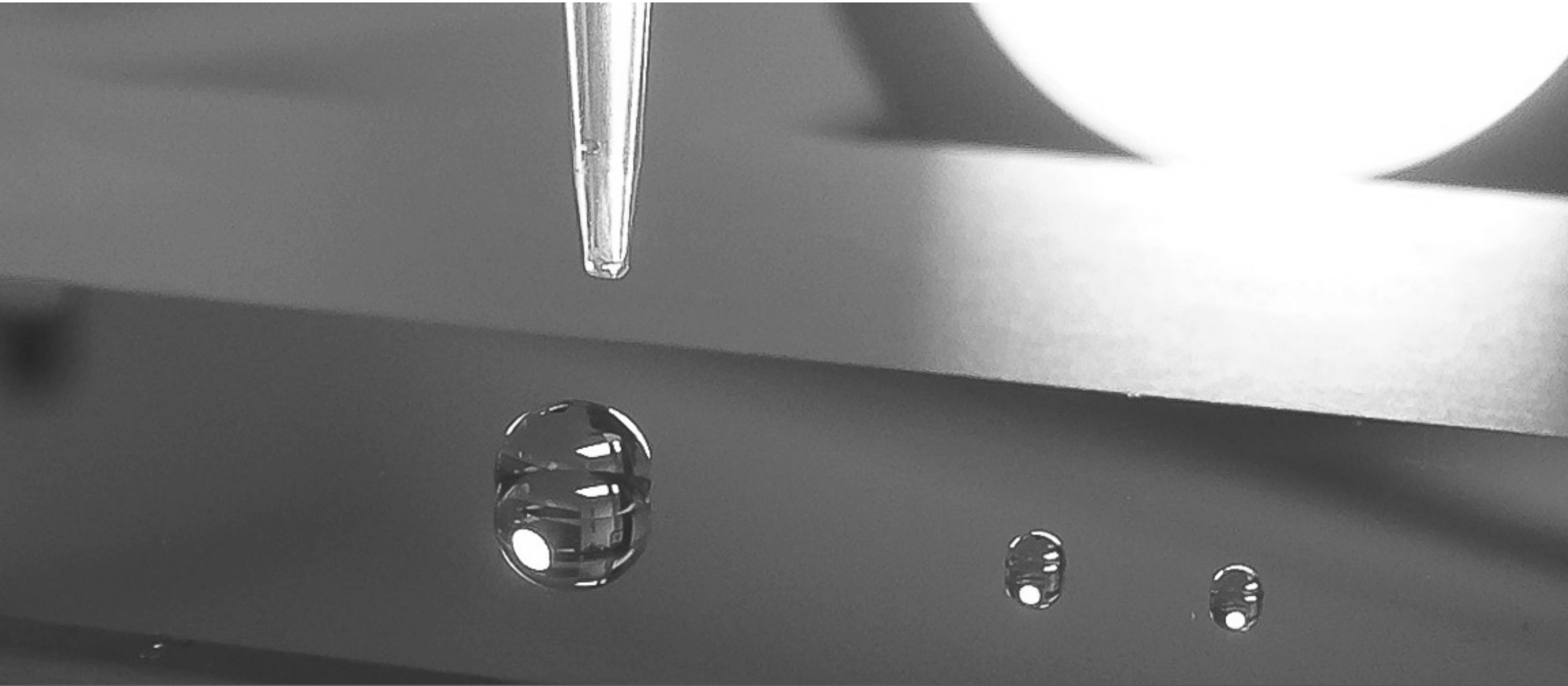

# SELF ASSEMBLED MONOLAYERS

# SAMS anatomy

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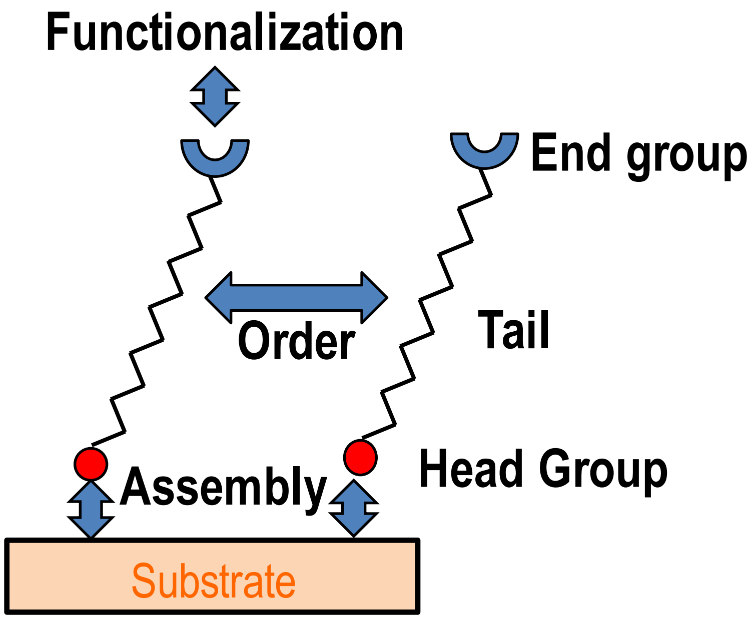
- Head group
  - Affinity to substrate to induce chemisorbed surface reactions
  - High energy chemical bound (100 kJ/mol) provides molecular stability (thermal, chemical, mechanical)
- Tail group
  - Closed-packed structure driven by Van der Waals interaction between alkyl chains
- End or Functional group
  - Defines properties of monolayer, e.g., hydrophobicity/hydrophilicity, affinity to anchor with biological entities




Single organic monolayer from ordered molecular 2D assembly formed spontaneously by the chemisorption of the head group

# SAMS precursors

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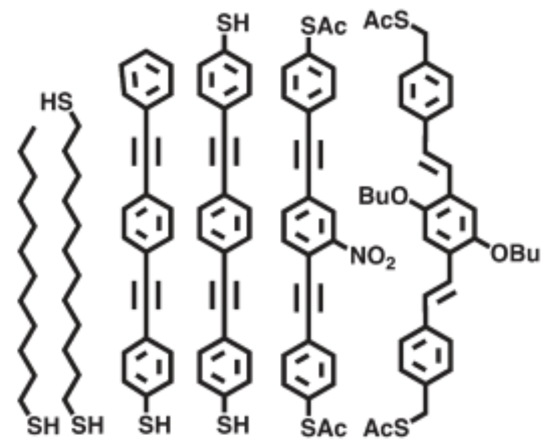
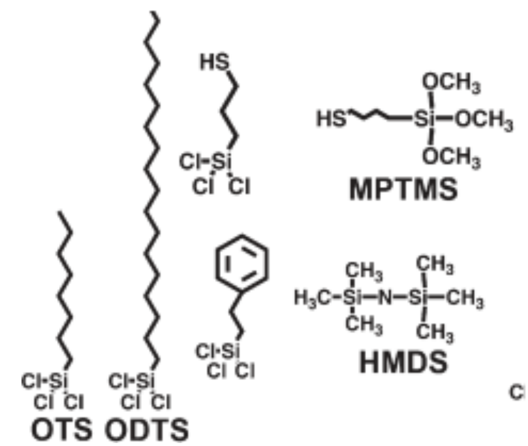
❑ Key selection criteria

- Head group determined by substrate
  - Thiols (organosulfurs) for metals
  - Silanes for (trichlorosilane, alkylsilane) for oxides
  - Phosphonates, carboxylates…
- Functional group
  - Non-polar hydrophobic: e.g., $-CH_3$
  - Polar hydrophilic: -OH, -COOH




Thiols for SAMs on Au surfaces

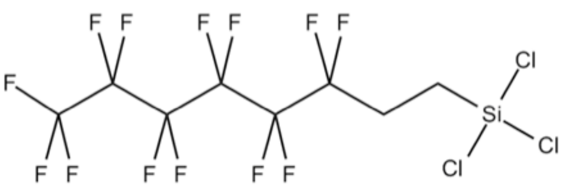


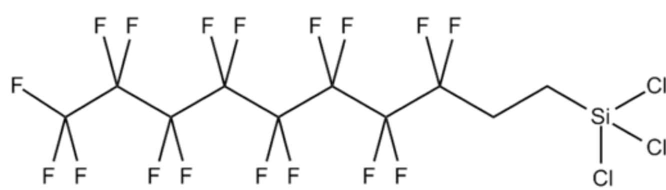

Silanes on oxide surfaces

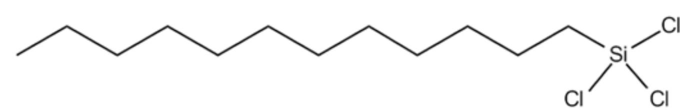
DiBenedetto, S.A., et al., Adv. Mater., 2009. 21(14-15): 1407-1433.

# Silane SAMS

| | FOTS | FDTS | DTS |
|---|---|---|---|
| Name | Tridecafluoro tetrahydrooctyl trichlrosilane | Heptadecafluoro tetrahydrodecyl trichlrosilane | Dodecyltrichlorosilane |
| Formula | $C_8H_4Cl_3F_{13}Si$ | $C_{10}H_4Cl_3F_{17}Si$ | $C_{12}H_{25}Cl_3Si$ |
| Gelest # | SIT 8174.0 | SIH5841.0 | SID4630.0 |
| Price | $28 / 10g | $84 / 10g | $10/10g |
| B.P. | 84˚C | 216˚C | 120˚C |
| Vap. Pr. | 4.2 Torr at 70˚C | 1.7 Torr at 80˚C | 0.5-1 Torr @100˚C |







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# APPLICATIONS

# Applications

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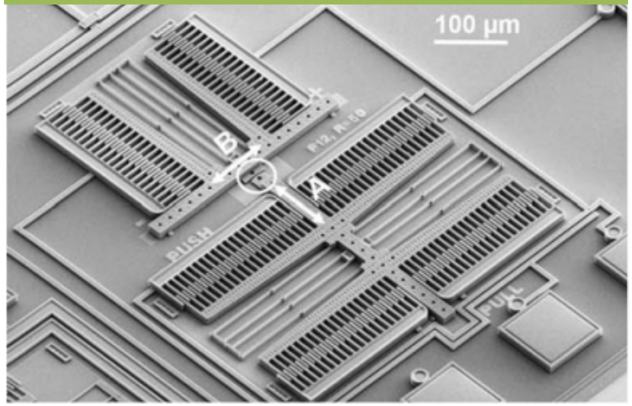
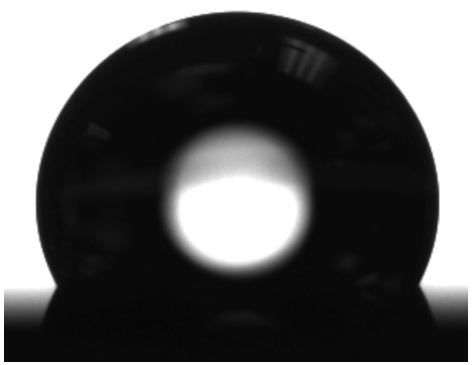
- ❑ Wetting control (hydrophobic, hydrophilic, oleophobic)
- ❑ Friction/anti-stiction/lubrication
- ❑ Nanostructure functionalization
- ❑ Building blocks for heterostructures
- ❑ OLED / Flexible electronics
- ❑ Cell adhesion/protein adsorption

## MEMS anti-stiction coating



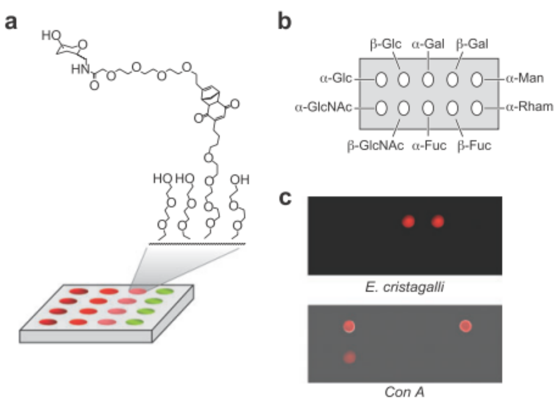

Asay and al., Tribol. Lett., 2008. 29(1): p. 67-74.

## Hydrophobic SAM on oxide



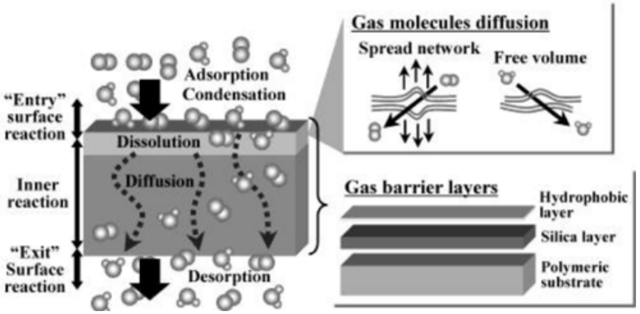
Ultratech, FDTS on Pt ALD (119˚)

## Biological assays



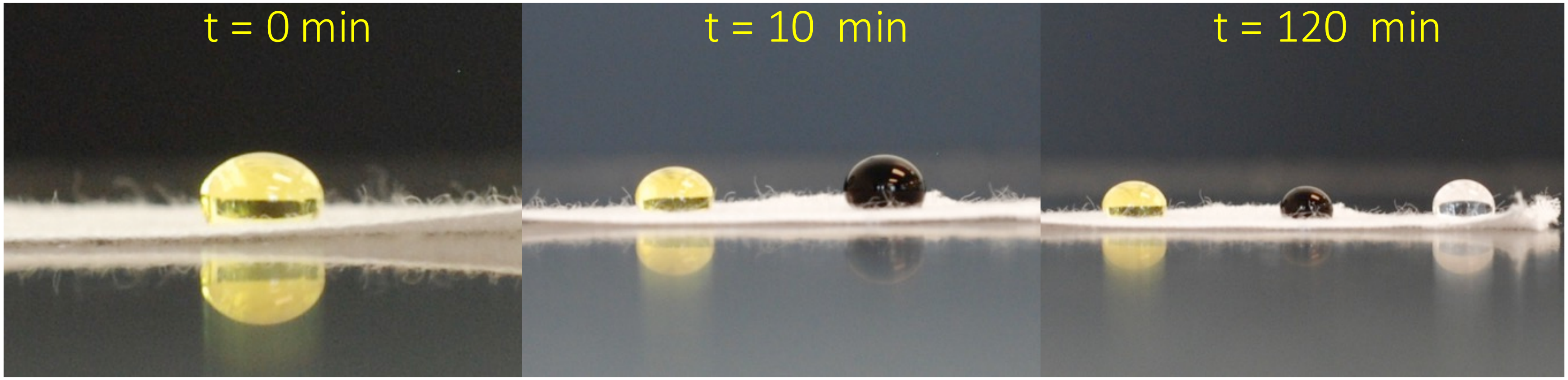

Gurard-Levin, et al.. Annual Rev. of Analyt. Chem., 2008. 1: p. 767-800.

## Gas permeation barrier



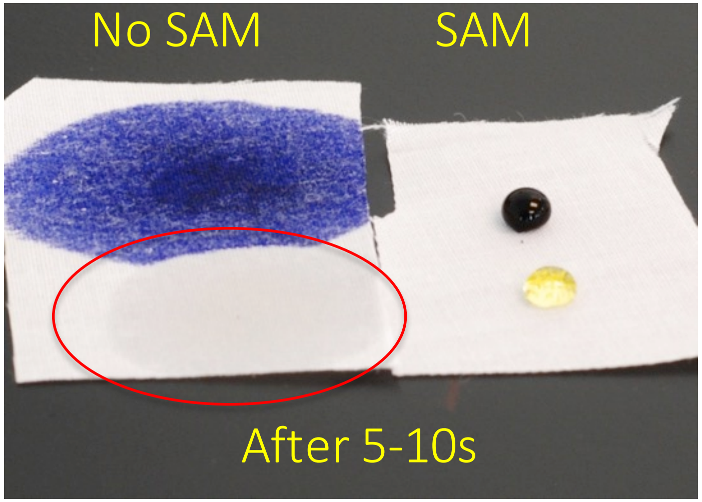

Teshima, K., et al., Langmuir, 2003. 19(20): p. 8331-8334.

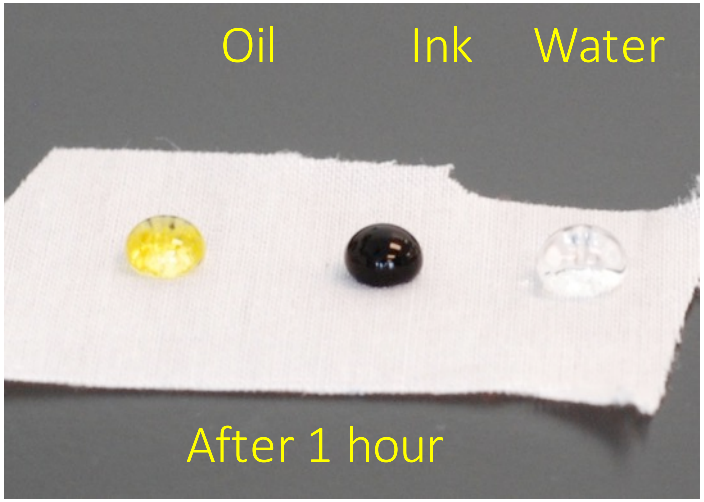
# FOTS on Cotton




Ink

Oil



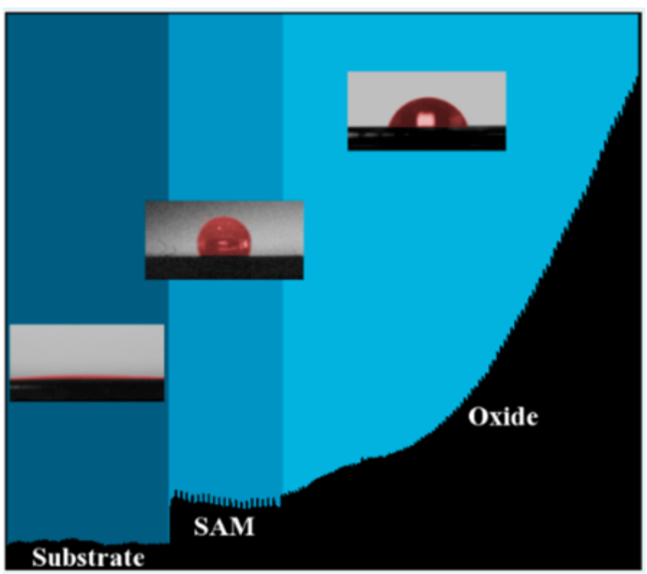




Deposition in Savannah S200 at 80˚C, 10 min. exposure

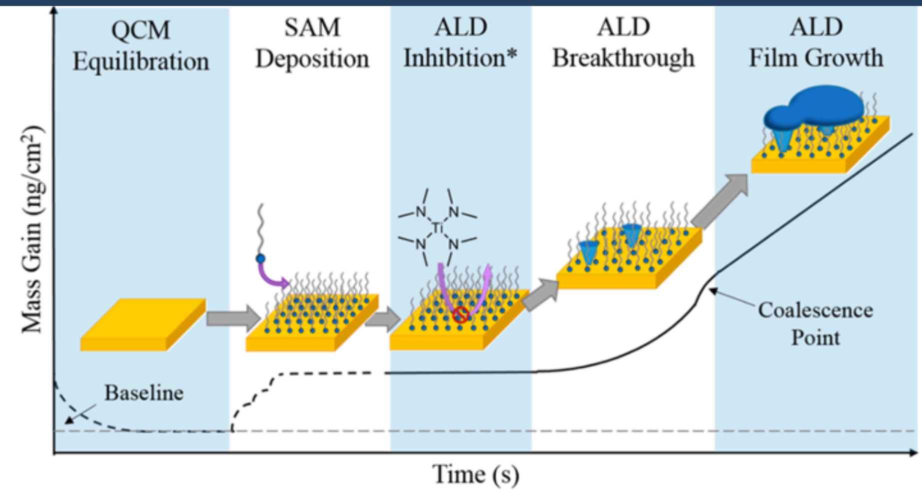
# In-situ QCM during ALD on SAMS

1. Avila, J. R. et al. Acs Appl Mater Inter 140721160005002 (2014).

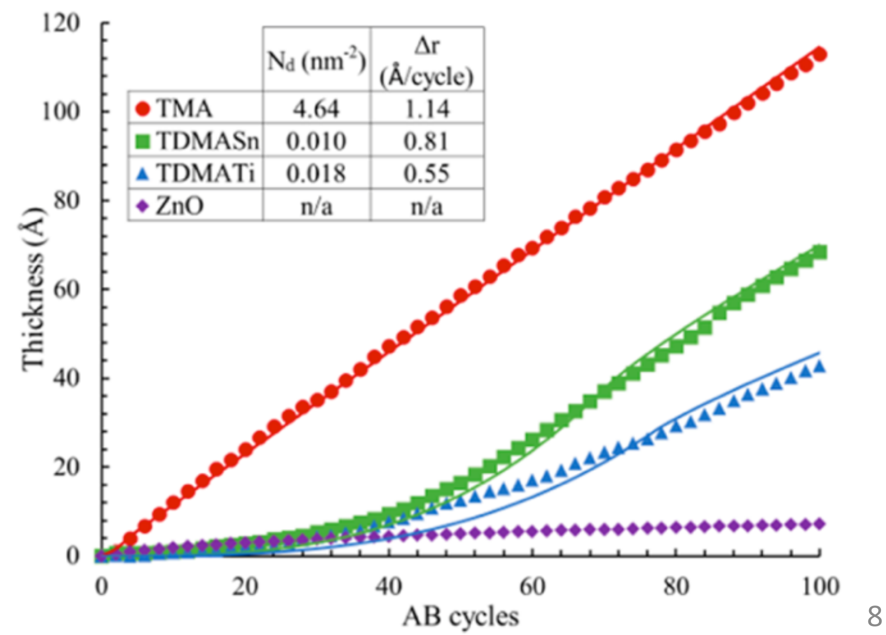
- In-situ QCM measurements during oxide growth by ALD on vapor-deposited alkanethiols
- Study in Savannah S200 with QCM integrated in lid
- Vapor deposited SAMS achieve ALD inhibition in min. vs days for solution-based SAMS




## Idealized QCM signature during SAMS / ALD



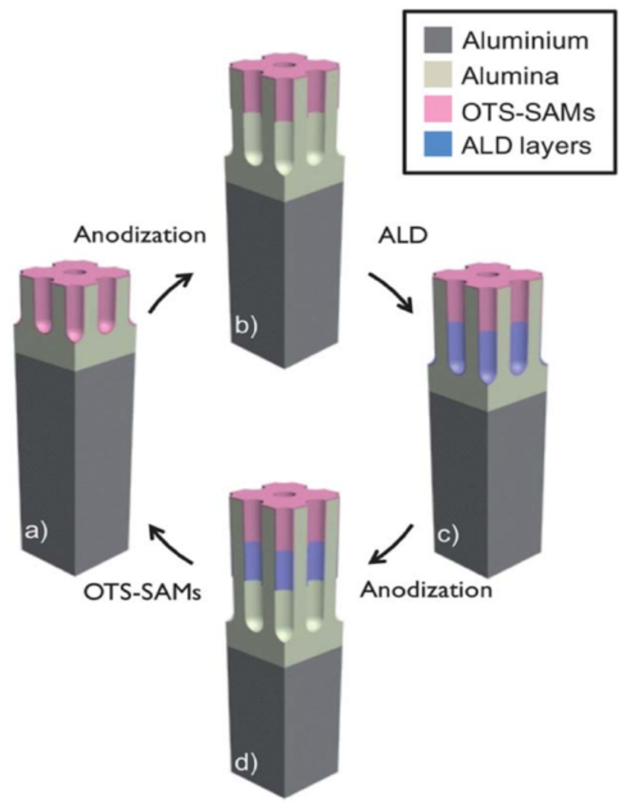

## In-situ thickness during ALD oxides on thiol SAM

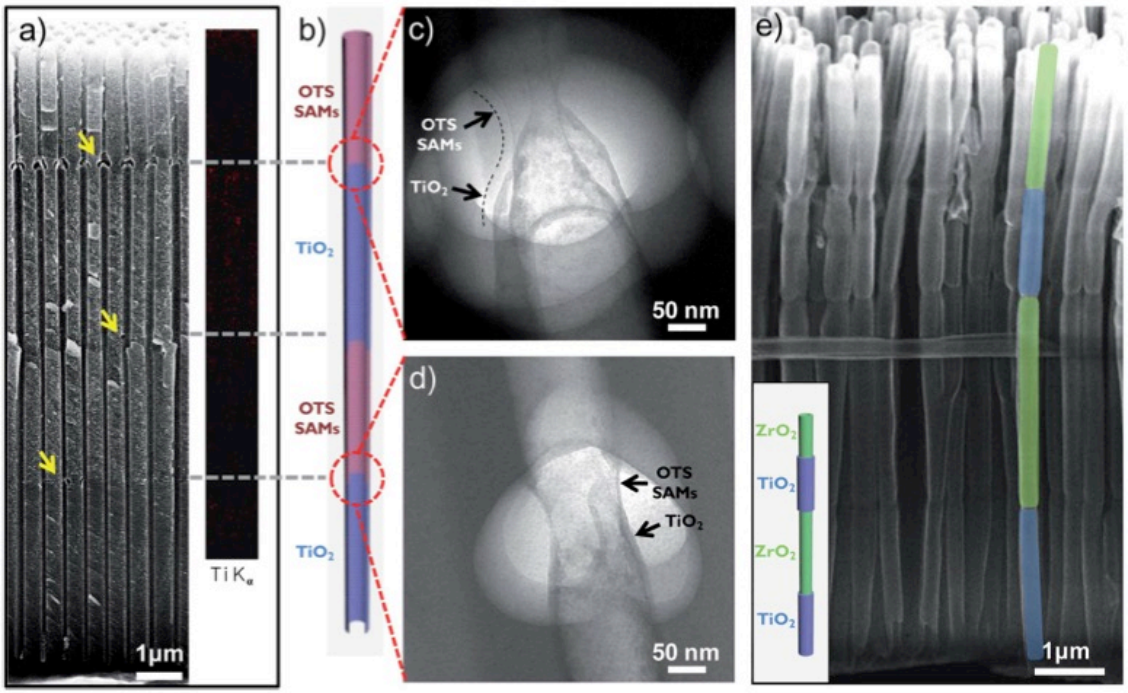


# Selective Area ALD

Fabrication steps of multi-segmented nanotubes using AAO, SAMS & ALD

Examples of $TiO_2$ / $ZrO_2$ segmented nanotubes deposited in AAO nano-termplate using OTS SAMS




Bae, C. et al. Multisegmented nanotubes by surface-selective atomic layer deposition. J. Mater. Chem. C 1, 621 (2012).

K. Nielsch's group, Hamburg U.

# SAMS in plasmonic hot electron PV

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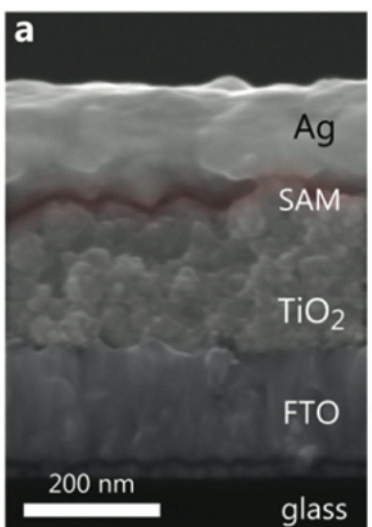
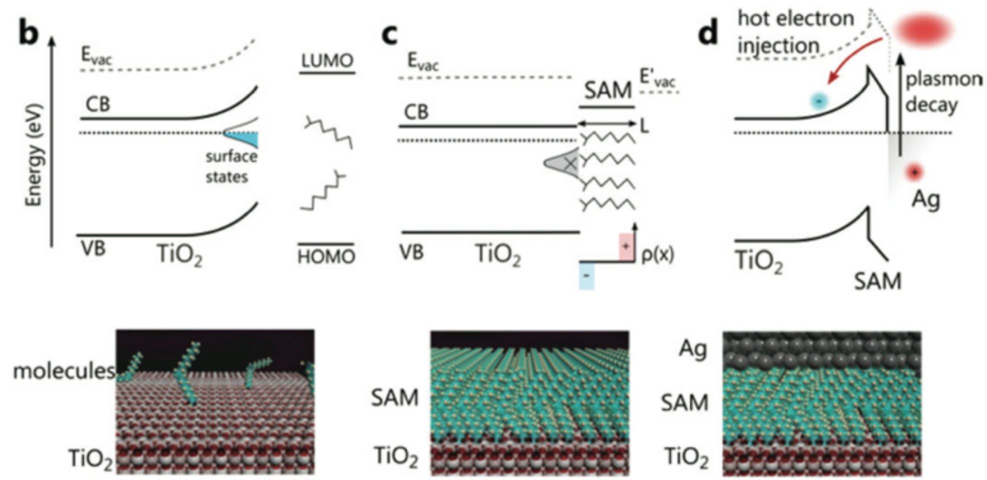
1. Pelayo García de Arquer, F., Nanoscale 7, 2281–2288 (2015).

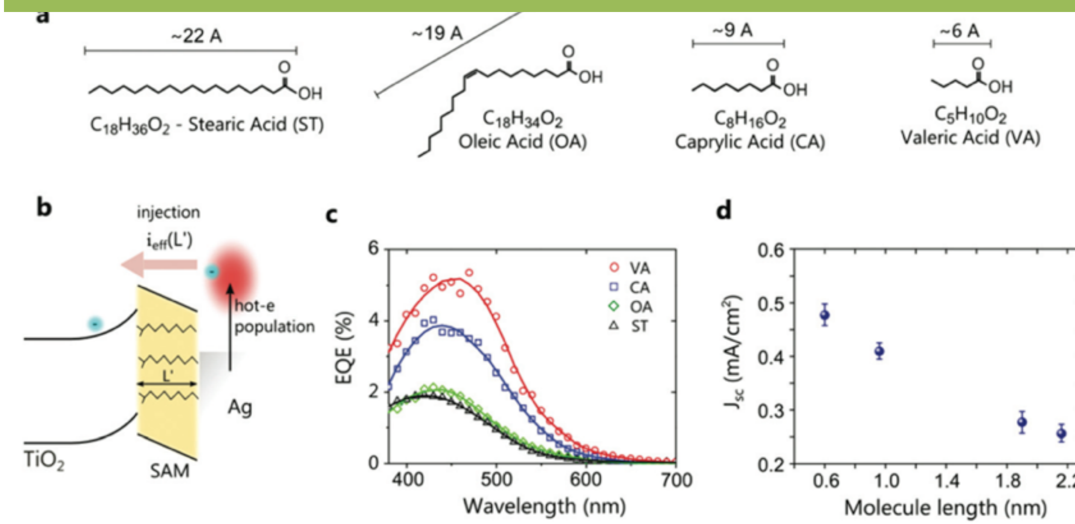
- Example of ALD / SAMS heterostructure using Savannah
- SAMS length control hot electron injection
- Open-circuit voltage function of SAMS dipole
- Short circuit current function of SAMS functionalization




## $TiO_2$ band diagram and passivation effect of SAMS




## Impact of SAMS length on injection efficiency, photon conversion efficiency and short circuit current



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# HARDWARE

# SAMS kit specs

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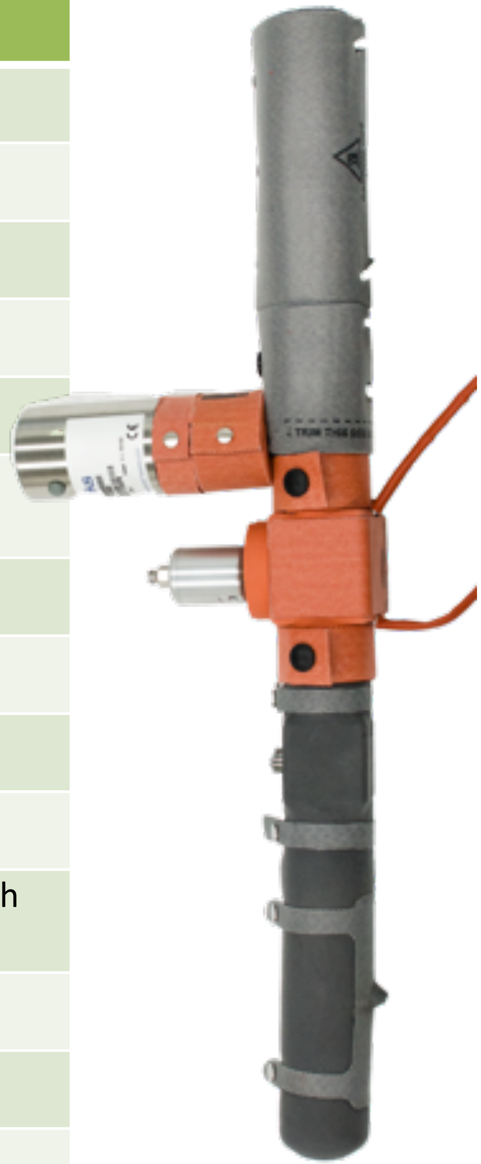
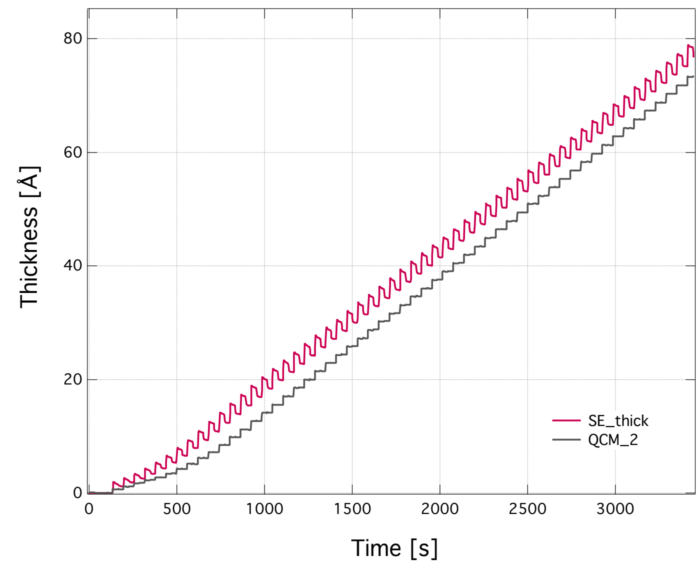
| Systems | Savannah S100, 200 & 300 |
|---|---|
| Max. # kits / tool | Up to 2 |
| Substrate size | Up to 300 mm for S300 |
| Typical run time | 5-20 min |
| Dose control | ±0.5µmol |
| Precursor Temp | Up to 200˚C |
| Accumulator temperature | • 100˚C with pressure gauge<br>• Up to 150˚C (w/o gauge) |
| Dose pressure range | 0-10 Torr with Baratron |
| Co-reactant | $H_2O$, ozone, air |
| Seed layers | ALD oxides and metals |
| Pump | Adixen 2021C2 with purge kit |
| Softw. Integration, end point control | Implemented in standard Savannah software |
| FDTS contact angle | >110˚ |
| FOTS angle | >105˚ |
| DTS angle | >100˚ |

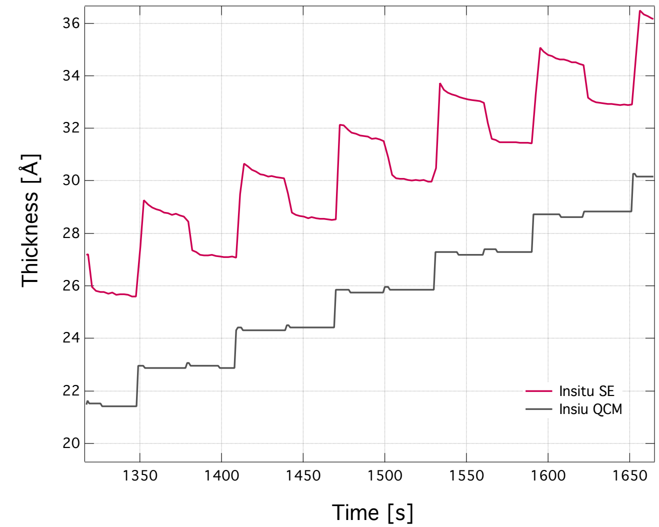


# In-situ diagnostic

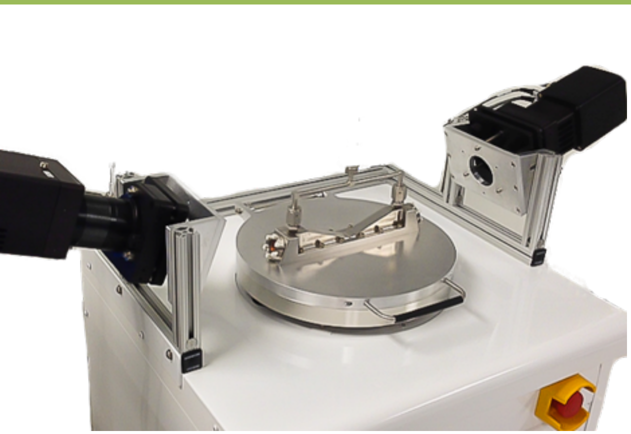
- Spectroscopic ellipsometry (Woollam M2000V)
- Quartz Crystal Microbalance
- Provide real-time sub-Å resolution and quick acquisition rate
- Ideal for thickness monitoring, rapid process optimization, growth characterization with multicomponent or heterogeneous films

## In-situ SE and QCM data during $Al_2O_3$ run




## In-situ SE and QCM on Savannah Gen2



Ultratech CNT data

# RESULTS

# DTS coating on ALD alumina

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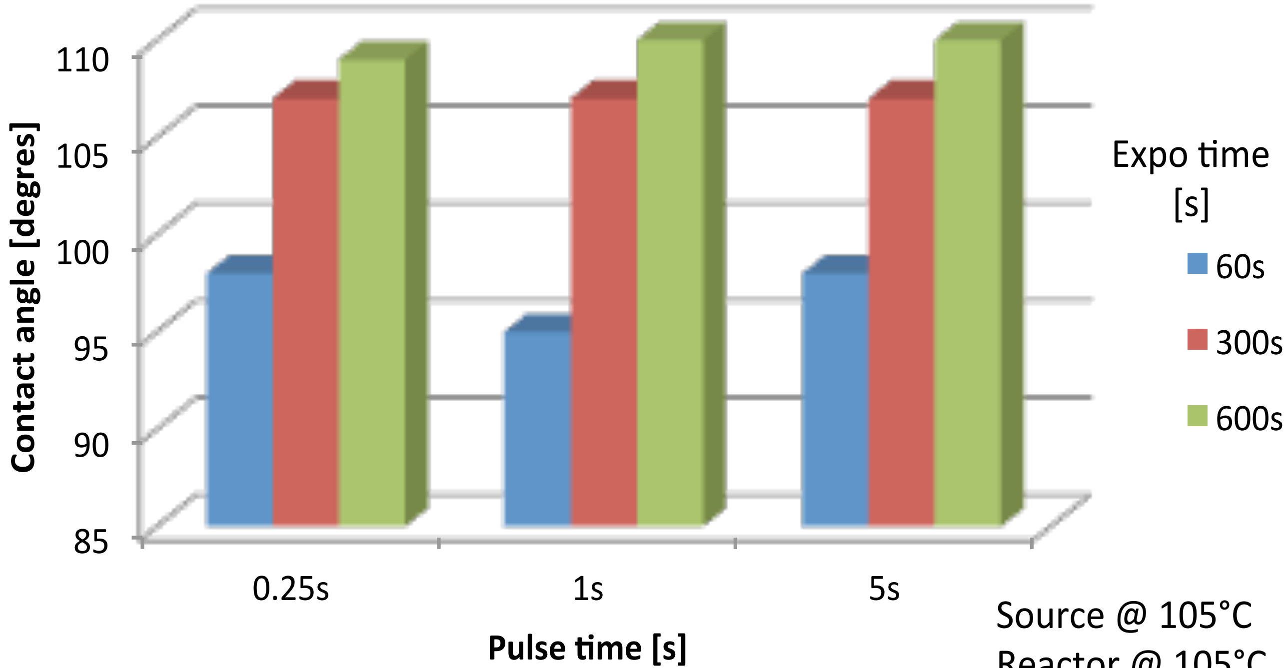
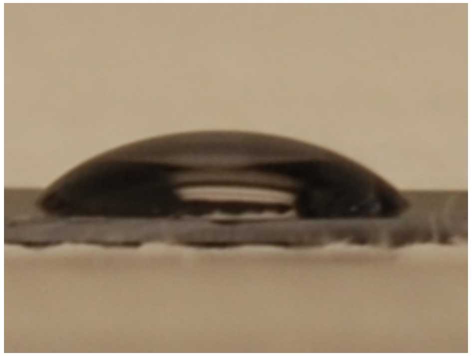
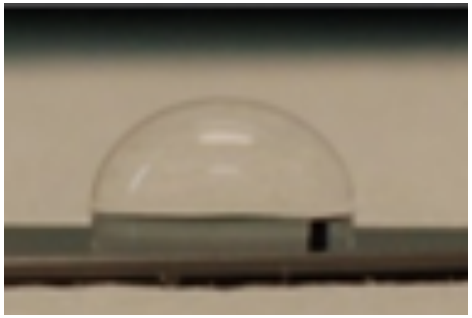
Water contact angles for DTS on $Al_2O_3$ ALD films as a function of dose (pulse time) and exposure time




Source @ 105°C
Reactor @ 105°C

Water on $Al_2O_3$ and $Al_2O_3$+ DTS

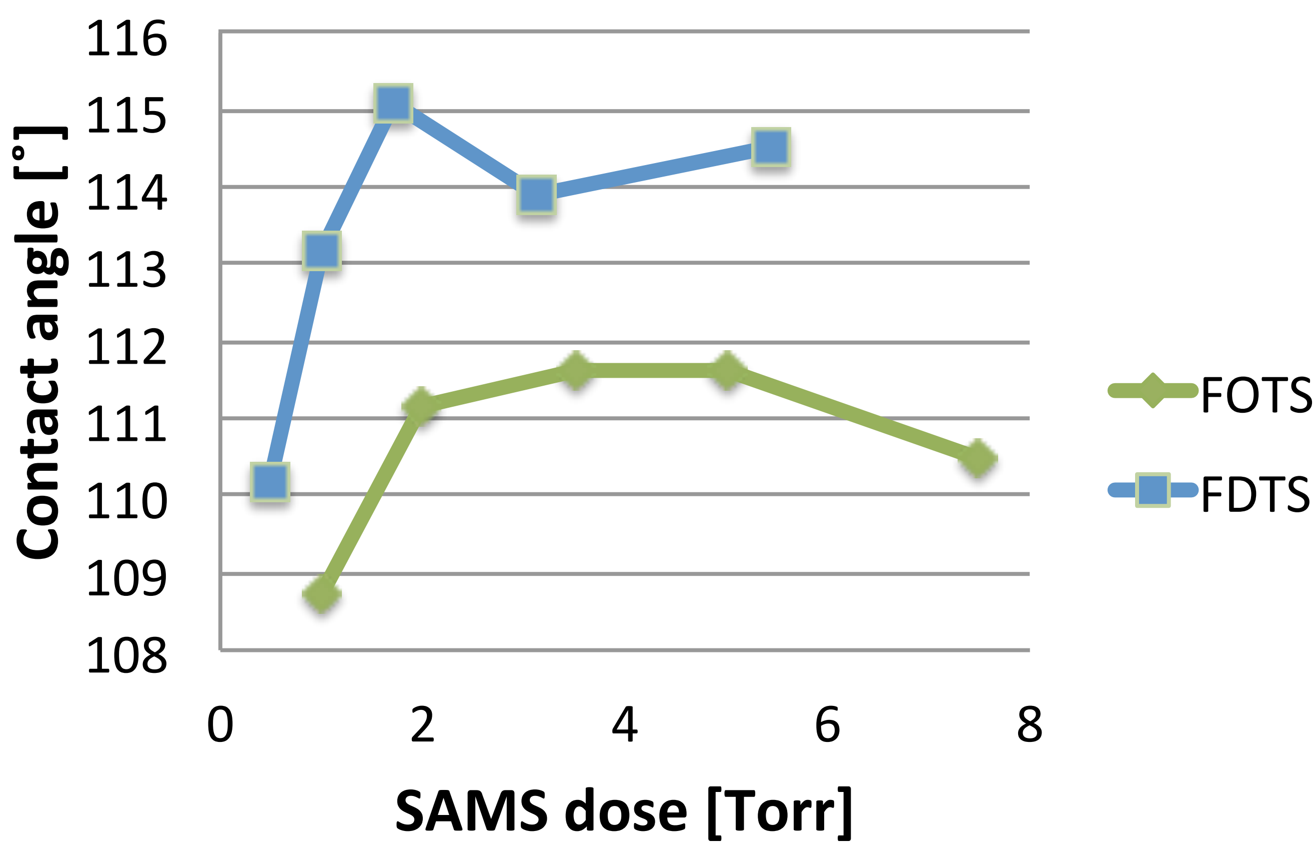




- Precursor: Dodecyltricholorosilane (DTS)
- Sample: Silicon with 20 nm ALD $Al_2O_3$
- Sample prep: none

# Impact of reactant dose





# DTS on $SiO_2$ Impact of seed layer

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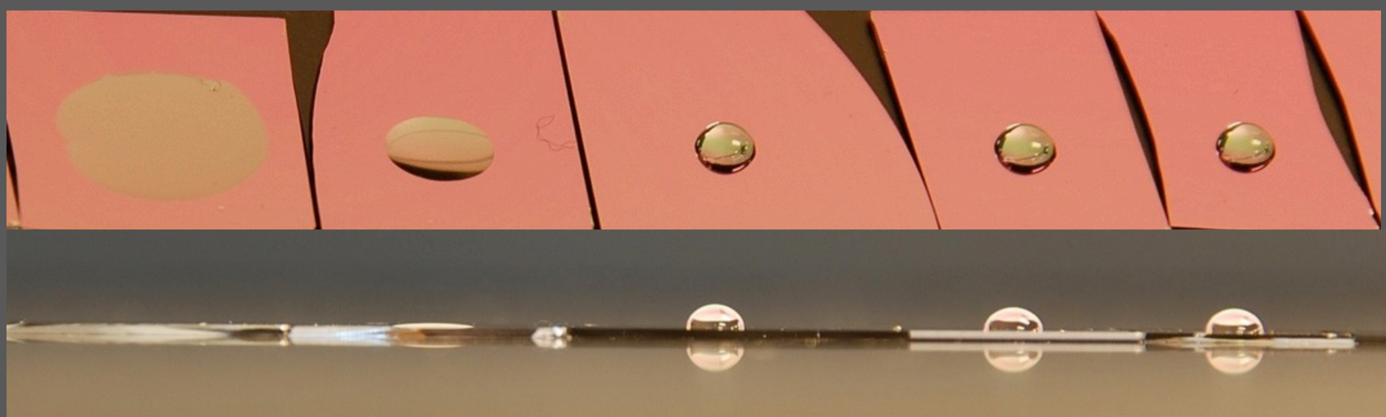
- Sample 10kÅ thermal $SiO_2$
- Deposit 1-10 cycles of ALD as a seed layer
- Vapor phase SAMS deposition for 10 min.



| $SiO_2$ | $SiO_2$ + DTS | $SiO_2$ + 1cy ALD + DTS | $SiO_2$ + 4cy ALD +DTS | $SiO_2$ + 10cy ALD +DTS |
|---|---|---|---|---|

Significant increase of water contact angle using ALD seed layer followed by DTS

# In-situ QCM characterization during FDTS growth

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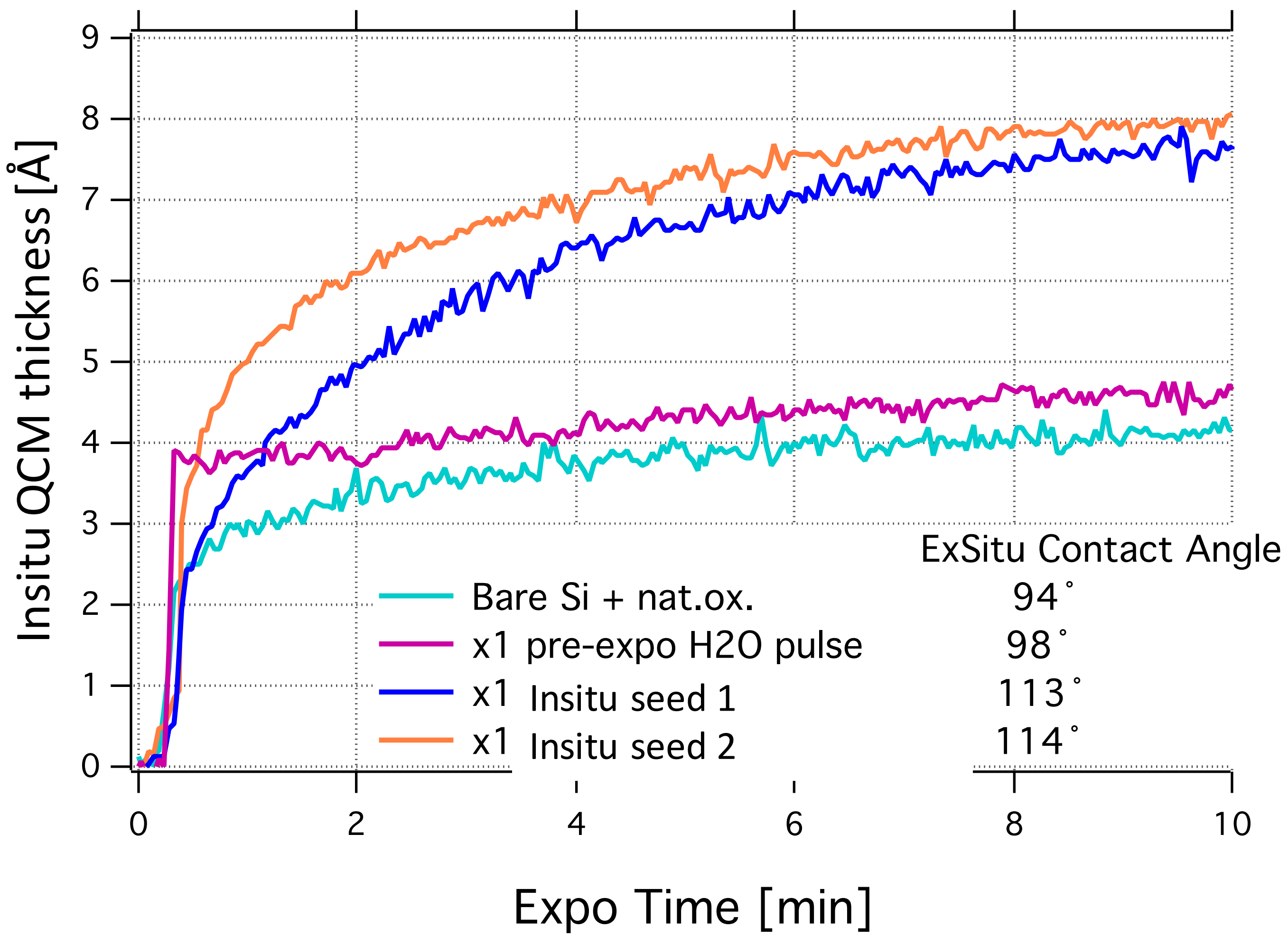
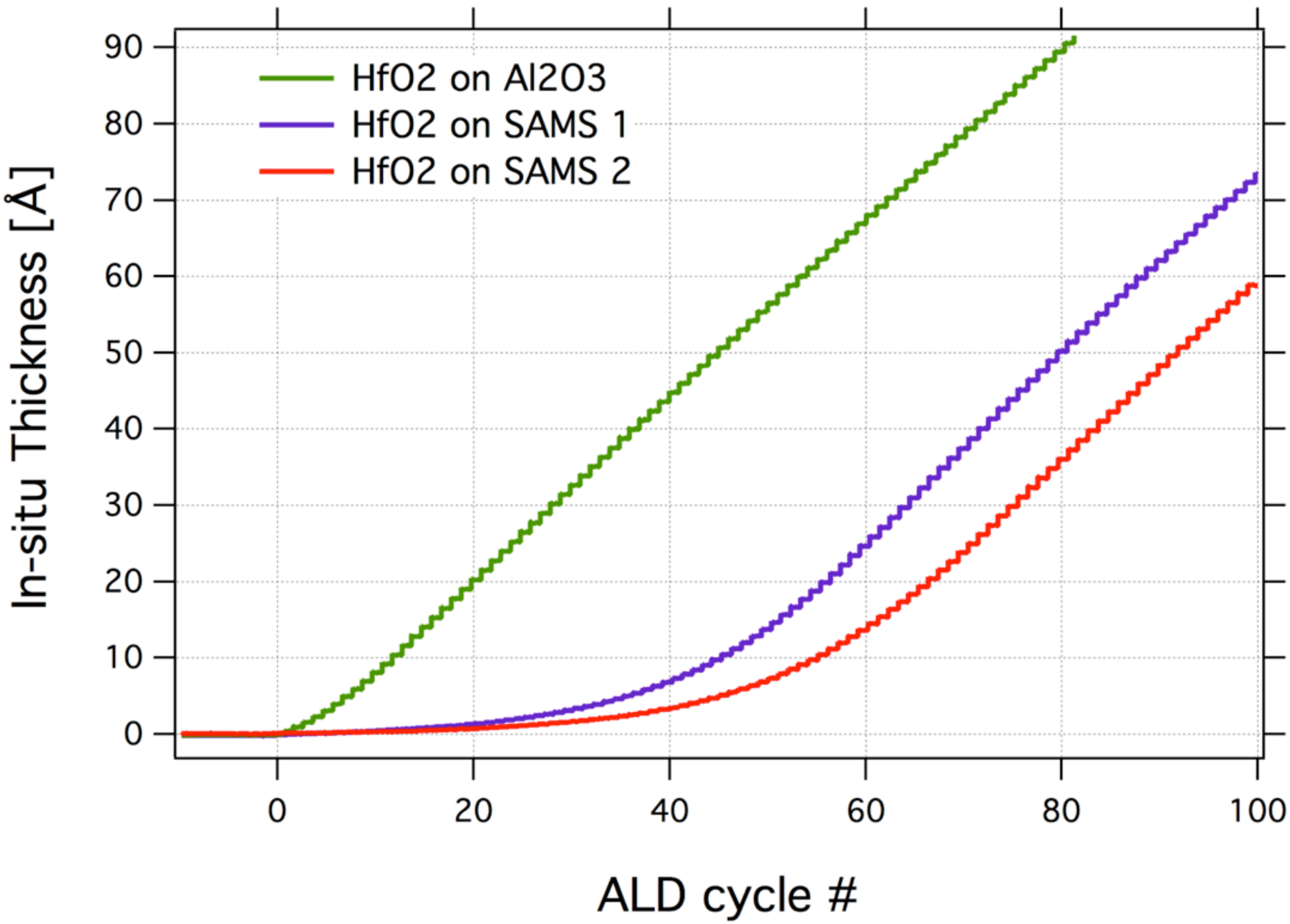


# In-situ QCM characterization during ALD on SAMS

Ultratech CNT



# Summary

Ultratech CNT

- ALD and SAMs provide a versatile set of solutions to coat & functionalize surfaces with organic and inorganic films
- Vapor-phase deposition of SAMS can be achieved in minutes and provides optimal coverage in high aspect ratio 3D nanostructures
- In-situ sensing (QCM, SE) provide unique opportunities to optimize both ALD and SAMs processes
- Vapor phase SAMS recipes developed in S200