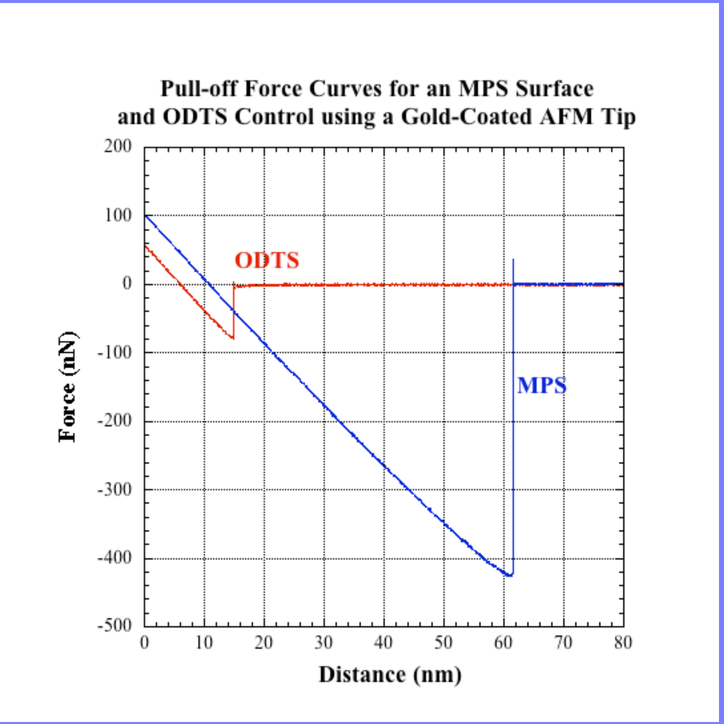
- Final work function value indicates gold not in electronic contact with substrate.

Force-Distance Measurements









Summary of Jump-In and Pull-Off AFM Studies for Gold-Coated Tips and Silane Films

Silane System	Mean Jump-In Force (nN)	Mean Pull-Off Force (nN)
Octadecyltrichlorosilane	133 +/- 46	107 +/-25
Mercaptopropyltrimethoxysilane	340 +/- 86	409 +/-48

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Conclusions

- Patterning of a wide variety of materials may be achieved if a sufficient contrast in wetting properties is obtained on the surface by chemical modification (e.g., thiol or silane SAMs).

- Silane SAMs on silicon oxide surfaces are substantially more thermally stable than thiol SAMs on metal surfaces.

- Light may be used on photocatalytic surfaces (e.g, TiO_2) to induce hydrophilicity - believed to be due to decomposition/desorption of hydrocarbons. Photomasking can be used to achieve contrast in hydrophobicity and patterning.

- Light switchable functionalization is being pursued for nanotransfer applications.

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