# Novel method to achieve area selective ALD on copper metal vs. $SiO_2$ using vapor-phase deposited SAMS

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# Bottom-up approach

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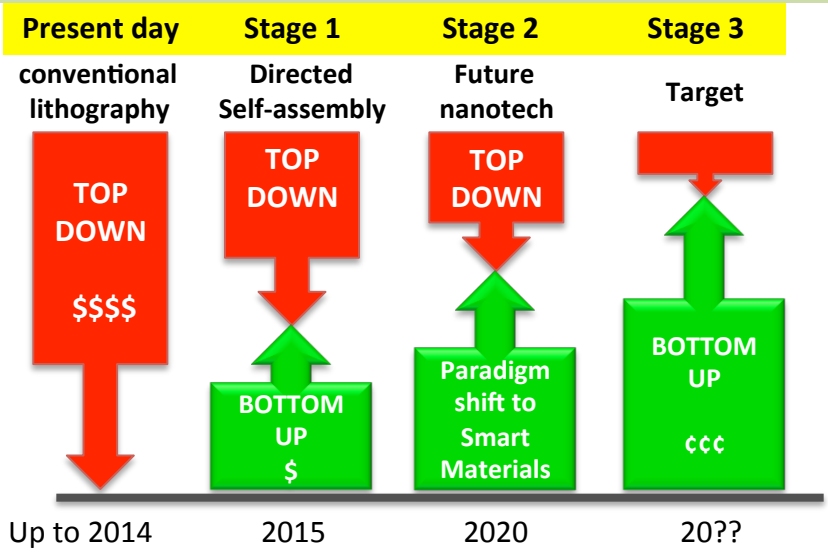
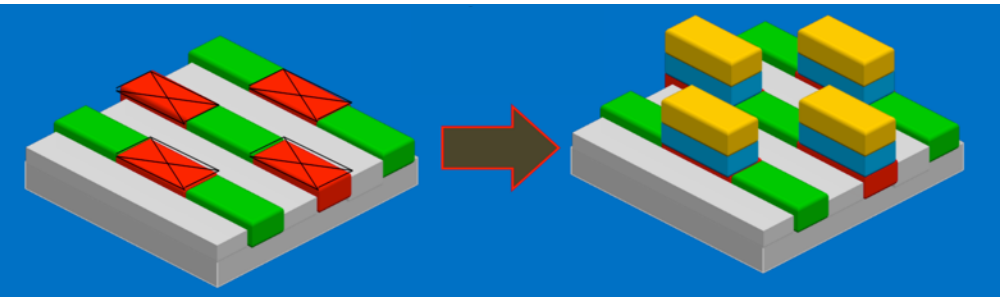
## Economic rational to bottom-up



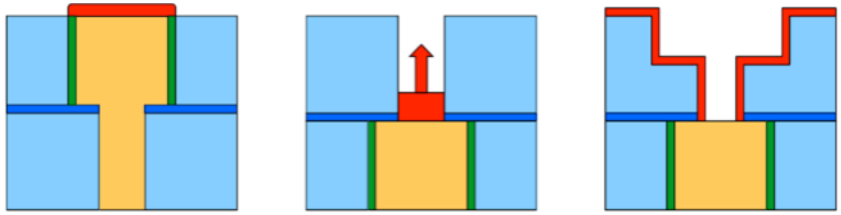

Source: R. Dammel, Semicon Korean 2015

## Selective area deposition



Source: T. Younkin (Intel), SPIE-2015, [9425-2], San Jose, CA, USA,

## Selective deposition schemes



Selectively deposited capping layer

Bottom-up trench fill

Selective side wall deposition

Source: J. Engstrom, Cornell Univ.

# SAMS as a barrier layer

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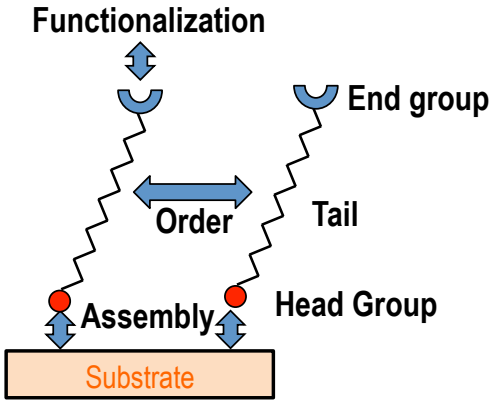
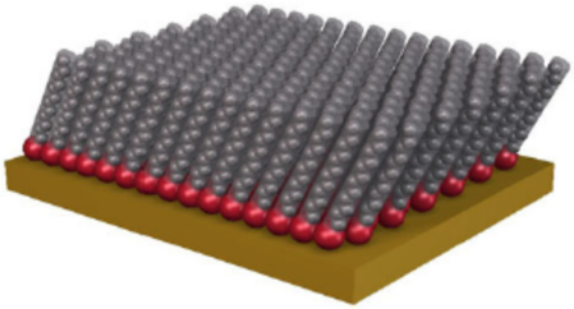
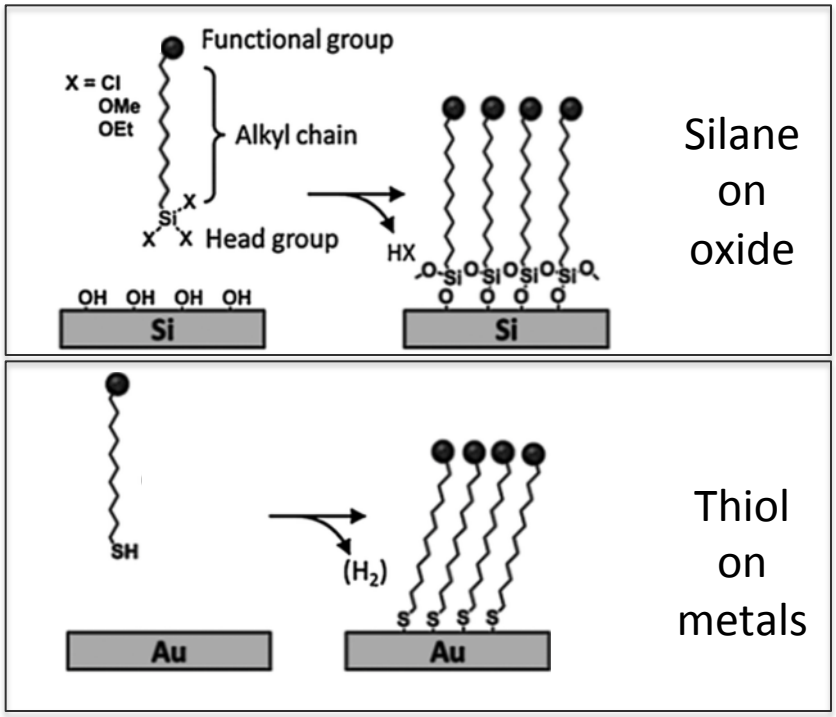
## SAMS anatomy




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

## Defect-free densely packed SAMS

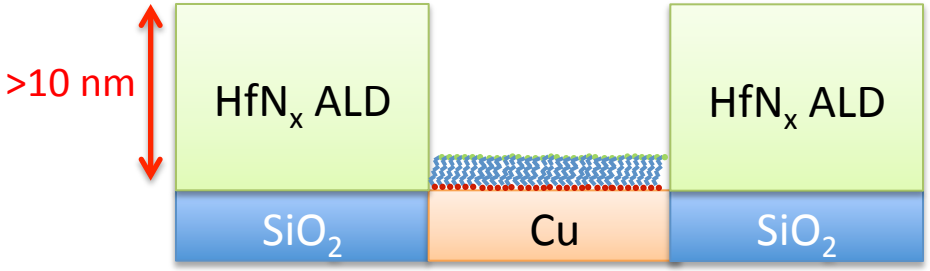





Silane on oxide

Thiol on metals

**Goal** – use thiol SAM to enable at least 10 nm of $HfN_x$ ALD on $SiO_2$ while blocking deposition on copper




**Source: C. Nicosia,** DOI: 10.1039/C3MH00046J

# What makes a good SAMS barrier

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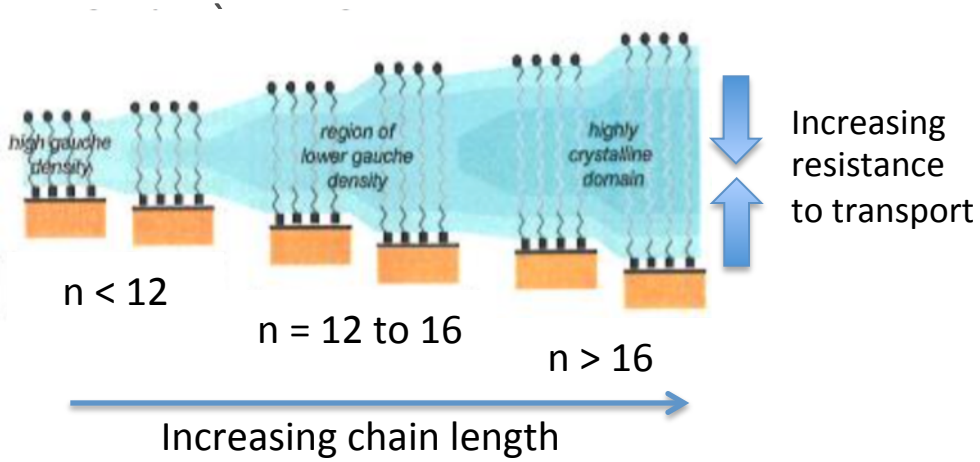
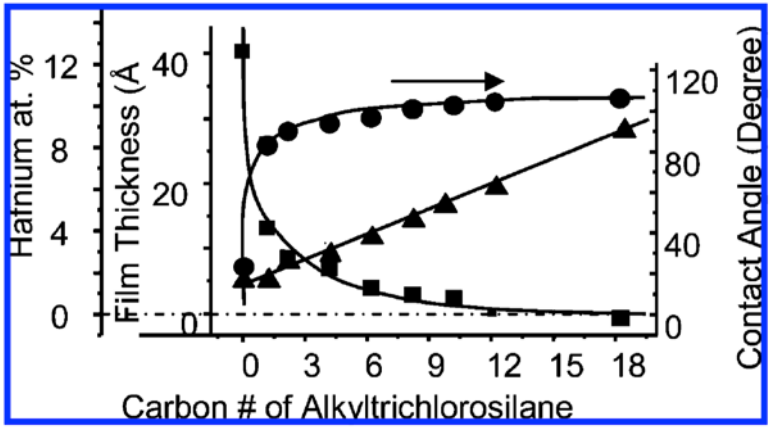
Source: Silvia Armini, IMEC




Ref: Jiang, X. & Bent, *J Phys Chem C* **113,** 17613–17625 (2009).




**Prior works**

- Good metal oxide and Pt ALD selectivity on oxides using silane SAMS deposited in liq. phase or MCP
- Little has been done on metals substrates [1]
- Almost none has been done in vapor phase [2]

1. Hashemi, F. S.. *ACS Nano* 150724143648006–8 (2015)
2. Farm, E.. Selective-Area Atomic Layer Deposition, Univ. of Helsinki Dissertation 2011.

**Vapor phase SAMS are**

- scalable for manufacturing
- work well in 3D
- allow rapid processing
- Compatible for ALD / SAMS codepostion

# Hardware setup

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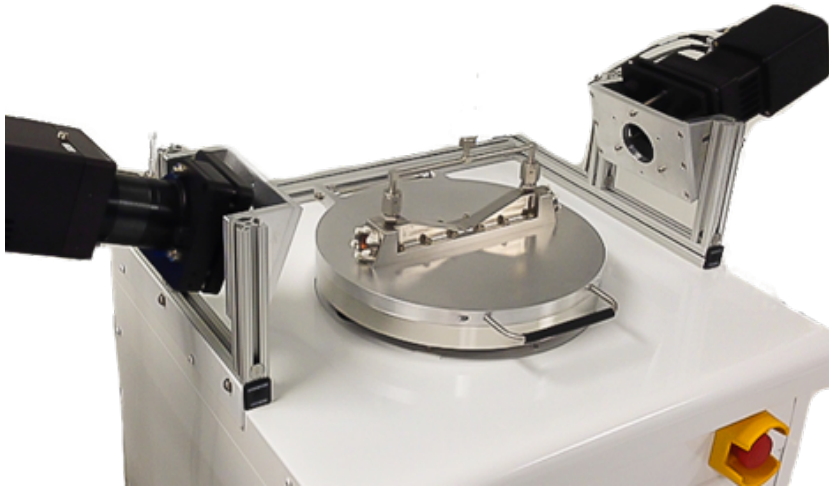

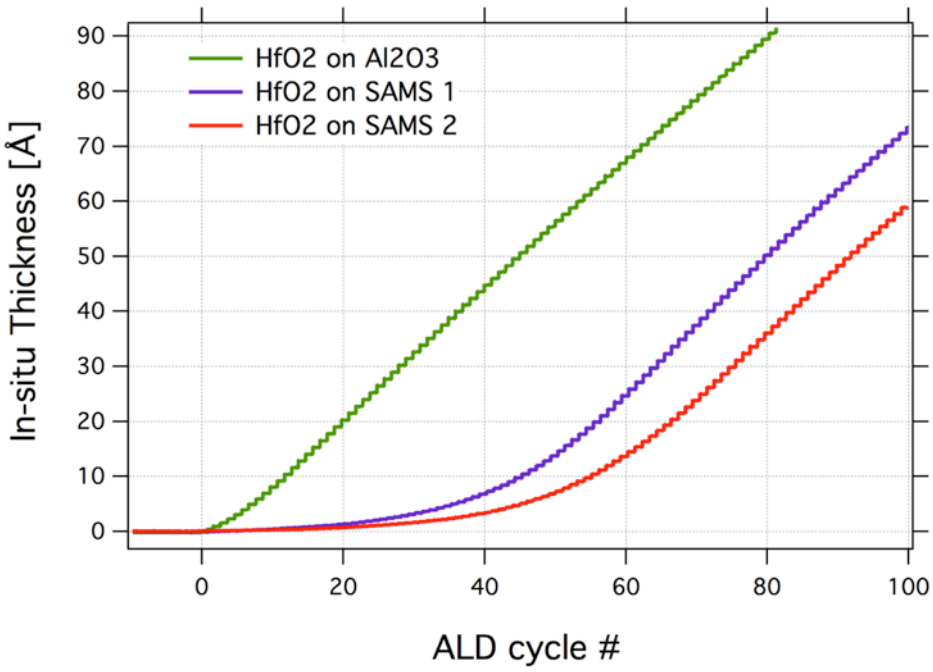


- Use same 200-mm Savannah* for thiol SAMS and $HfN_x$ ALD
- Depositions at 170˚C
- $HfN_x$ - TDMAHf and $NH_3$ thermal ALD
- C18 Thiol SAMS precursor (ODT)
  - 1- Octadecanethiol $CH_3(CH_2)_{17}SH$
  - Vapor pressure @130˚C ~1 Torr
  - But evaporation rate x10 slower than C10-C12 SAMS
  - High temp. pressure endpoint delivery SAMS kit
- ☹ No glove box configuration
- ☺☺ Insitu thickness monitoring via Woollam M2000 ellipsometer

  Insitu SE is critical to monitor both the SAMS growth and $HfN_x$ inhibition in real-time

* IMEC: 300-mm glovebox Savannah

# $HfN_x$ ALD on $SiO_2$ exposed to C18 thiol

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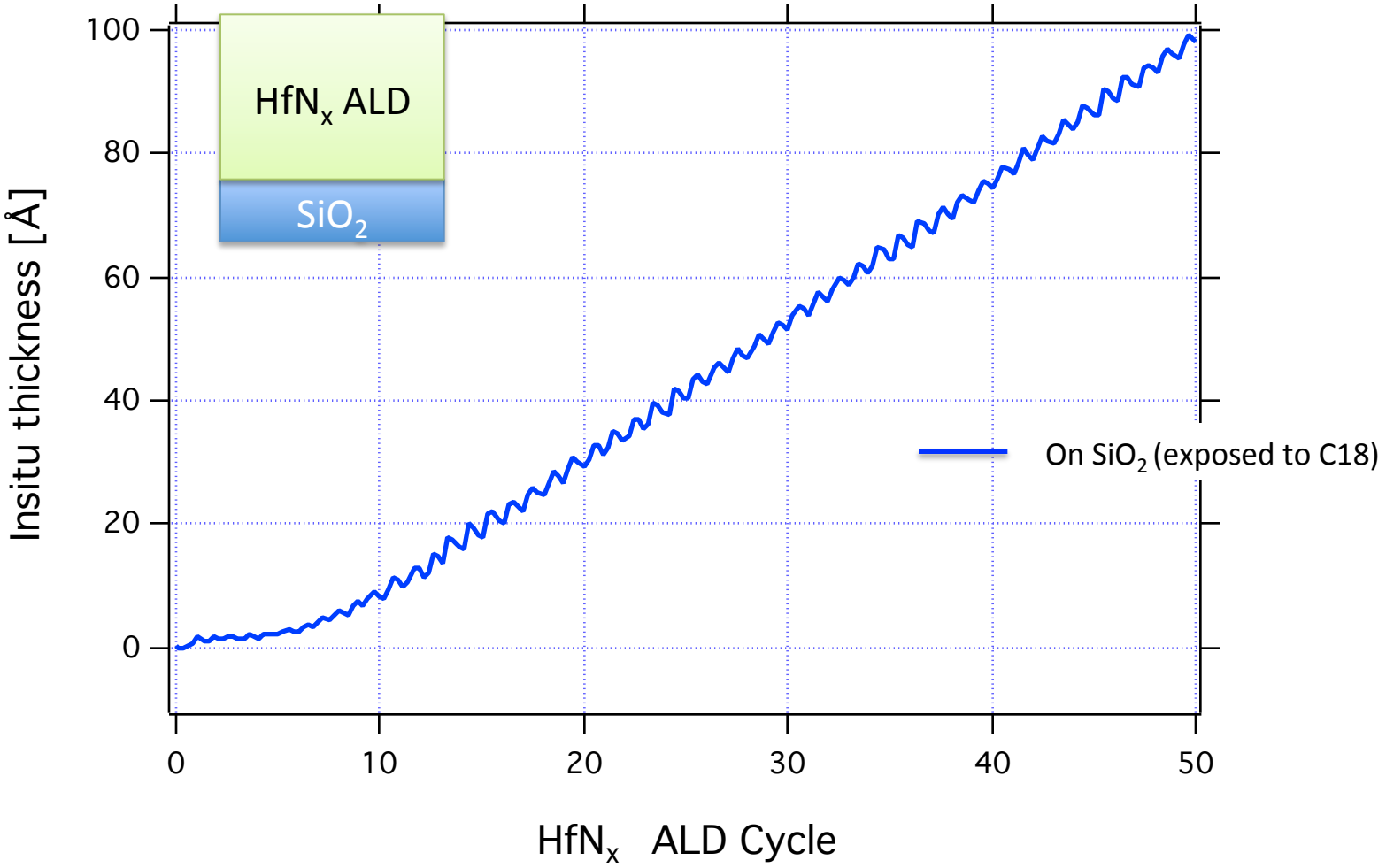
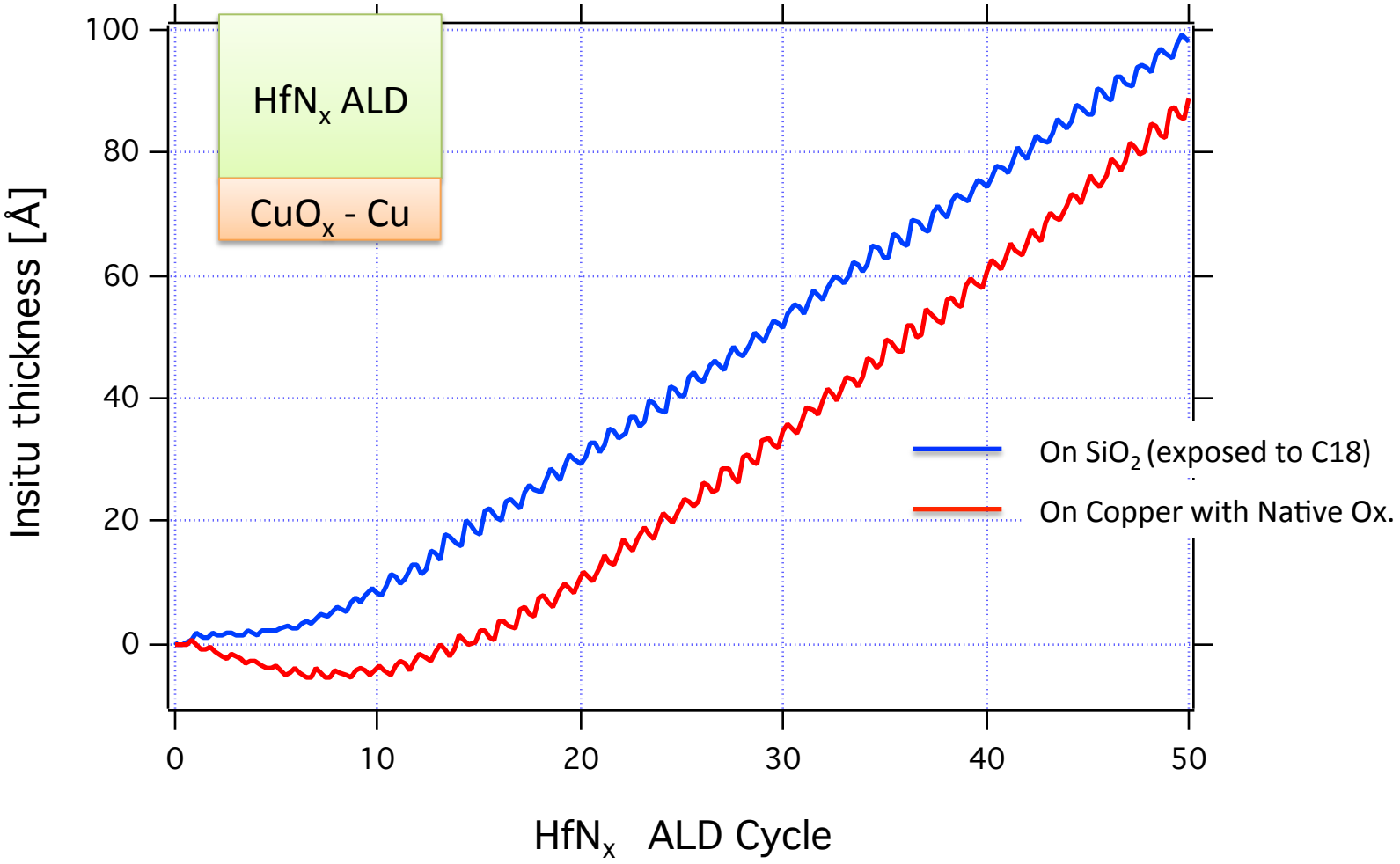



- C18 thiol doesn't bound to $SiO_2$
- $HfN_x$ shows 5-10cycle growth inhibition

# $HfN_x$ ALD on copper with native oxide

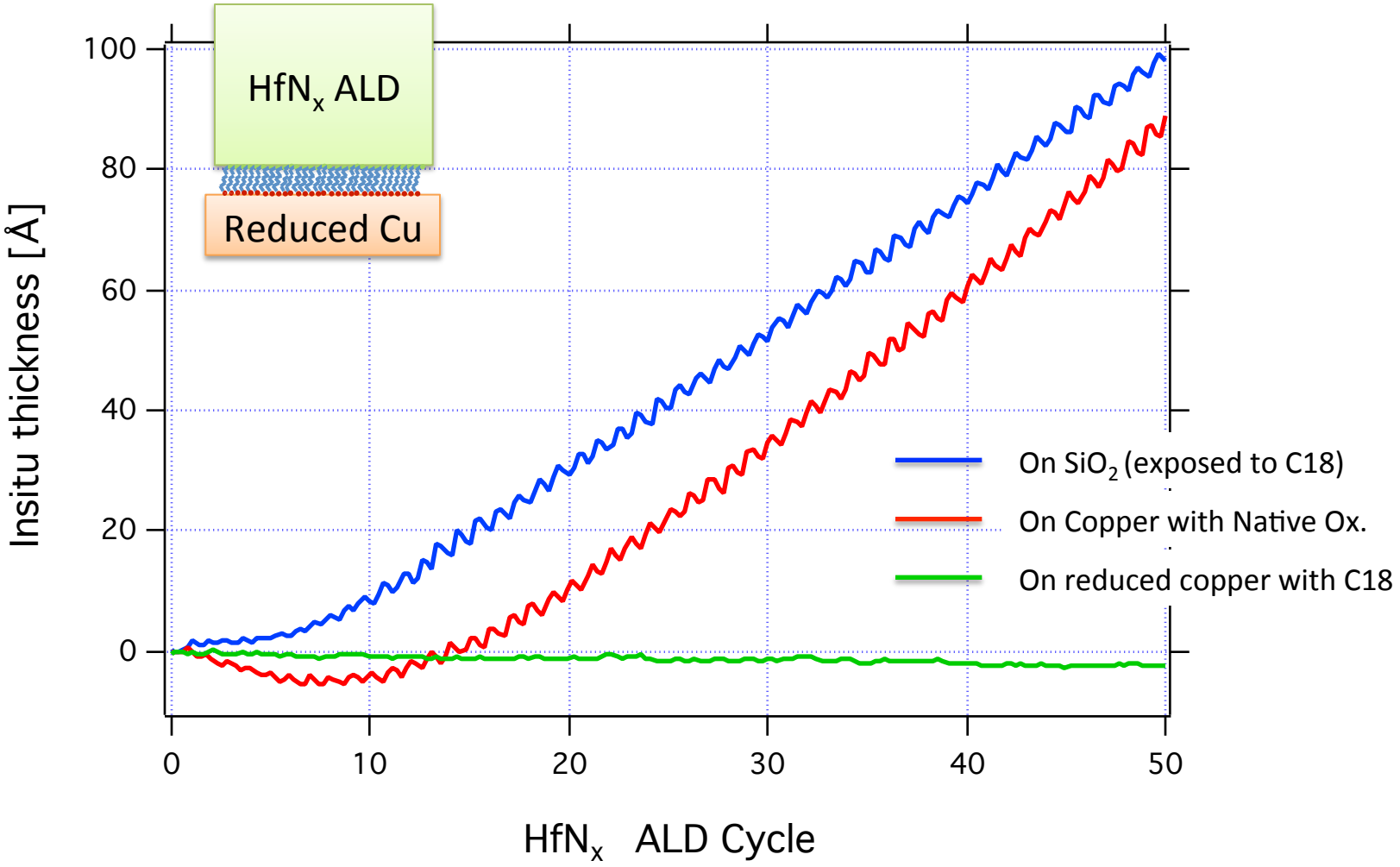
Ultratech CNT




- $HfN_x$ chemistries react on as-is copper leading to likely reduction of $CuO_x$

# $HfN_x$ ALD on reduced copper exposed to C18 thiol

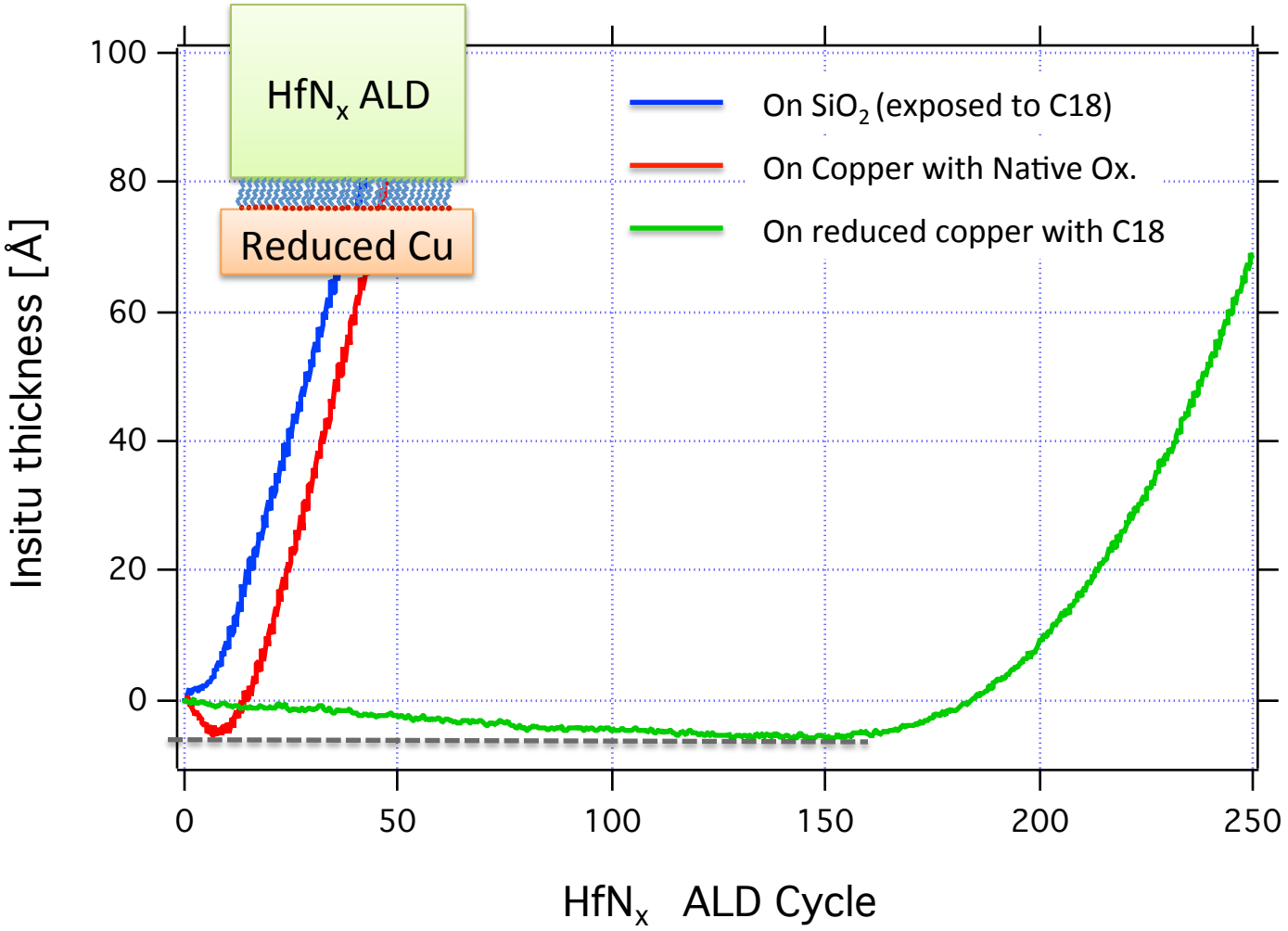
Ultratech CNT




- $HfN_x$ on reduced Cu + C18 SAMS is inhibited for > 50 cycles
- >10nm ALD selectivity is achieved

# $HfN_x$ ALD on reduced copper exposed to C18 thiol

Ultratech CNT




- Retardation extends to >150 ALD cycles
- Underlying reaction during first 150 cycles

# In-situ reduction of native copper oxide

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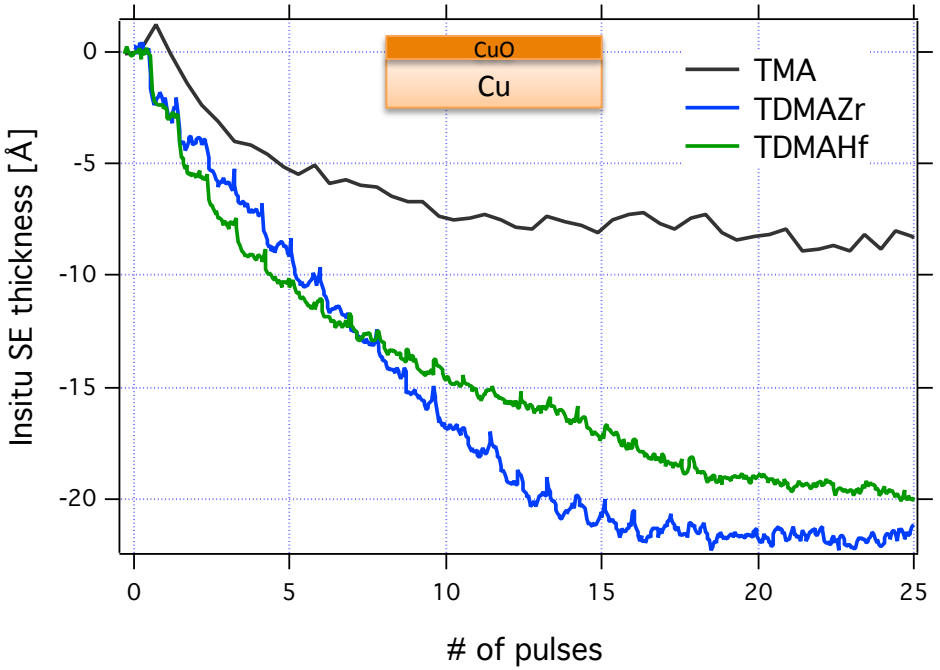
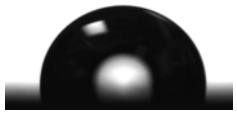
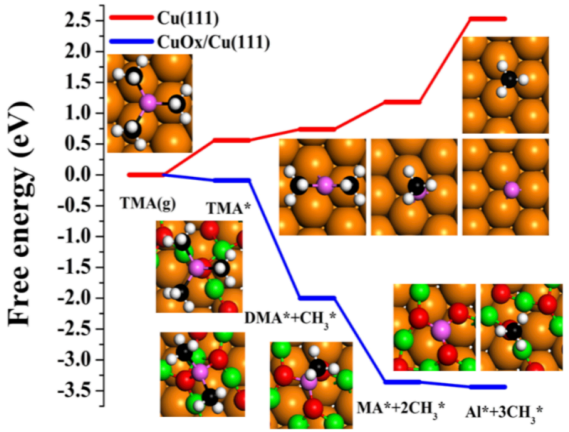
Insitu SE thickness change during
0.1 s metalorganic pulses @ 170˚C on $Cu/CuO_x$



Cu + nat.ox | Cu after insitu TDMAHf | Cu after exsitu HCl wet clean
WCA 92˚ WCA 31˚ WCA 32˚




Proposed reduction pathway

$2Cu\,O + Al(CH_3)_3$
$\rightarrow CuAlO_2 + 3Cu + 2CH_4 \uparrow + CH_{ads}$

Gharachorlou, A. *et al*. *Acs Appl Mater Inter* **7,** 16428–16439 (2015).

Above 150˚C, metal organic pulses (TMA, TDMAZr, TDMAHf) leads to “partial” reduction of copper native oxide conducive to thiol reaction on reduced Cu

# Insitu SE during undecanethiol depositions

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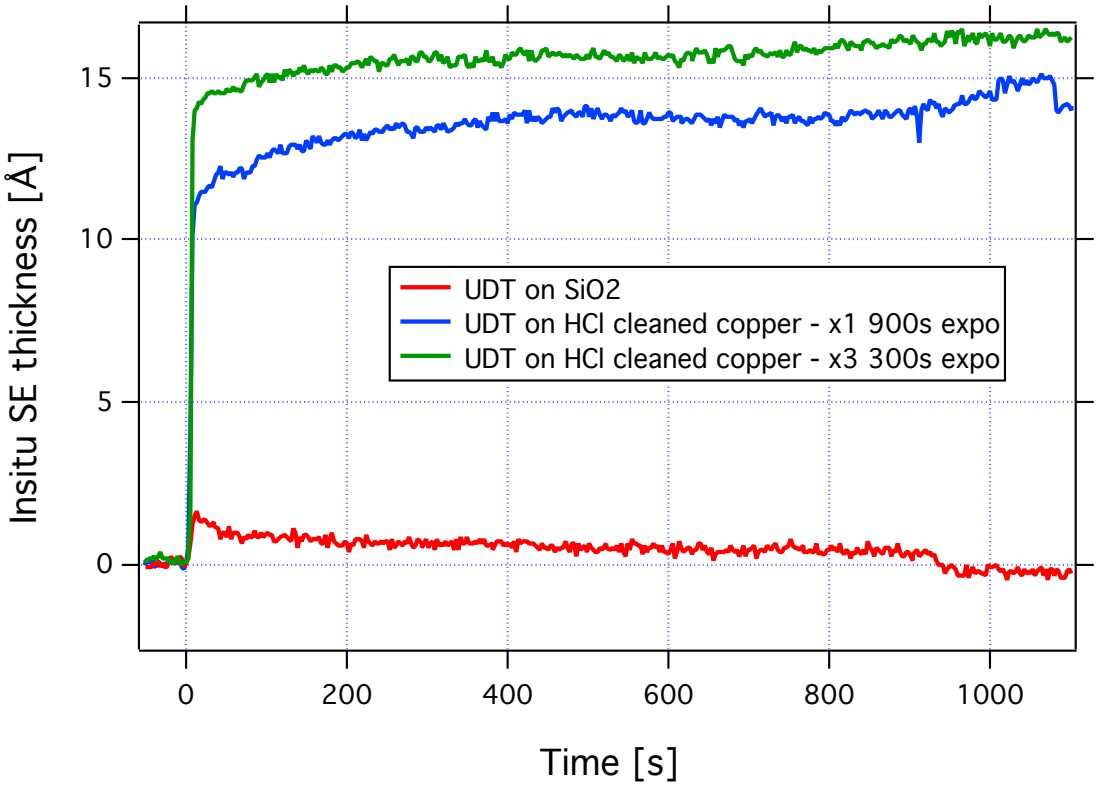
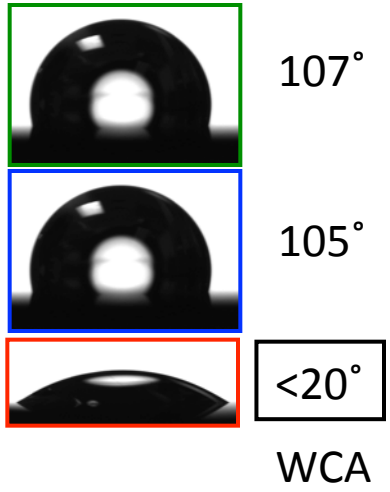
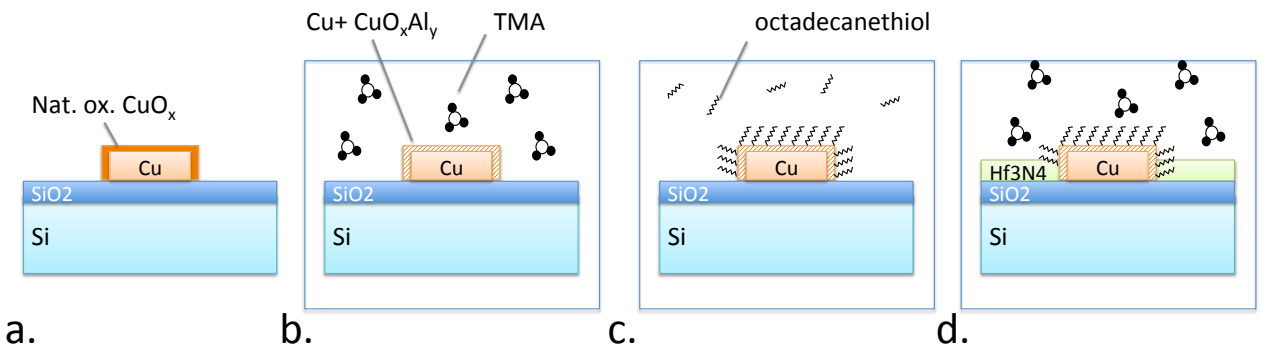



- Use C11 Undecanethiol
  - Too short for efficient blocking action (20-30 cycles) but enables rapid characterization of SAMS growth behavior due to x10 refill rate
- No C11 growth observed on $SiO_2$
- Self-limited C11 growth within 10 min. on reduced copper

# Summary




- Copper oxide is reduced in-situ above 150˚C using TMA/ TDMAHf or TDMAZr
- A dense self-limited ODT SAMS is selectively deposited in <15 min in vapor phase on reduced copper vs. $SiO_2$
- The SAMS layer acts as an efficient barrier blocking $HfN_x$ ALD for >150 cycles
- Selective ALD deposition of more than 10nm $HfN_x$ on $SiO_2$ vs copper is demonstrated
- All the steps were performed in-situ in a single tool
- ODT delivery is challenging and will require improved delivery systems
- Process integration in a glove box will be beneficial (IMEC platform) due to rapid oxidation kinetics of copper

*Patent application # 62/244,467 "Methods of forming an ALD-inhibiting layer using a self-assembled monolayer"*