Low ESH-impact Gate Stack Fabrication by Selective Surface Chemistry

(*Task Number: 425.026)*

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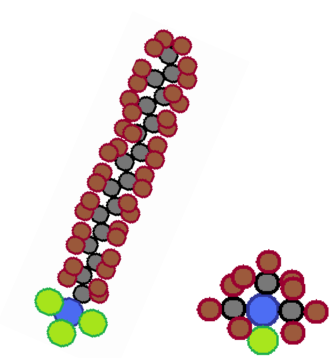
Industrial partners:
ASM

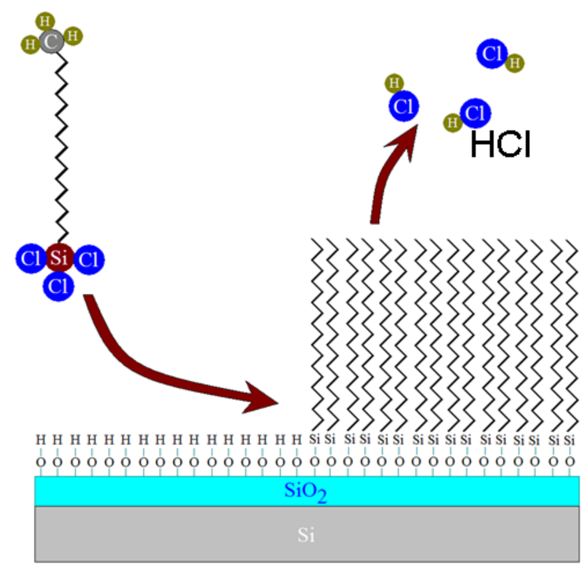
ESH Metrics and Impact: Cost Reduction

- Replace multiple patterning steps with single selective chemistry approach
  - Reduce chemical waste in dielectric/metal deposition process

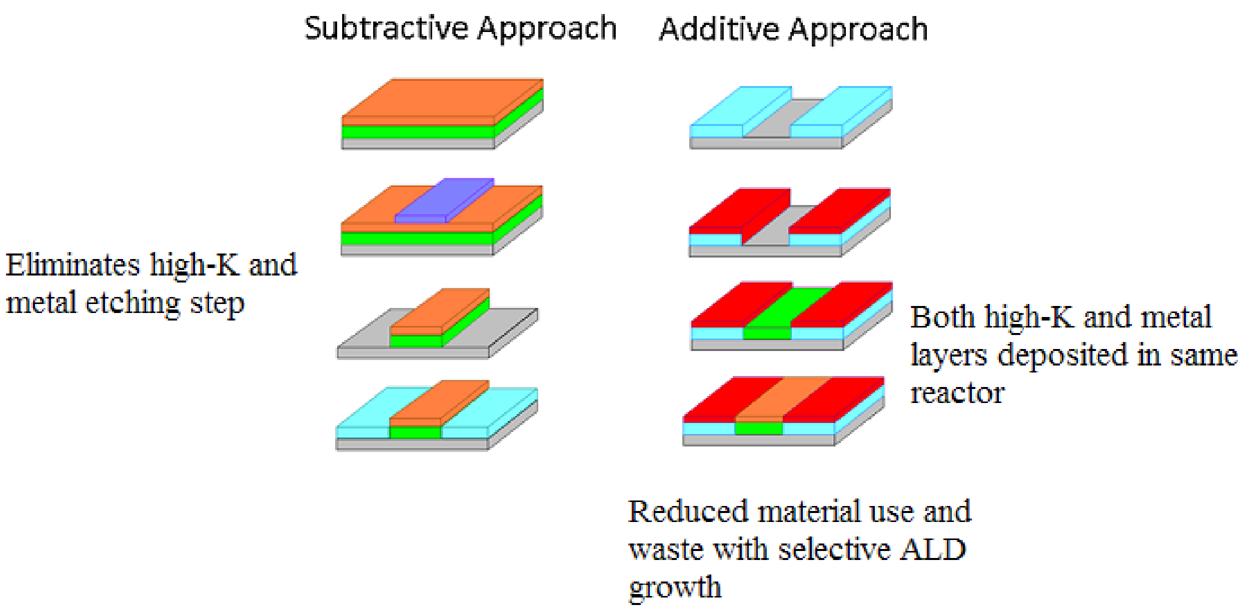
- Safety of SAM solution
  - Chlorosilanes dissolved in toluene
    - Chlorosilanes reacts with water, air sensitive, and combustible
      - OTS (octadecyltrichlorosilane)
      - TMCS (trimethylchlorosilane)
    - **Batch processing must be done in vented environment with controlled humidity and no spark or open flame**
    - **Vapor process could eliminate solvent**
  - Carbon and HCl are only byproducts of the surface reaction



OTS TMCS



ESH Metrics and Impact: Cost Reduction

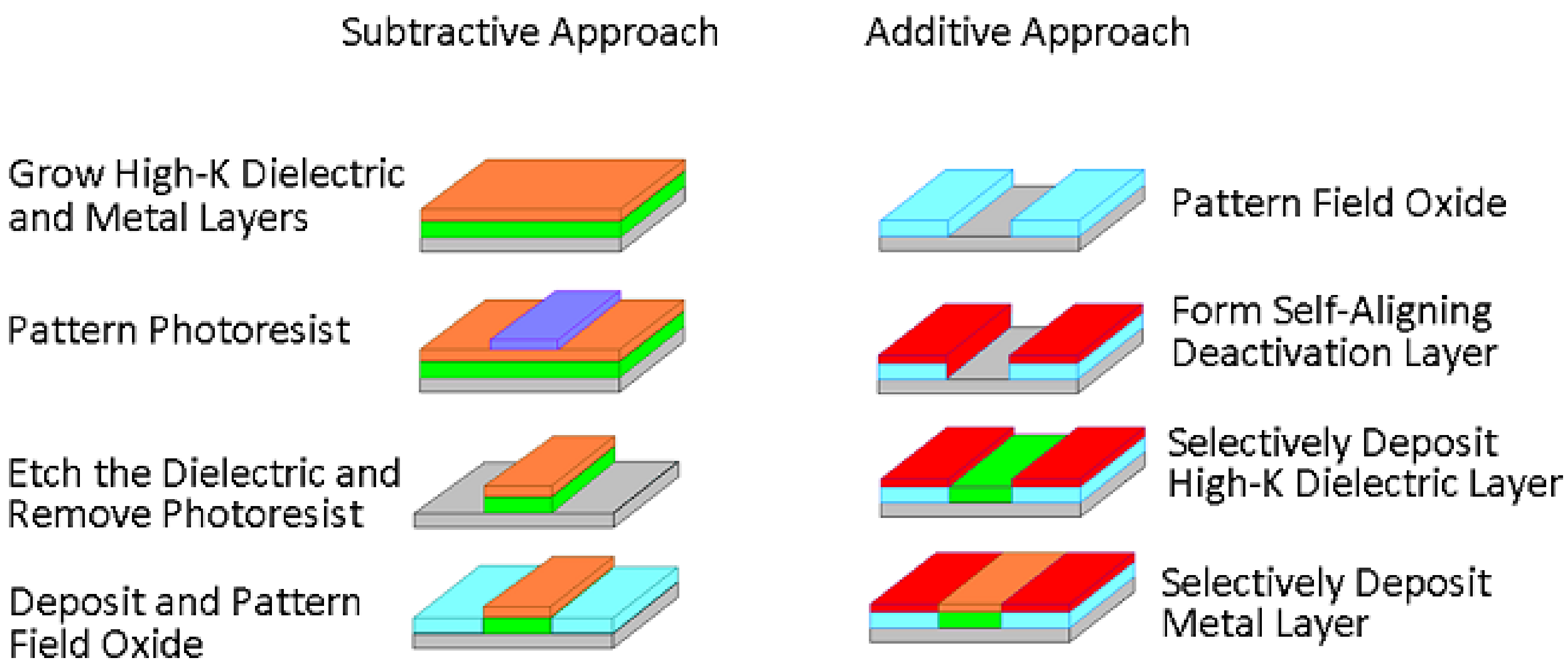


- SAM prevents aqueous solutions from interacting with hydrophobic surfaces
  - Coat metal parts or work surfaces exposed to water-based solution reduces need for cleaning
  - Coat ALD reactor walls with SAM to extend up-time, reduce cleaning, and improve throughput

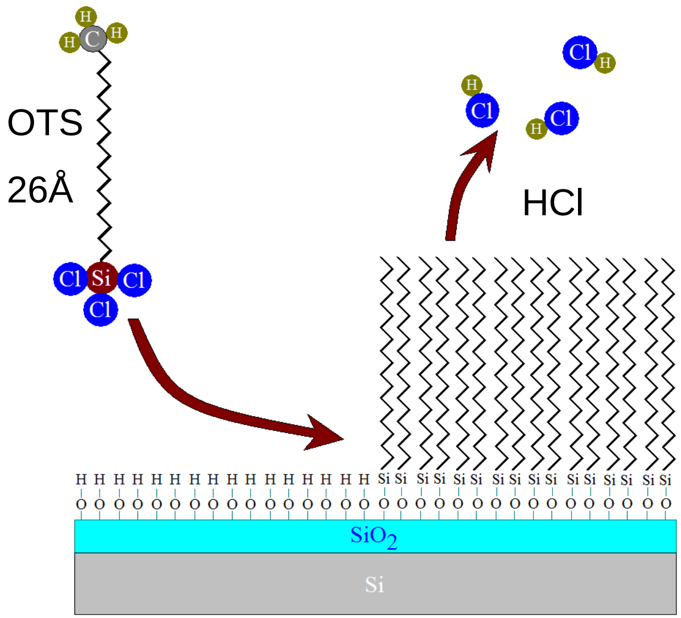
Overall Objectives

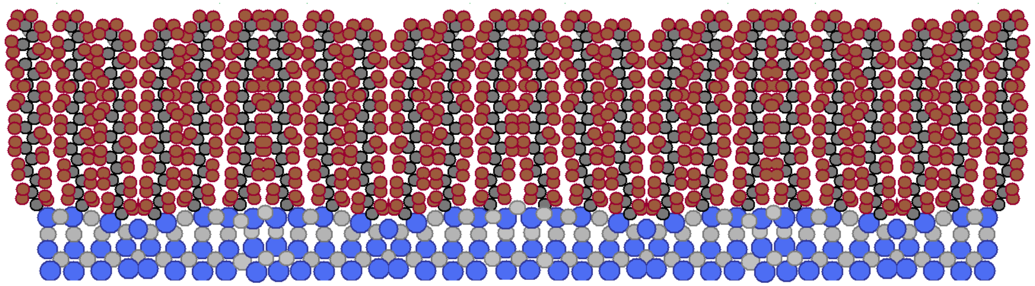
- **Simplify multistep subtractive processing used in microelectronic device manufacturing**
  – Develop new additive processes that can be integrated into current devices flows

- **Focus on high-k gate stack testbed**
  – Fabricate low defect high-k/semiconductor interfaces



Technical objective

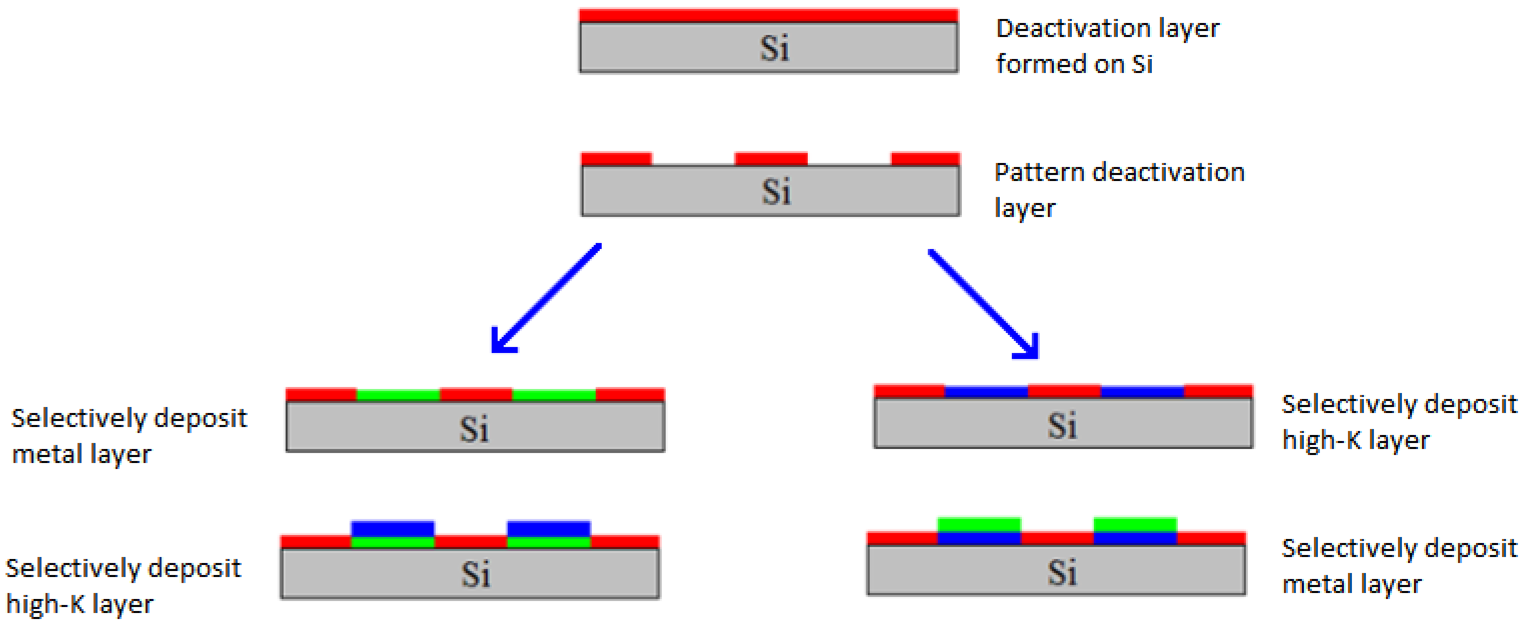




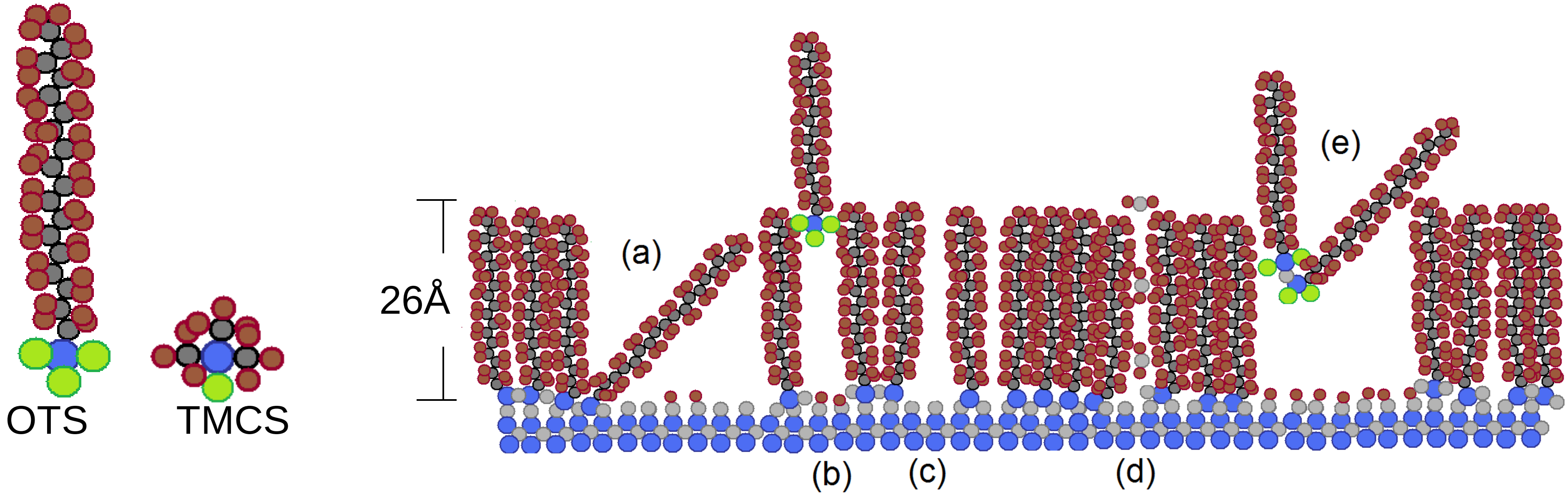
- Use a self-assembled monolayer (SAM) as a chemically inert layer to selectively block ALD deposition
  - Identify and solve defects in SAM layers that result in deactivation failure
  - Pattern SAM layer for device manufacturing
  - Integrate vapor phase SAM formation with ALD system

Novel Device Manufacturing

- Single patterning step for deactivation layer
- Use selective ALD of metal and high-k dielectric layer

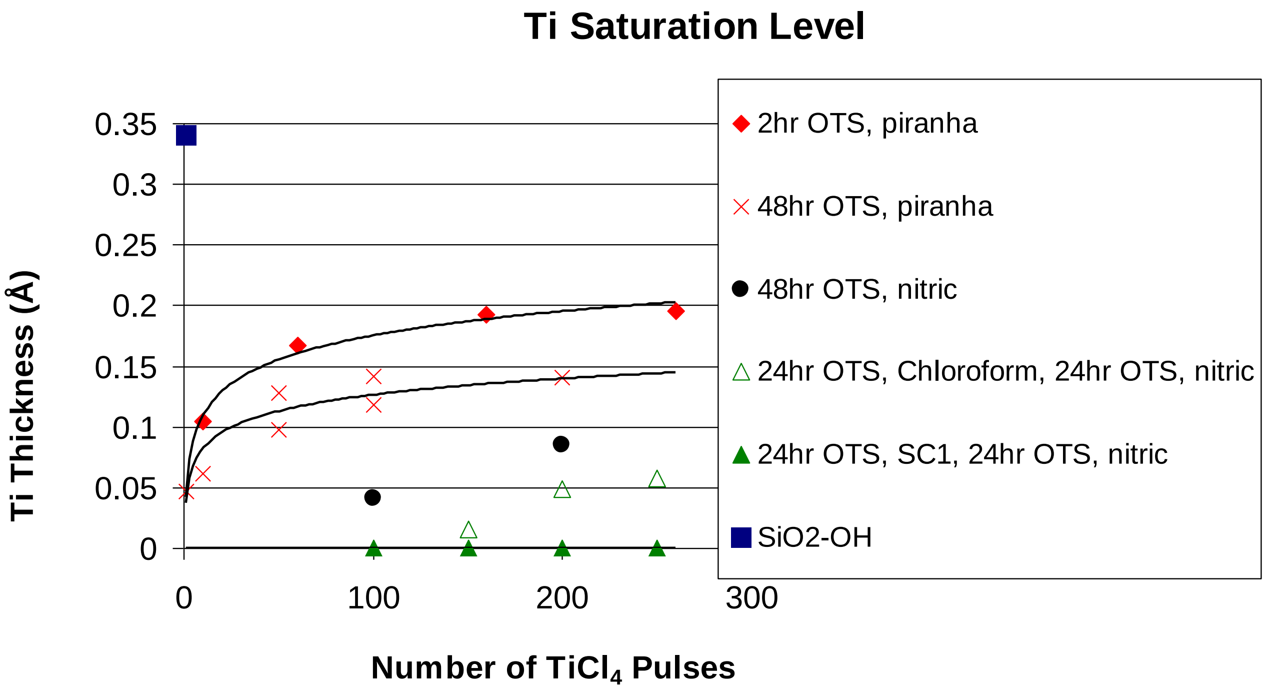


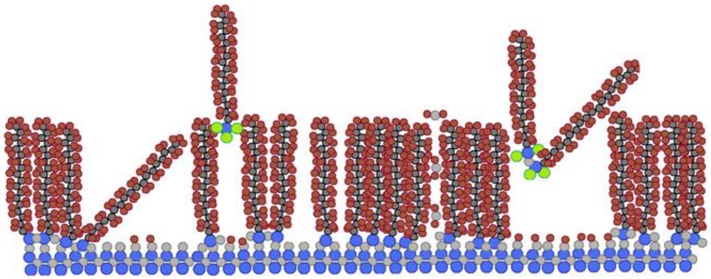
SAM Defects



- (A) Poor alignment at island boundaries block surface sites (poor uniformity)
- (B,C) Gaps in SAM too small for primary SAM molecule
- (D) Water absorbed/adsorbed in SAM layer
  - Either during SAM formation or during ALD process
- (E) Polymerized SAM molecules on surface
  - Block surface sites
  - Excess polymer increases thickness and water contact angle
  - Could generate particles

Defect monitoring using $TiCl_4$ pulses

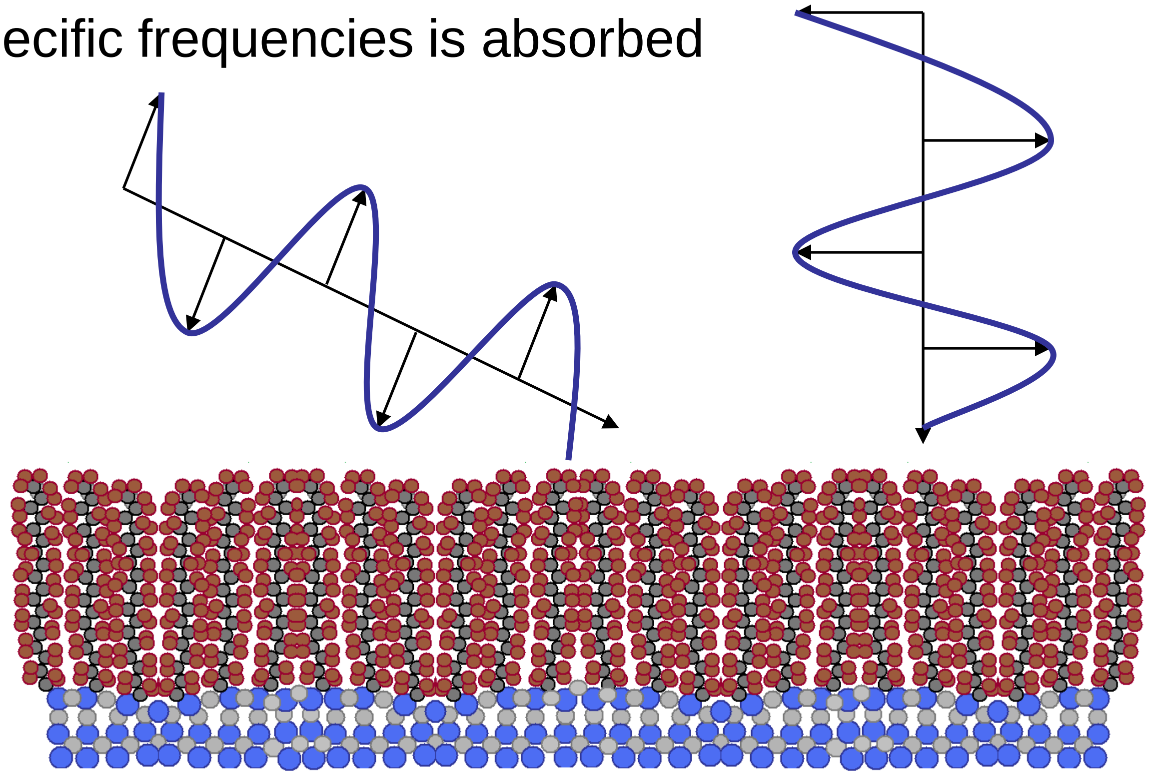




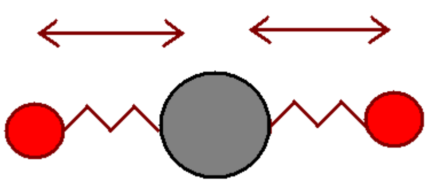
- Defect level in SC1 re-hydroxylated samples was below XPS limit for up to 250 seconds of $TiCl_4$ exposure
- FTIR used to determine why nitric acid out performed piranha as starting surface treatment

SAM Alignment: FTIR

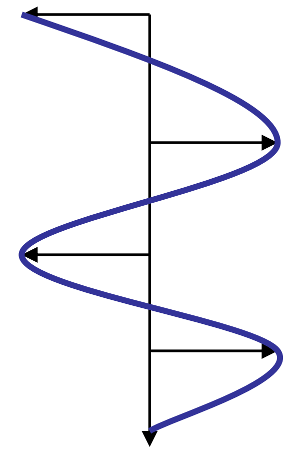
- EM field is perpendicular to the incident light
- Electric field provides an oscillating force at the atomic level
- Atomic bonds vibrate at specific resonant frequencies
  - Light of these specific frequencies is absorbed

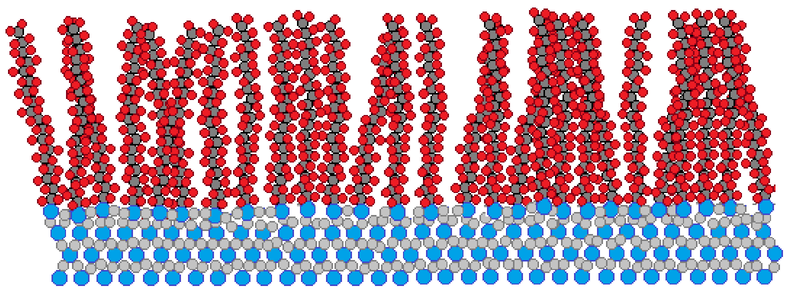


Symmetric 2850cm^{-1}
Antisymmetric 2919cm^{-1}

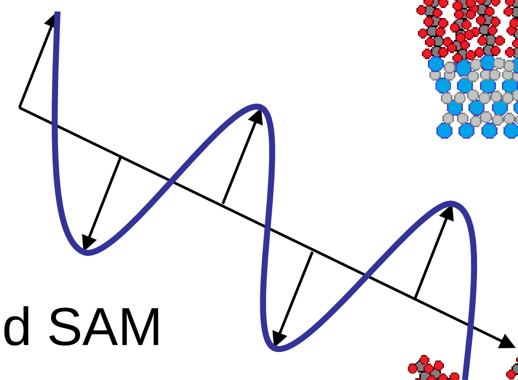


SAM Alignment: FTIR

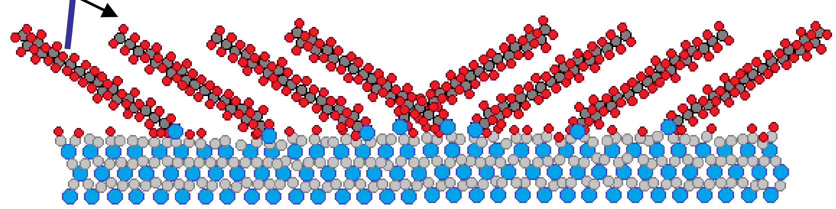




- Vertically aligned SAM
  - Normal incidence absorption greater than Brewster incidence absorption
  - Brewster peak area divided by normal peak area <1



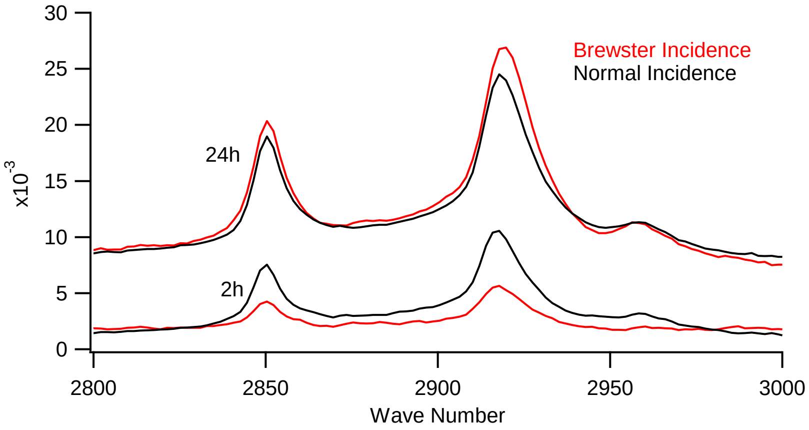
- Non-vertically aligned SAM
  - Brewster incidence absorption greater than normal incidence absorption
  - Brewster peak area divided by normal peak area >1



Analysis of CH_2 peaks Brewster Incidence/Normal Incidence

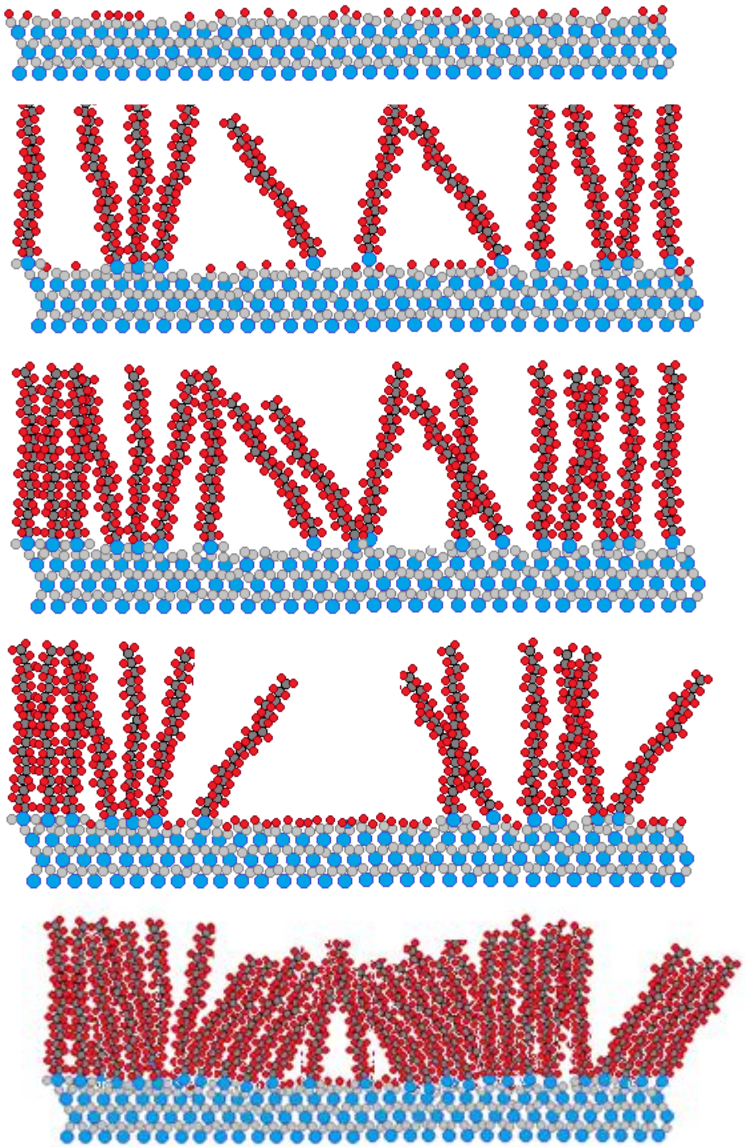
Peak at $2850cm^{-1}$

	2h	**24h**	24h sc1	24h sc1 / 24h
OTS on nitric acid etched SiO_2	0.2919	**0.5202**	3.1325	3.2451
OTS on piranha etched SiO_2	0.3555	**1.2263**	2.2984	2.7108



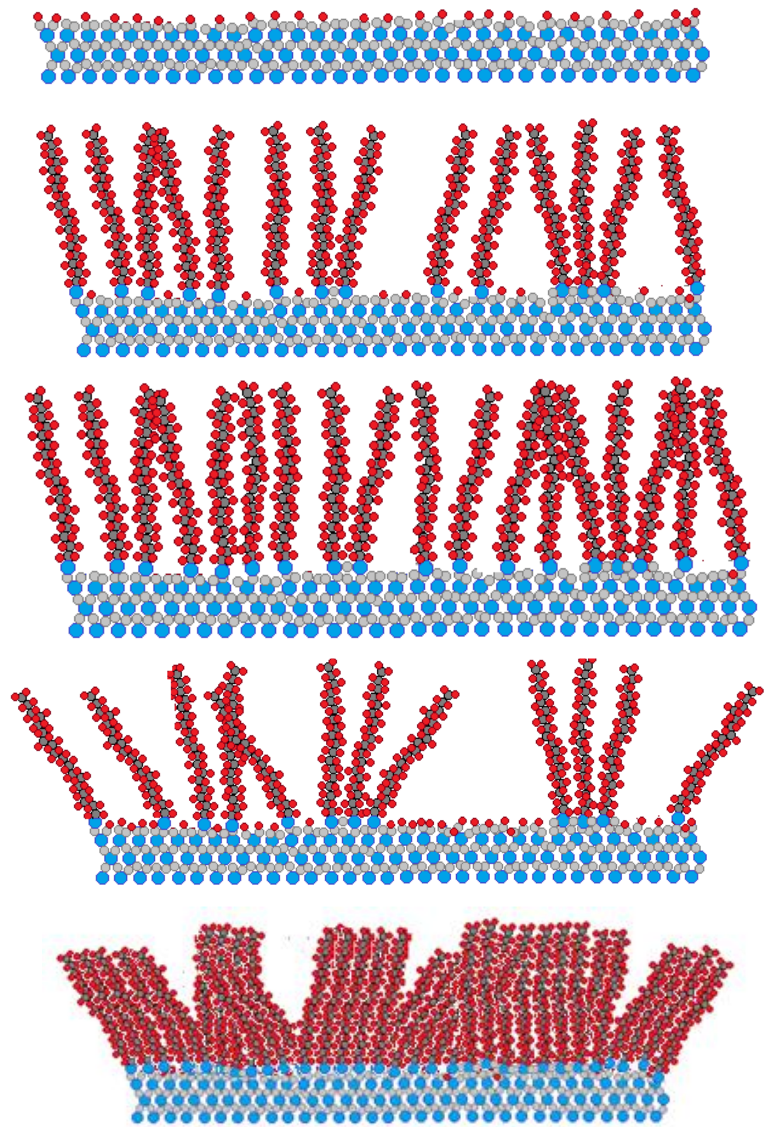
SAM growth mechanism

Piranha SiO_2 staring surface

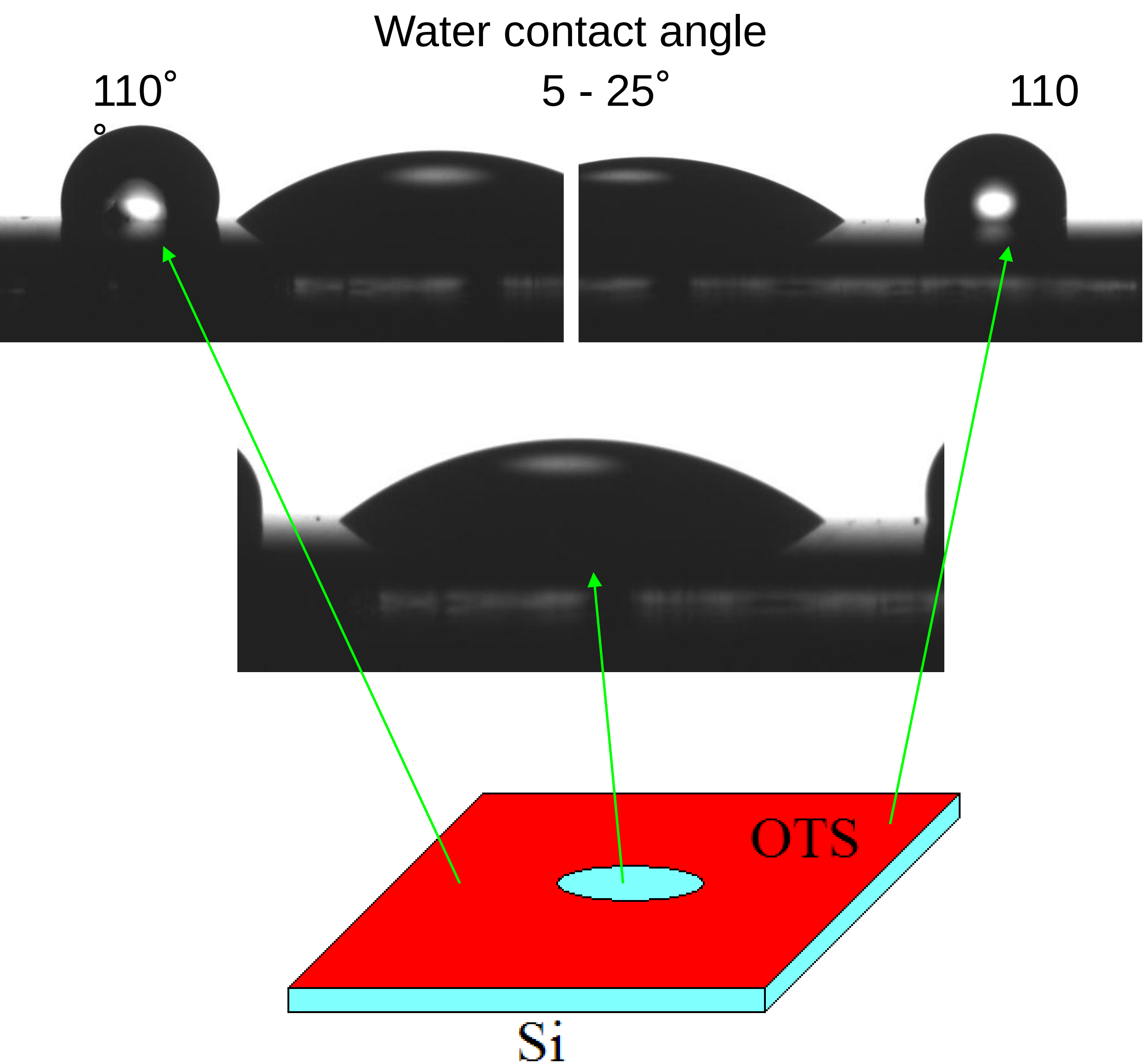


- Initial hydroxylation
- 2h SAM attachment
  - Vertical alignment of SAM
- 24h SAM attachment
  - Loss of hydroxyl binding groups
- SC1 re-hydroxylation
  - Opens and re-hydroxylates defect boundaries
  - Less vertically aligned
- Additional 24h SAM attachment
  - Higher density SAM but less vertically aligned

Nitric acid SiO_2 starting surface



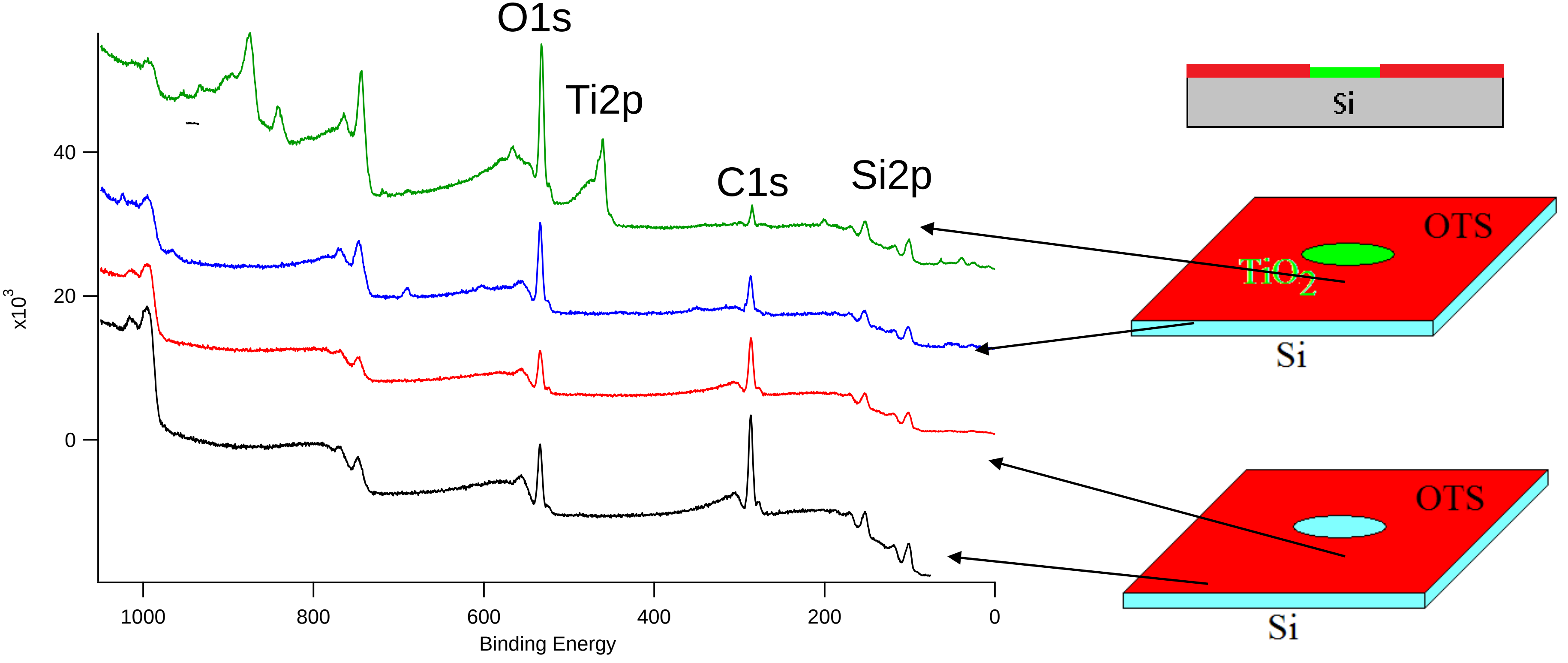
Selective high-k deposition



- SAM surfaces exposed to UV in air for 2.5 h through a simple mask
- Removal of SAM occurred only in UV/air exposed areas
- Surface was hydrophilic in UV/air exposed areas and hydrophobic on remaining OTS areas

Direct SAM patterning

- Selectively deposited 30Å of TiO_2 only in open areas of OTS coated Si surface
- Pattern formed without photoresist



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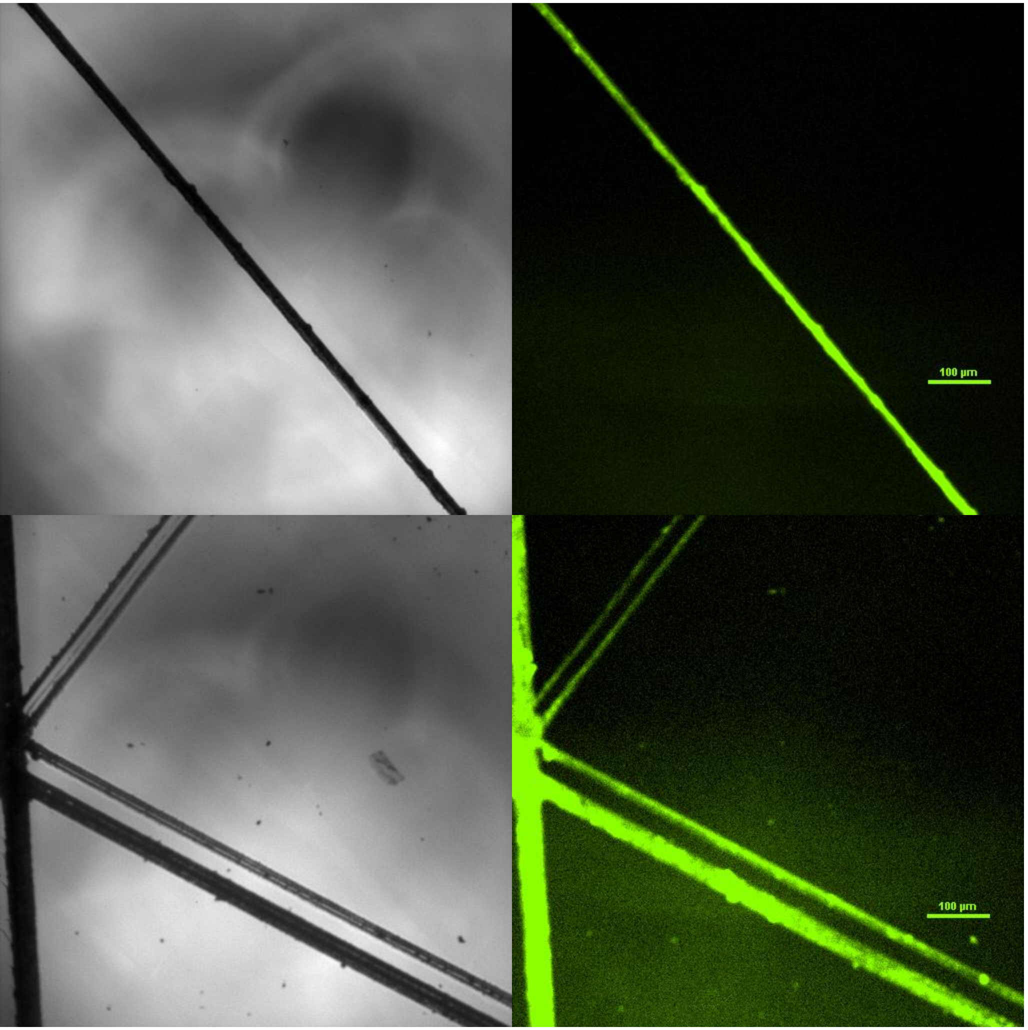
SEM images

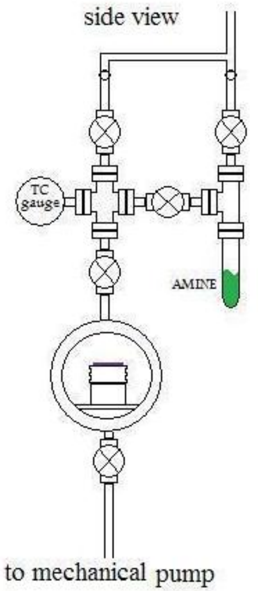
- UV light shown through an electro polished stainless steel mask
- Ozone generated at surface etches the OTS layer
  - One edge of the mask was lifted 200 μm off the surface (bottom image)
  - Effect of mask undercutting is visible in SEM (proportional to mask surface separation)
- Dark areas are TiO_2 light areas are OTS

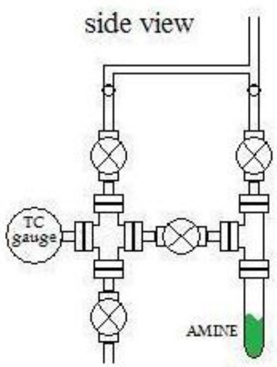
Quantum dot selective deposition

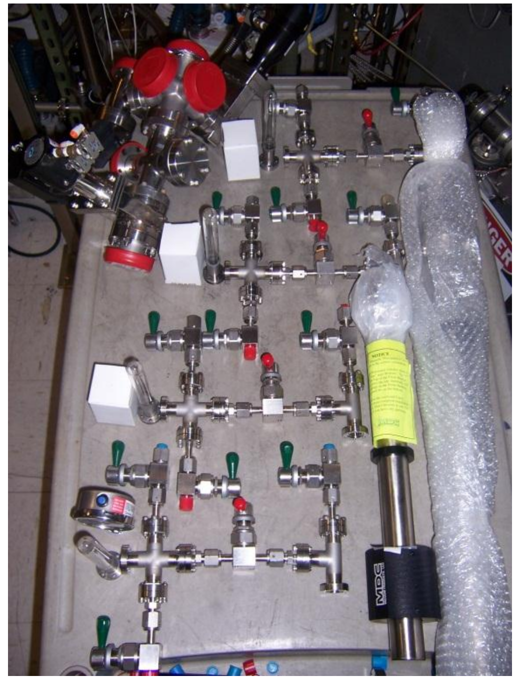


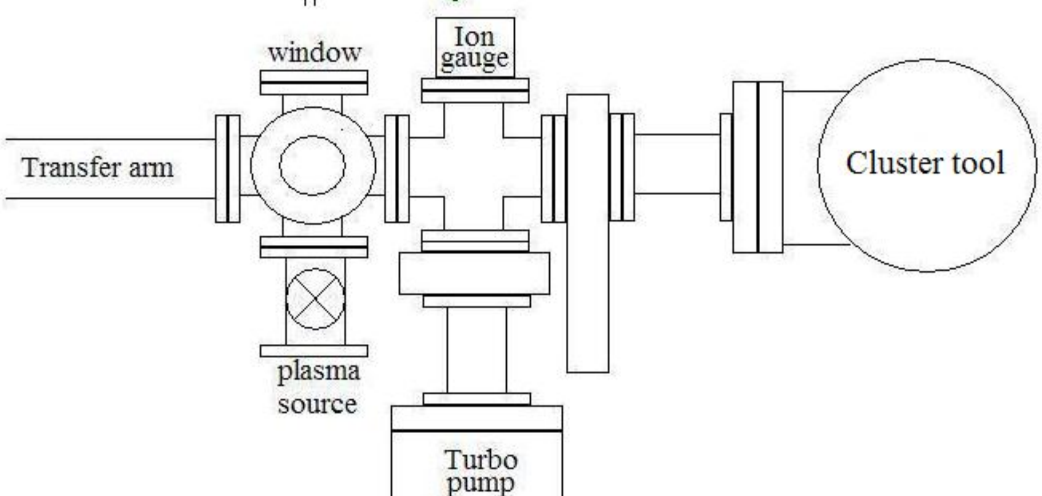
- OTS pattern hydroxylated in SC1 for 5 min
- QD solution spread over pattern and dried under IR lamp
  - Solvent rinsed and polished, leaving behind filled pattern
- On chip QD sensitized TiO_2 light sensors for optical processing/data transfer

New SAM Vapor/In-situ Hydroxylation Reactor









- Safe to install on cluster apparatus
  - Polymerization not seen in previous reactor
- Provides more versatile vapor delivery
- Allows higher temperature testing
  - 300° C
- In-situ hydroxylation
- Connected in-situ to ALD reactor
- Vials are well isolated from other chemicals

Conclusions

- Demonstrated controlled selective deposition of high-k dielectric layer
  - Characterized effect of extraction and re-hydroxylation using FTIR
    - Majority of the SAM binds in first 2h of OTS exposure
    - SC1 re-hydroxylation has similar effect on SAMs formed on both nitric acid and piranha SiO_2 starting surfaces
    - Reduces SAM alignment but increases density by opening defect areas and adding hydroxyl binding sites
    - Can be integrated with current manufacturing piranha hydroxylation process
  - Reduced SAM defects (200+ ALD $TiCl_4/H_2O$ cycles)
  - Only one patterning step required for metal, dielectric, or nano-particle deposition (self-aligning high-k growth)
- Simplifies the front end gate stack manufacturing process
  - Reduced cost
  - Reduced material usage
  - Improved environmental performance

Future Work

- Continue to investigate the line spreading and line edge roughness for different patterning approaches
- Develop an industrially viable method for vapor phase delivery of SAM molecules
  - Pulse and purge both water and SAM molecules as opposed to sealing vapor in a reactor for extended time
  - Extend re-hydroxylation process to vapor phase SAMs
- Characterize SAM layers
  - Thermal stability for deactivation
  - Durability for large numbers of ALD cycles
  - Lifetime of SAM solution
- Investigate selective deposition/etching method on III-V semiconductor surfaces