NIST Combinatorial Methods Center

Polymers Division

Combinatorial Surface Energy Libraries: Micropatterned Self-Assembled Monolayer Gradients

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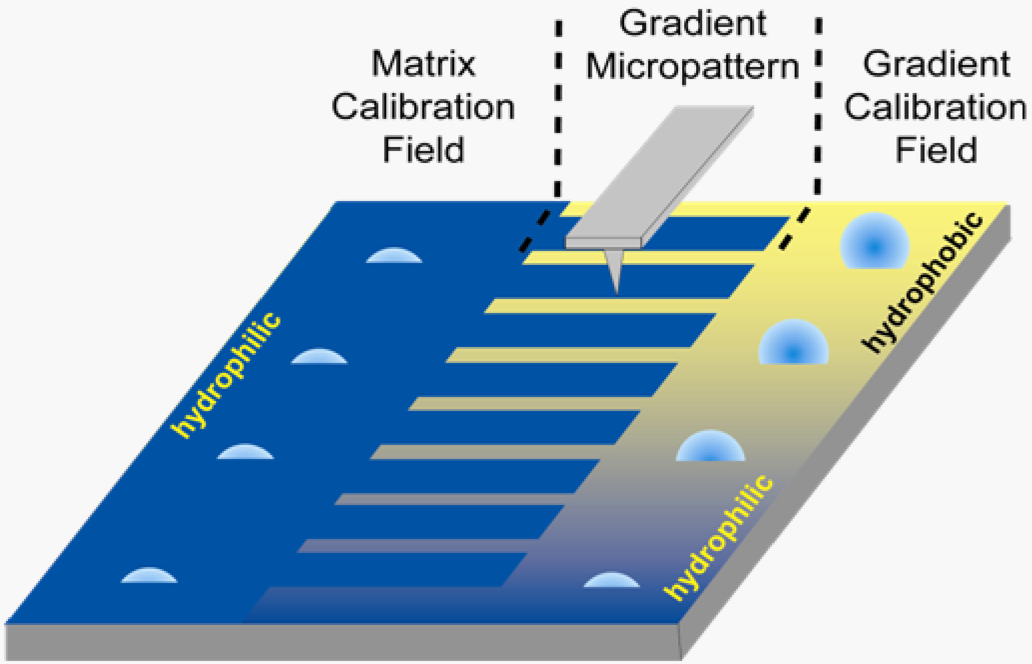
Motivation

GOAL : To design and demonstrate combinatorial surface energy libraries that accelerate the discovery and optimization of biomimetic surfaces

To tune the surface chemistry of biomedical implants to control the selective response of biological molecules for various applications, such as biofouling of implants, tissue regeneration, and targeted delivery.

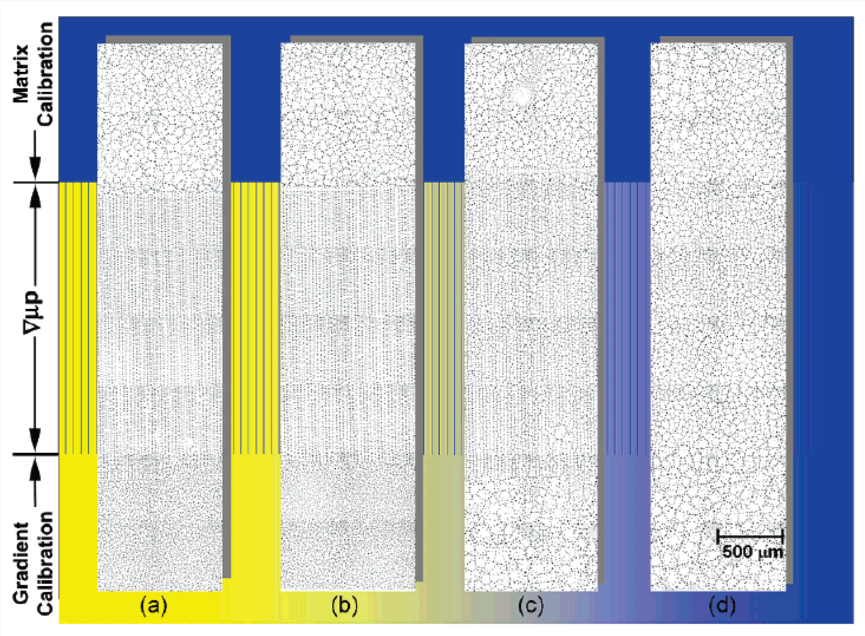
Combinatorial Measurements of:

- Biosurfaces
- Biofouling
- Nano-defect assessment
- Nano-film stability
- Grafted functional layers
- Self assembled films
- Responsive surfaces
- Catalysis

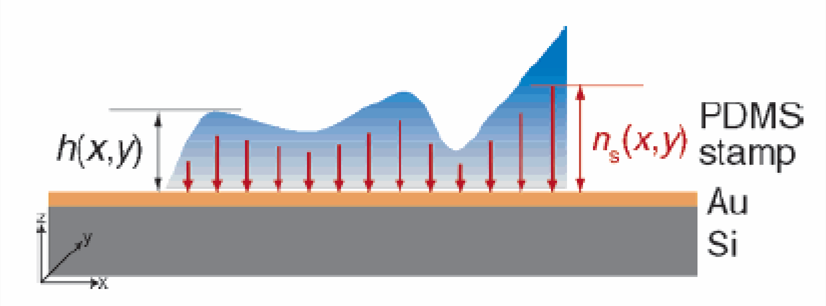


Previous Gradient Libraries

Example: Library of nano-film wetting behavior



D. Julthongpiput et al. *Nano Lett*., **2005**, 5, 1535



T. Kraus *et al. Langmuir* **2005,** *21,* 7796

ODS to Silicon by burning off SAM using UVO lamp

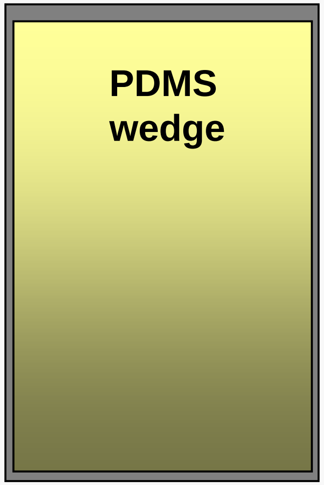
- Quick, easy
- Surface degrades over short storage times (~1 month)
- Limited surface chemistry and library possibilities

Diffusion-controlled depletion printing

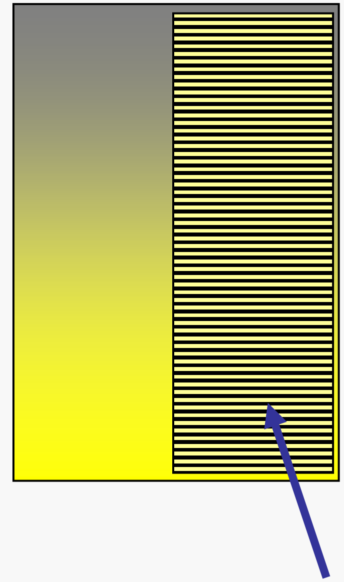
- Thermal stability limited on gold-thiol systems
- Greater flexibility in surface chemistry and geometry but limited in substrate surfaces

Experimental Approach

Mask substrate with Polydimethyl-siloxane (PDMS) wedge and deposit SAM A via vapor



Remove wedge, mask with micropatterned stamp, backfill with SAM B

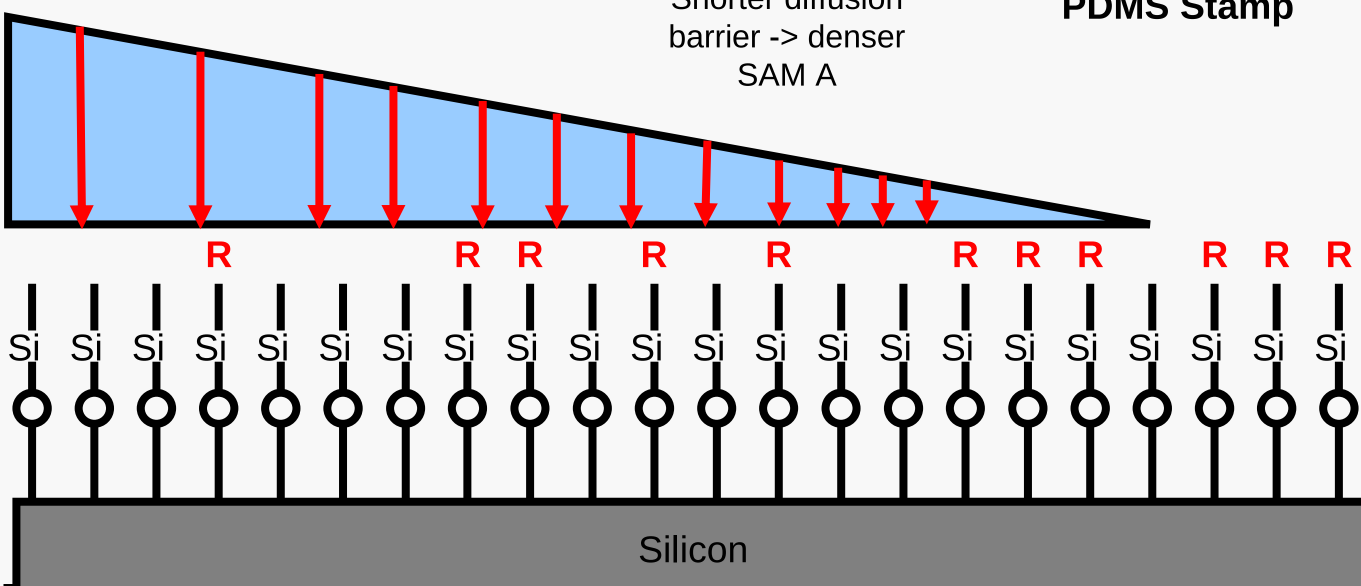


Corrugated PDMS Stamp

- Vapor deposition allows for multiple samples fabricated under same conditions
- Produces linear gradient on silicon substrate
- Backfill step allows for inclusion of micropattern

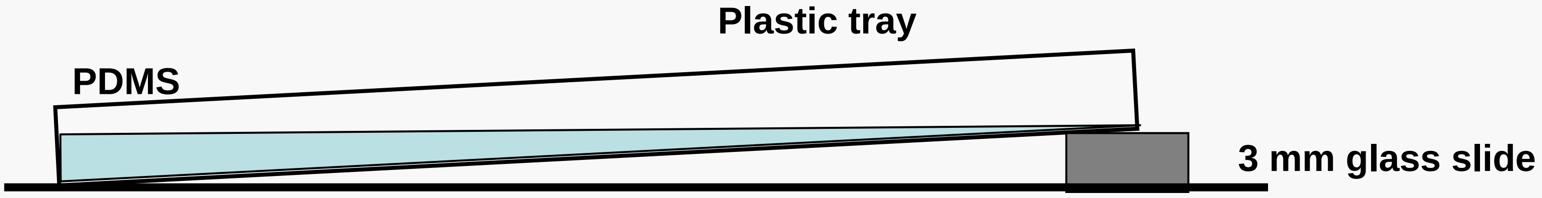
Longer diffusion barrier -> less dense SAM A

Shorter diffusion barrier -> denser SAM A

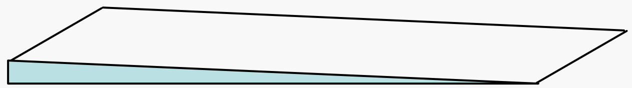


Homogeneous reference SAM (no barrier)

PDMS Wedge Fabrication

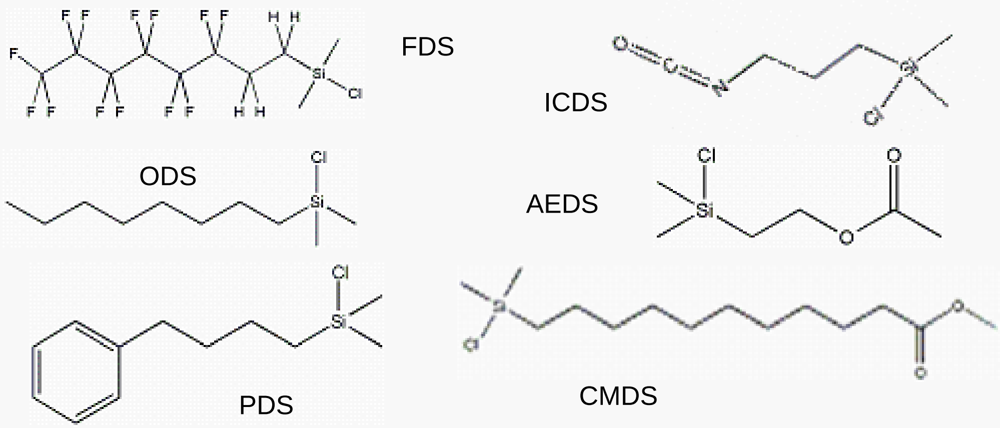


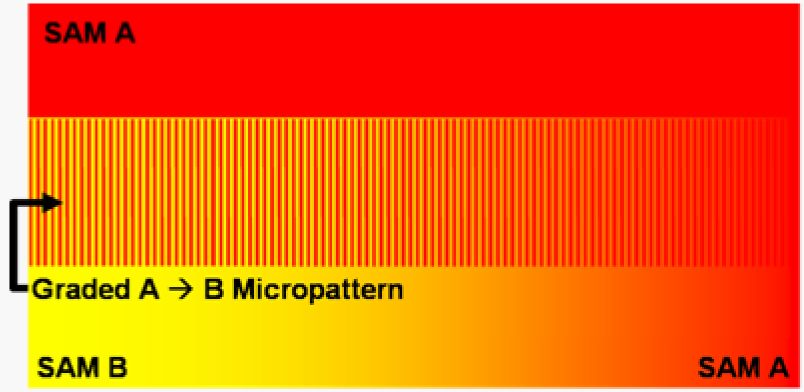
- PDMS cured in tilted tray overnight to form wedge
- Wedge final dimensions 70 x 30 x 3 mm



- Ligamer to crosslinker ratio varied (8:1, 10:1, 12:1) to examine effect of wedge modulus on gradient formation
- Wedges soxlet extracted 72 hrs in toluene and dried under vacuum for 2 hrs

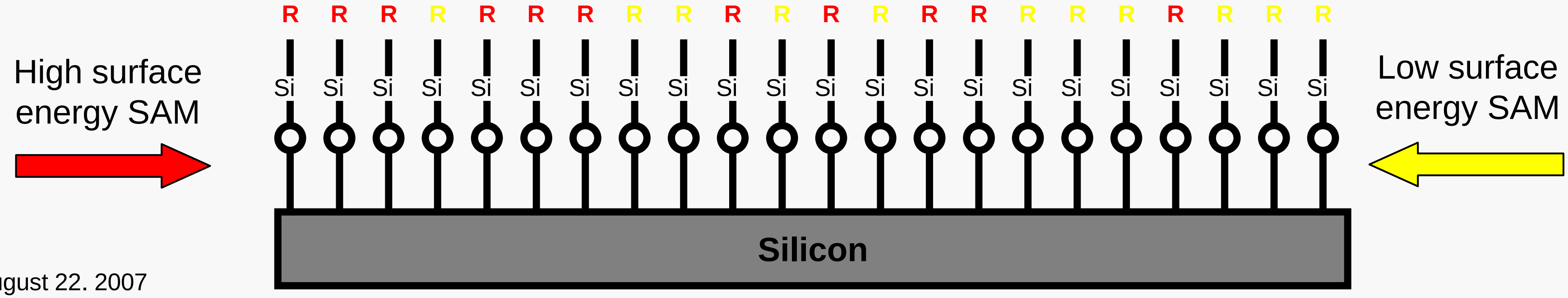
Experimental Details





Self-assembled monolayers (SAM) **R** :
4-phenylbutyldimethylchlorosilane (PDS),
n-octyldimethylchlorosilane (ODS),
Acetoxyethyldimethylchlorosilane (AEDS),
10-(carbomethoxy)decyldimethylchlorosilane (CMDS),
3-isocyanatopropyldimethylchlorosilane (ICDS)
(tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane (FDS)

Graded deposition of patterned SAMS provides rapid prototyping and testing of advanced surface library designs.

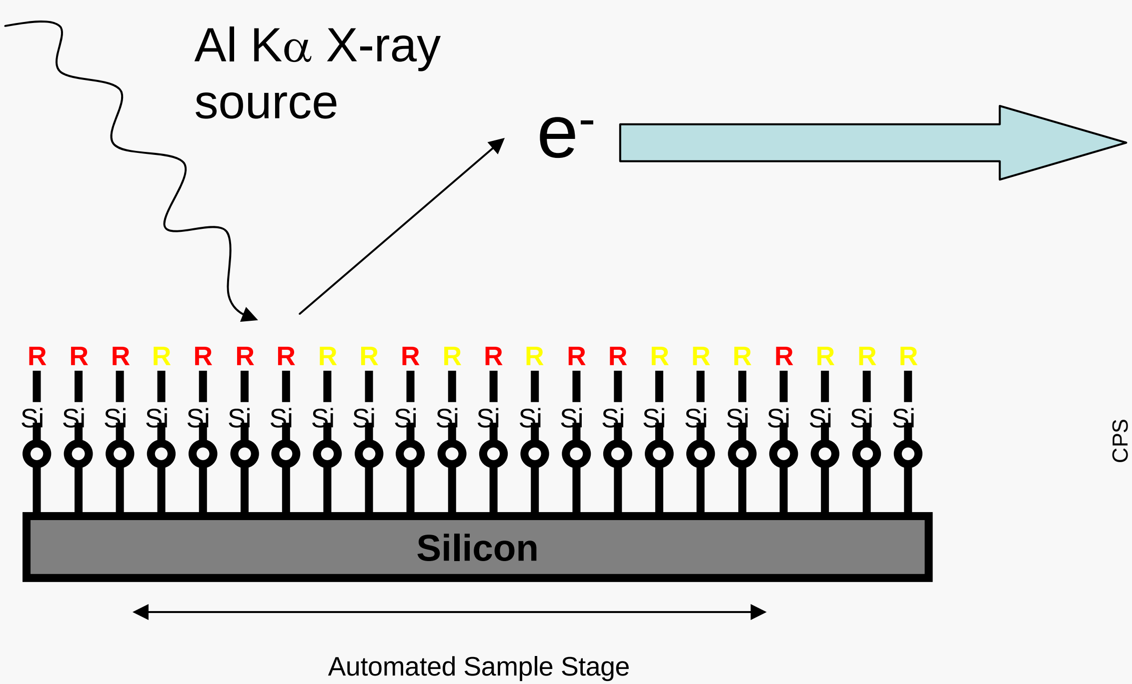


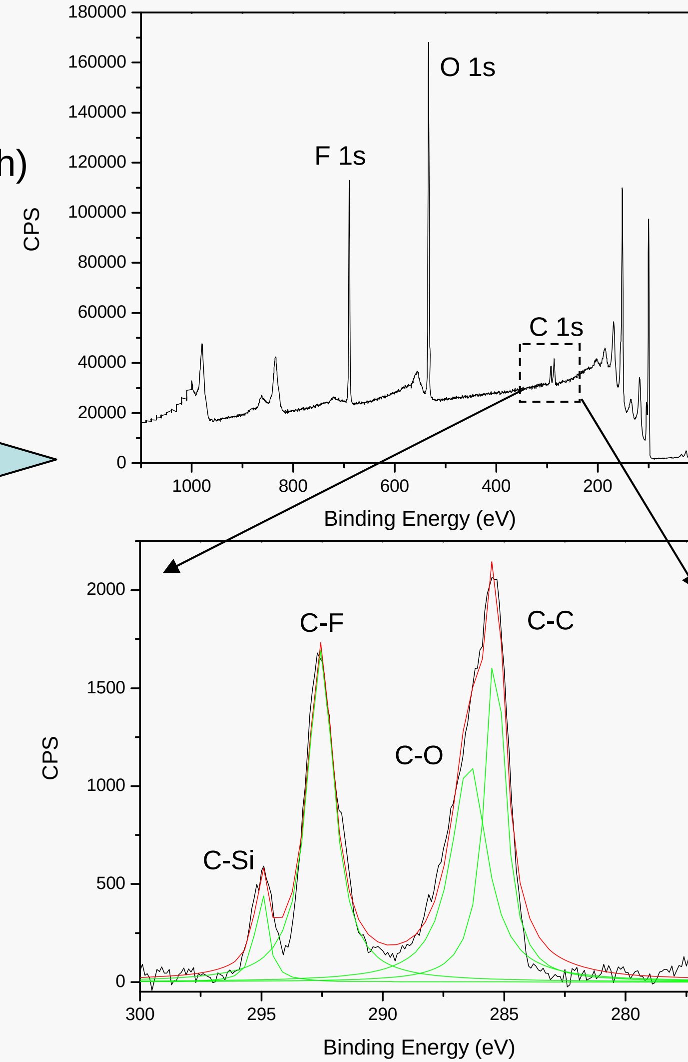
Automated X-ray Photoelectron Spectroscopy

- High Throughput XPS using automated stage (program steps 2-3 mm apart along gradient axis
- Spot size 300x700 µm

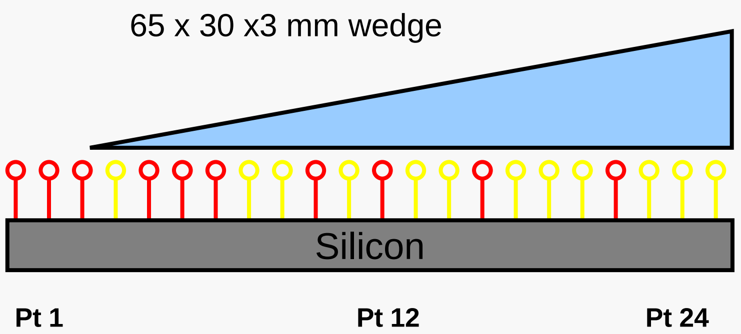
Photoelectrons ejected from near surface (region 10nm depth)

photoelectron=$E_{X\text{-ray}}$ – e^{-}Binding Energy

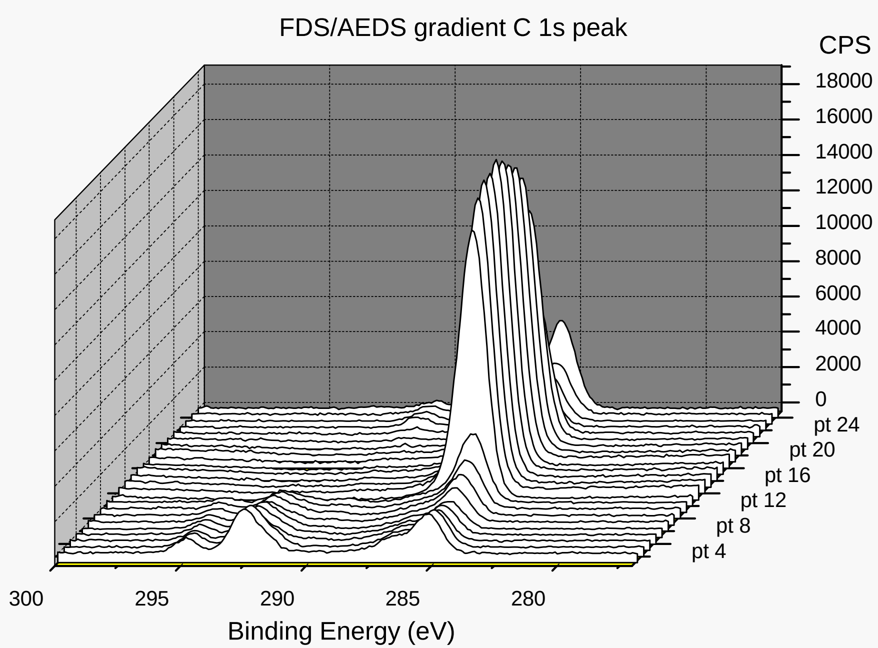


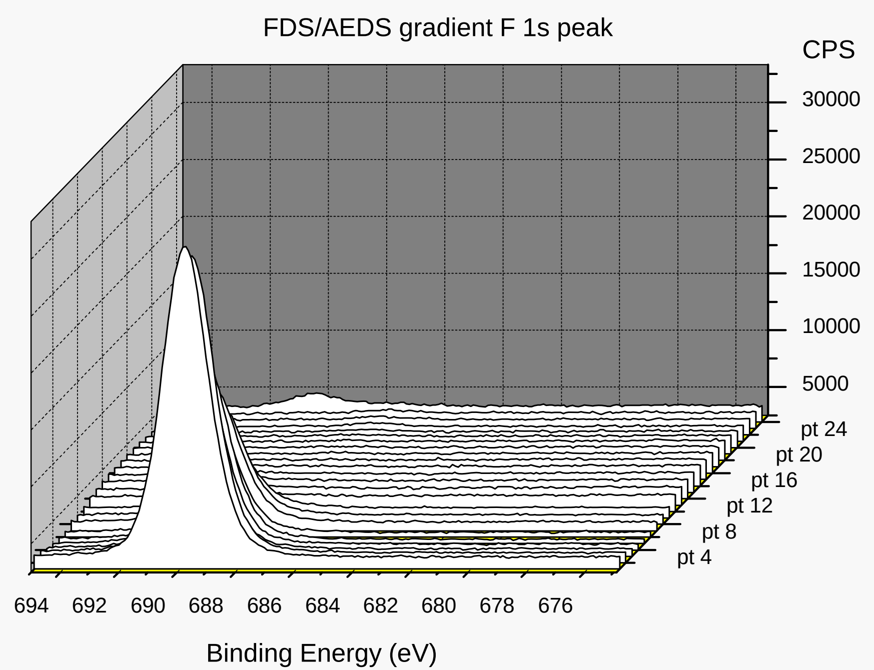


Diagnostic example: FDS/AEDS gradient



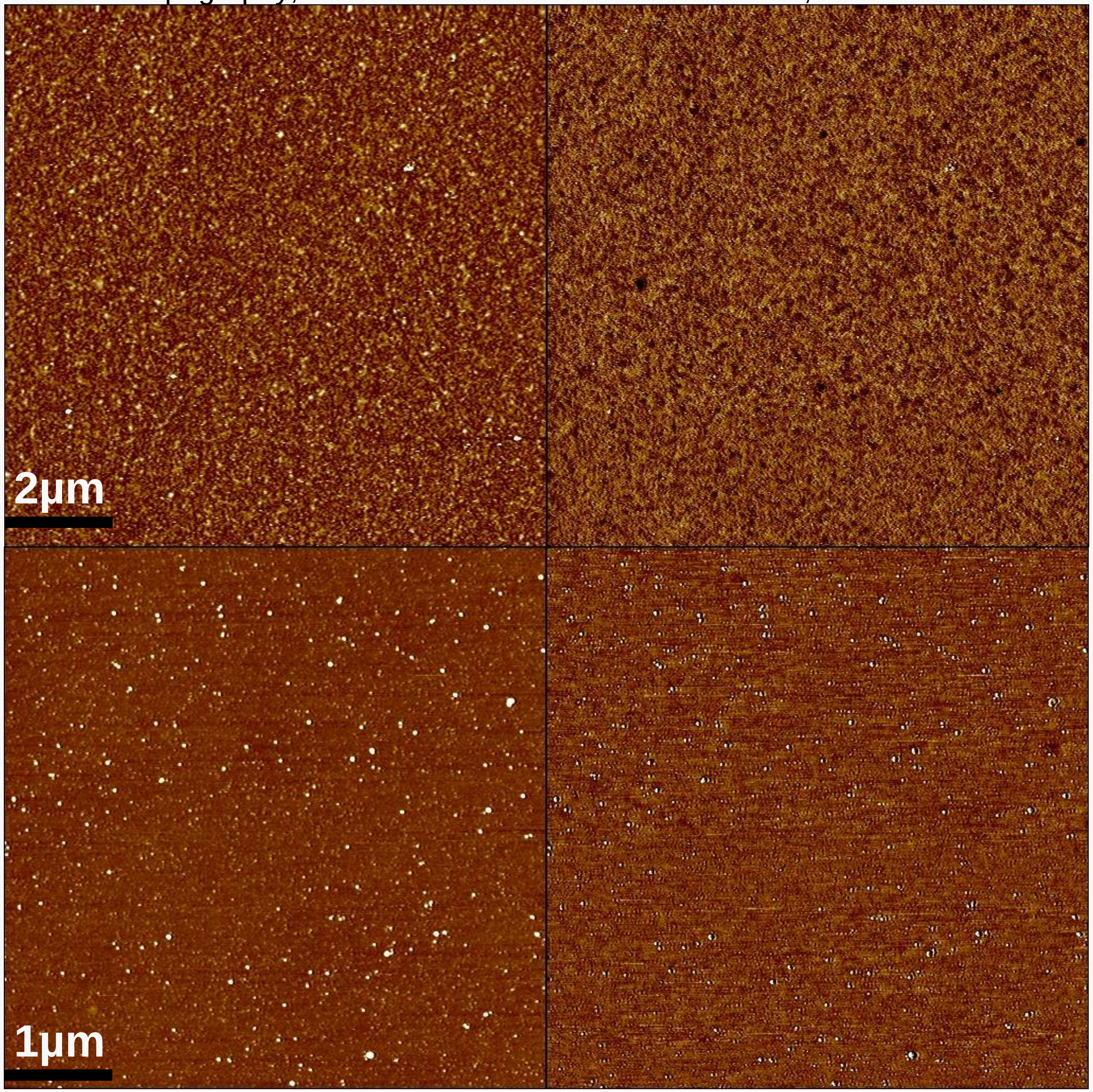
- Linear trend more visible in F peaks then C peaks
- Gradient linearity highly dependent on wedge geometry and deposition time
- 2 hours optimal for 3:60 mm wedge
- Diffusion coefficients effect overall deposition times





SAM Quality test: AFM of FDS/AEDS

Topography, z = 10nm
Phase, z = 40°



Topography, z = 5nm
Phase, z = 10°

90:10 FDS/AEDS (NS)

RMS roughness 0.23 nm

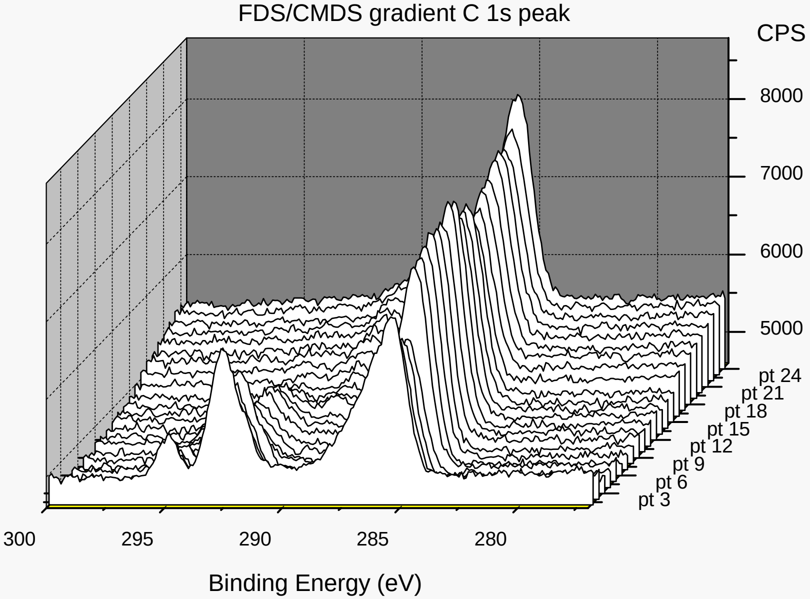
50:50 FDS/AEDS

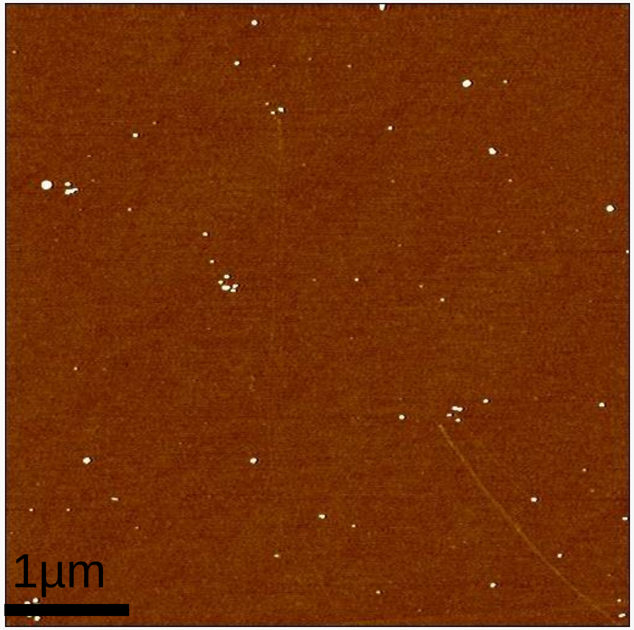
RMS roughness 1.06 nm

10:90 FDS/AEDS

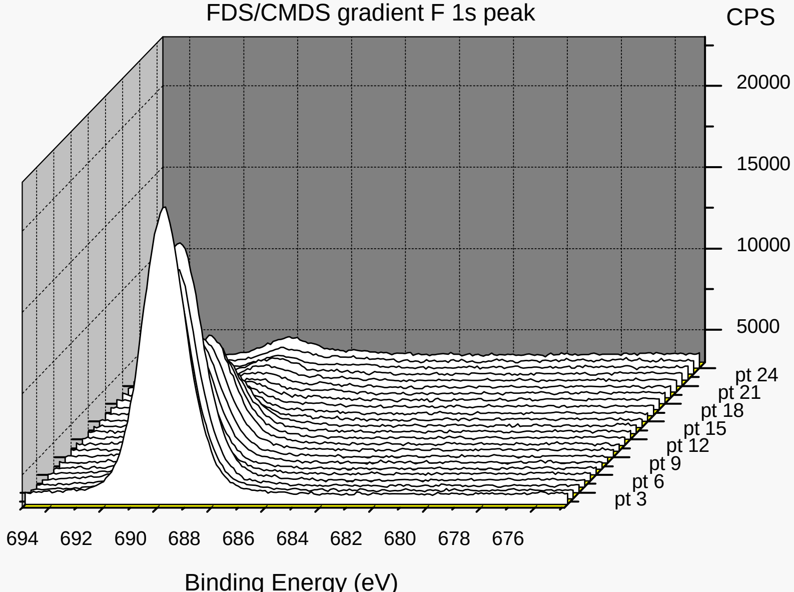
RMS roughness 0.29 nm

Improved Gradient: FDS/CMDS gradient





Topography, z-range 5nm



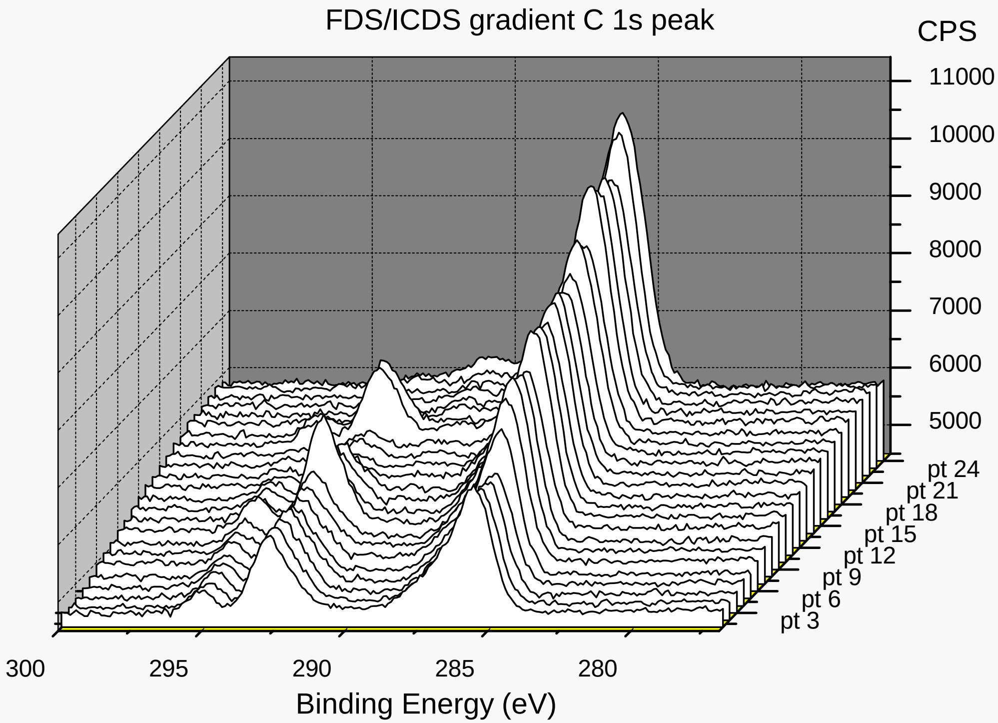
Improved surface roughness for FDS/CMDS gradients (monolayer quality)

- 90:10 r = 0.15 nm
- 50:50 r = 0.11 nm
- 10:90 r = 0.11 nm

Gradient exhibits some step-like character

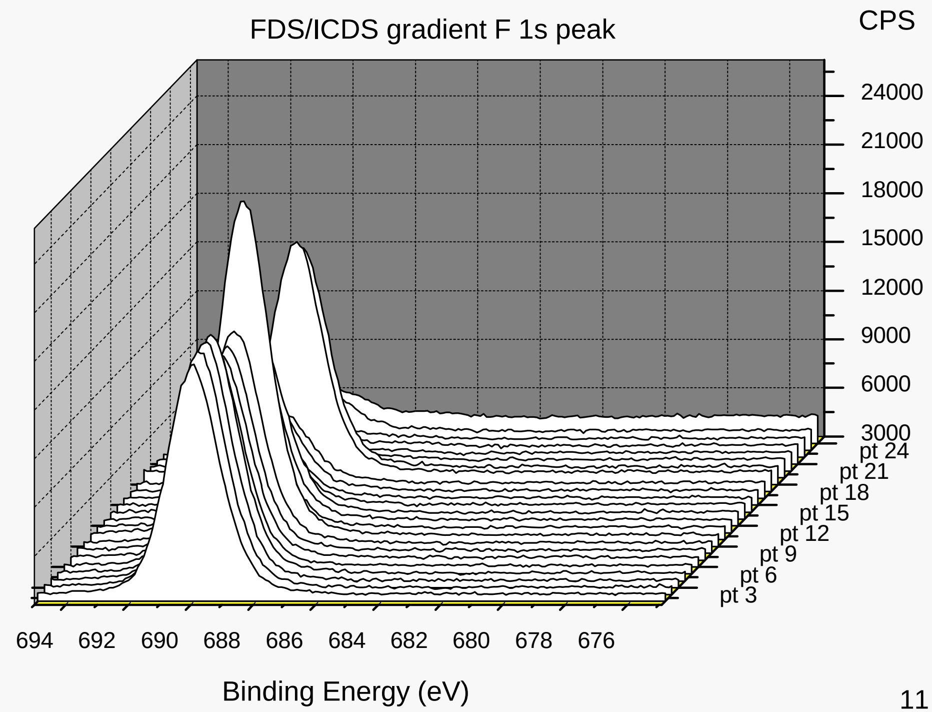
- Attributed to stiffer wedge (8:1 L:C ratio)

Example: FDS/ICDS gradient



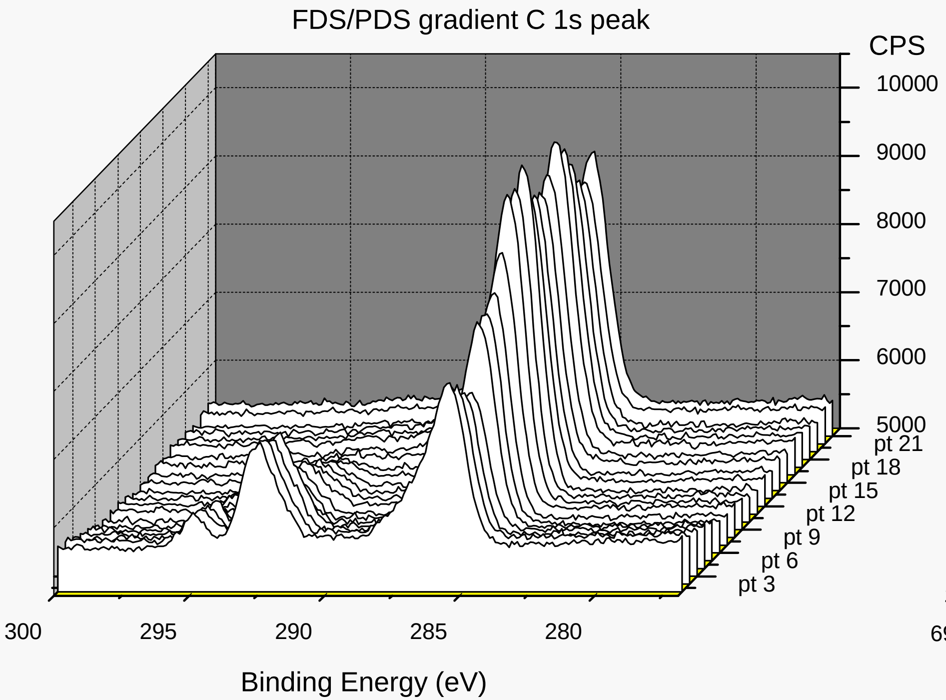
- XPS mapping :Step trend in gradient composition
- AFM: Similar surface roughness to FDS/CMDS gradient

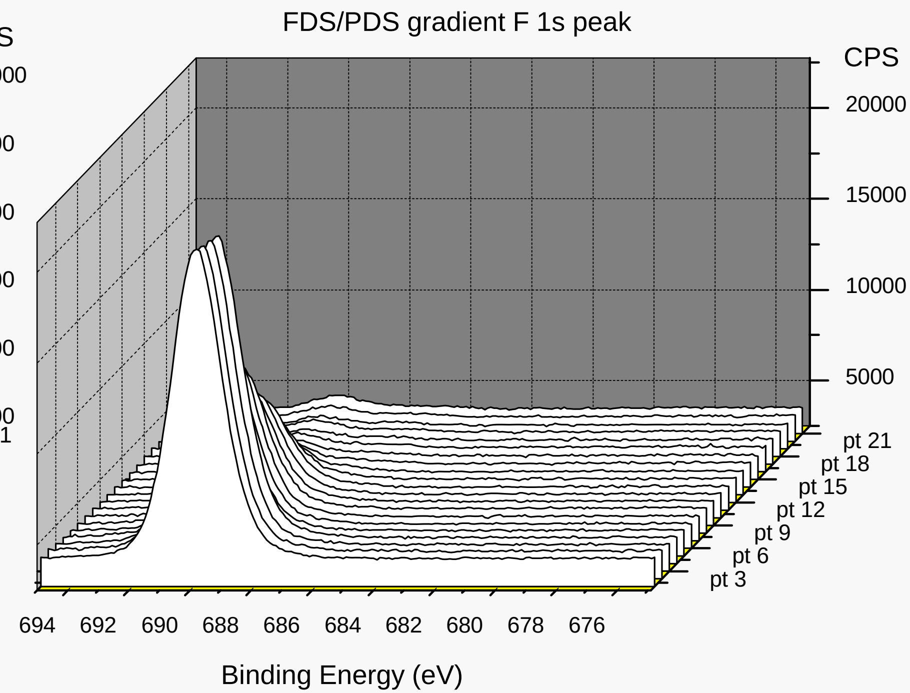
- Difficult to identify N bonds, quantification from C, O, and F peaks only
- Wedge did not fully adhere to substrate during FDS deposition disrupting gradient



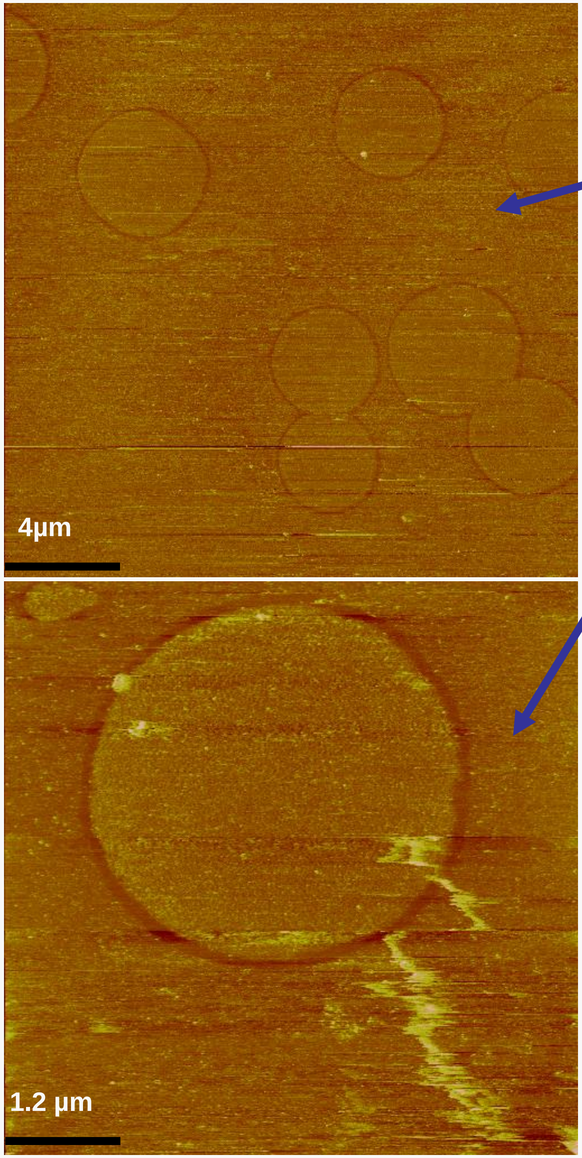
Example: FDS/PDS gradient

- Backfill quality (uniform mixing) not effected by size or chemistry of end functionality of second species
- Difficult to quantity gradient composition without fluorinated SAM as species A or B
  - Intensity from carbon backbone obscures signal from end functionality





Confirmation of pattern



- Low contrast region (10%CMDS/FDS background)
  - Lower friction between pattern regions
- High contrast region (90%CMDS/FDS background)
  - Higher friction between pattern regions
- Sequence on deposition (wedge/stamp or stamp/wedge) can be varied

- Friction images, Z = 0.1 V

Summary of Key Library Design Factor: Gradient Linearity

- All samples show decreasing trend (20-30 degrees)
- Small rise in contact angle for end of gradient due to PDMS release from sample prior to complete deposition
- Lateral diffusion is controlled by increasing size of wedge and modifying edges
- Contact angle lower for FDS and higher for backfill SAMs due to less dense packing

Water contact angle

mm from start	FDS/ PDS	FDS/ ICDS	FDS/ CMDS
5	87.0	95.1	93.4
10	92.0	93.5	91.8
15	93.8	95.0	92.5
20	87.1	94.0	87.0
25	88.5	90.8	88.3
30	87.3	90.0	82.1
35	70.8	80.0	78.9
40	70.7	72.3	65.1
45	69.2	71.4	59.4
50	67.2	74.9	63.0
55	65.2	74.5	62.4
60	66.7	70.0	58.8
65	69.3	70.2	61.6

Summary, Conclusions and Future Directions

- Surface chemisty gradients (flat or micropatterned) can be created using two disparate chlorosilane species
- Surface roughness varies along the gradient due to difference in silane species length
- PDMS wedge geometry can be tailored to create libraries with desired parameters
- Variance in gradient linearity due to difference in SAM diffusion coefficients through PDMS
- Homogeneity and quality of gradient monolayer dependent on sequence of SAM deposition
- Next step: test cell response

Acknowledgements

- NRC-NIST postdoctoral fellowship
- Matt Becker and Derek Patton