Low ESH-impact Gate Stack Fabrication by Selective Surface Chemistry

(Task Number: 425.026)

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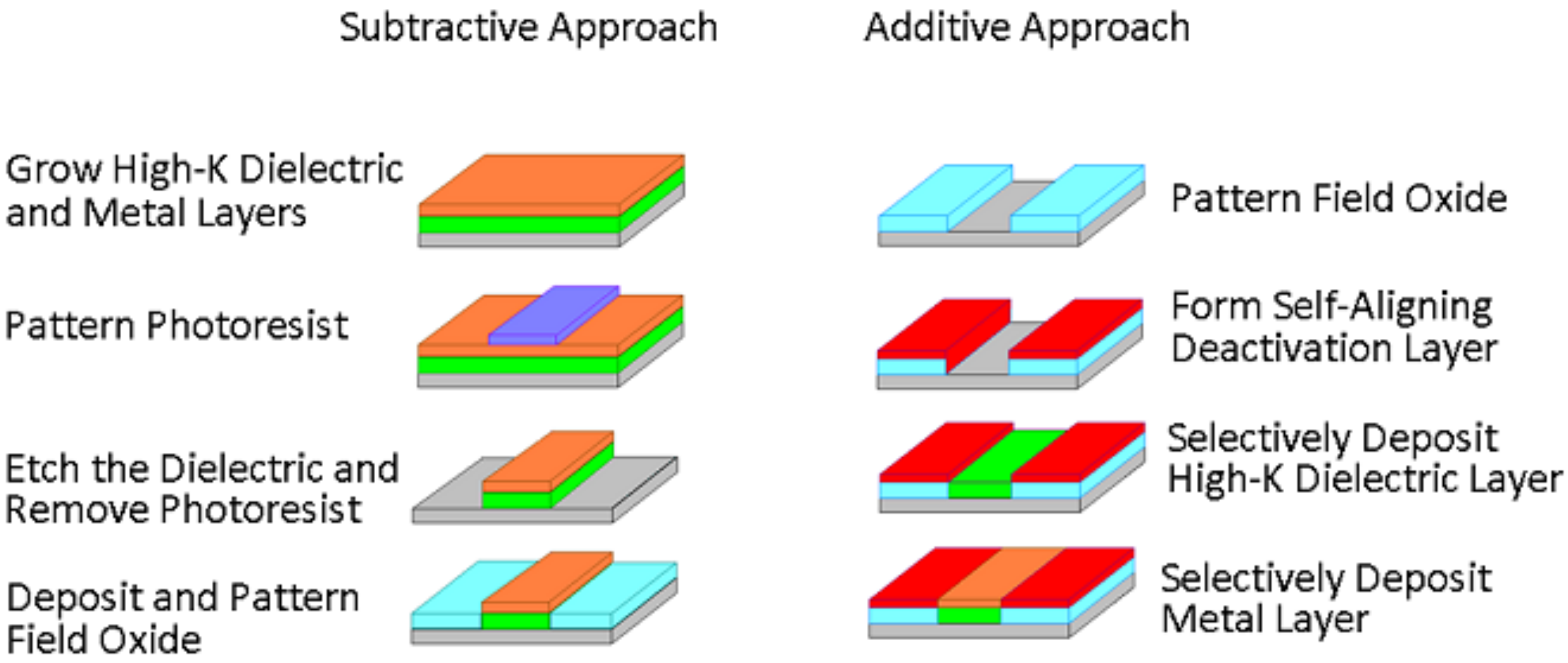
ERC Teleconference
Feb, 9th 2012
Tucson, AZ

Industrial partners:
SFAZ
ASM

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



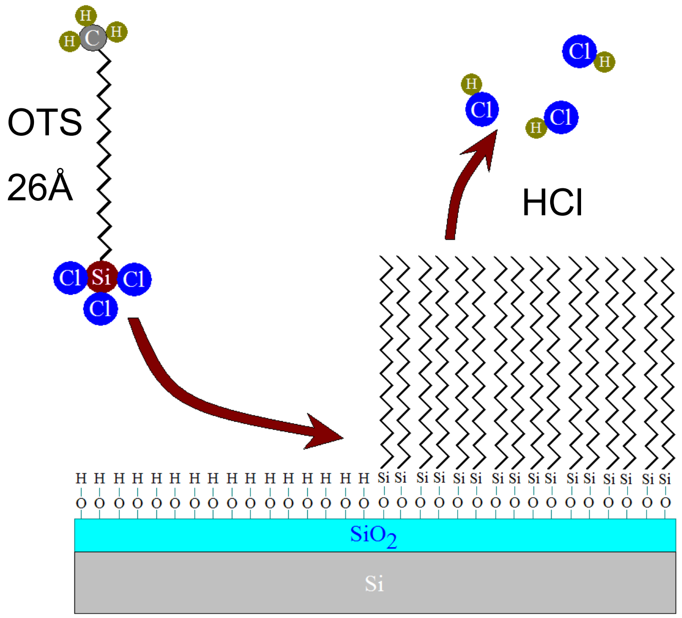
Subtractive Approach

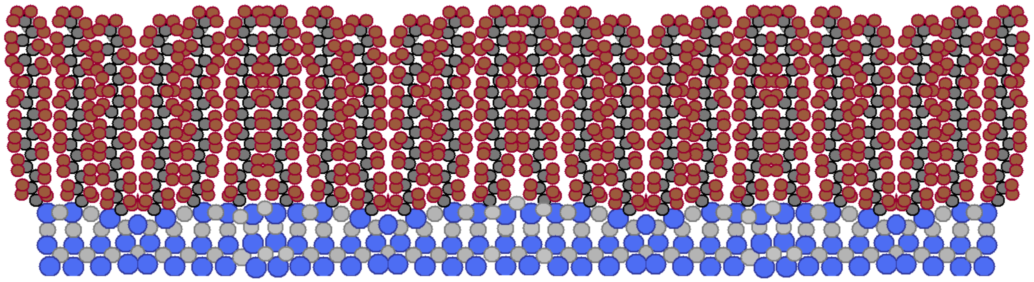
- Grow High-K Dielectric and Metal Layers
- Pattern Photoresist
- Etch the Dielectric and Remove Photoresist
- Deposit and Pattern Field Oxide

Additive Approach

- Pattern Field Oxide
- Form Self-Aligning Deactivation Layer
- Selectively Deposit High-K Dielectric Layer
- Selectively Deposit Metal Layer

Technical objective

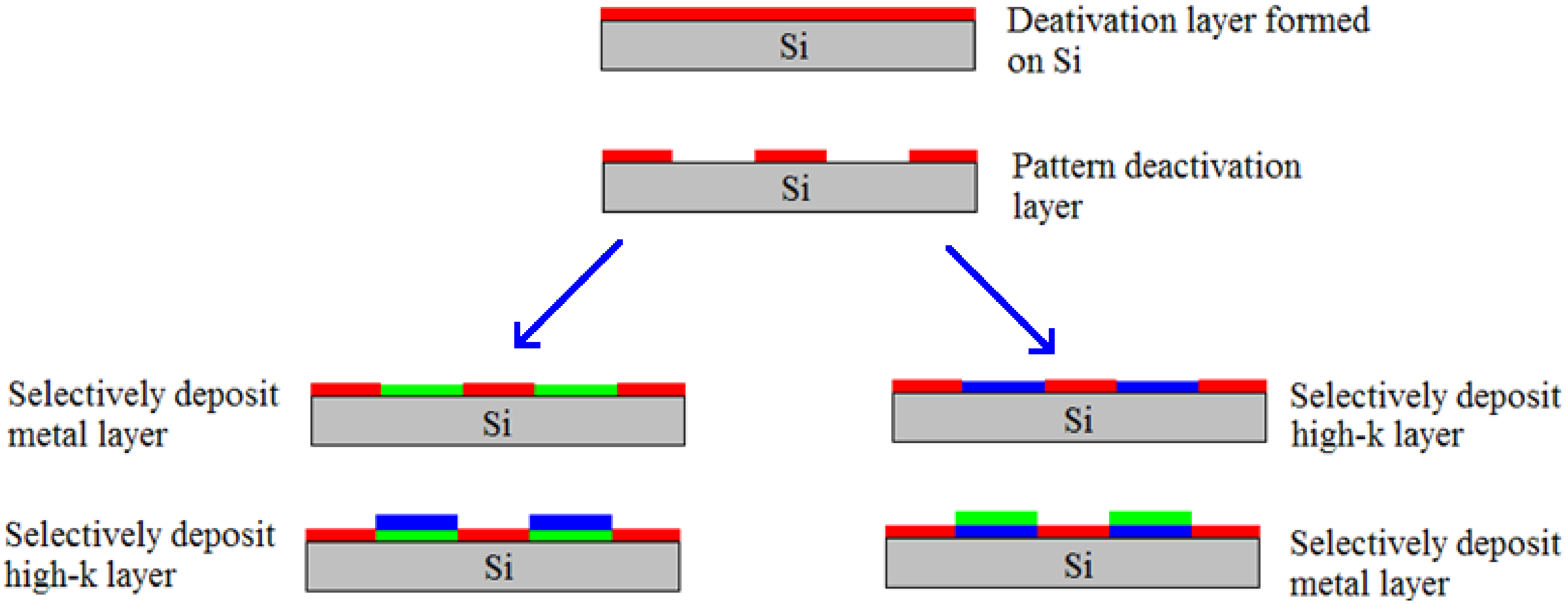




- Use a self-assembled monolayer (SAM) as a chemically inert layer preventing ALD deposition from occurring on surfaces
  - Identify and solve defects in SAM layers which result in deactivation failure (completed)
  - Pattern SAM layer for device manufacturing
  - Vapor phase SAM formation integrated with ALD system

Novel Device Manufacturing

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



Deativation layer formed on Si

Pattern deactivation layer

Selectively deposit metal layer

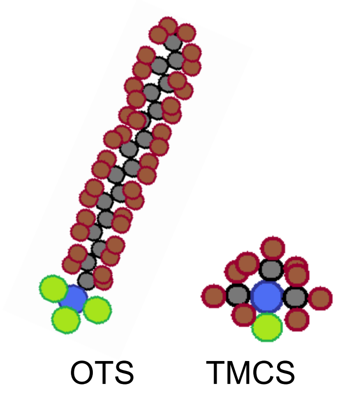
Selectively deposit high-k layer

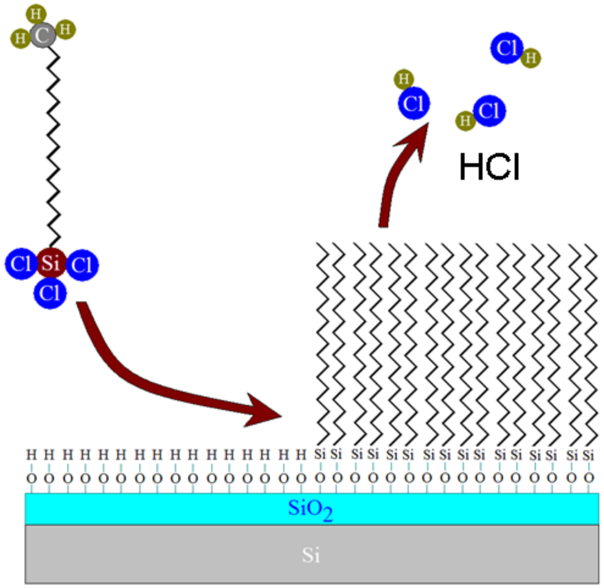
Selectively deposit high-k layer

Selectively deposit metal layer

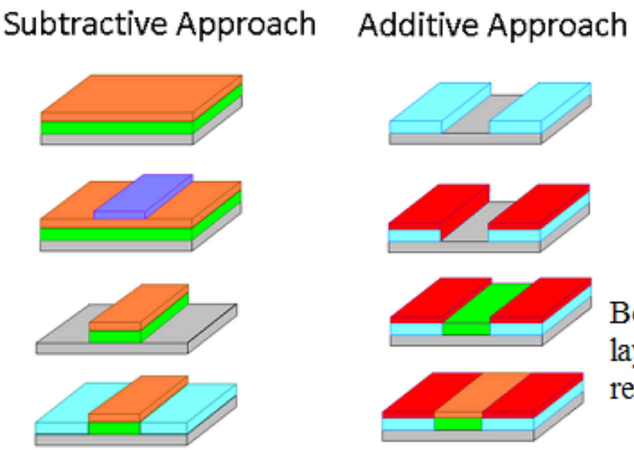
ESH Metrics and Impact: Cost Reduction

- 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





ESH Metrics and Impact: Cost Reduction



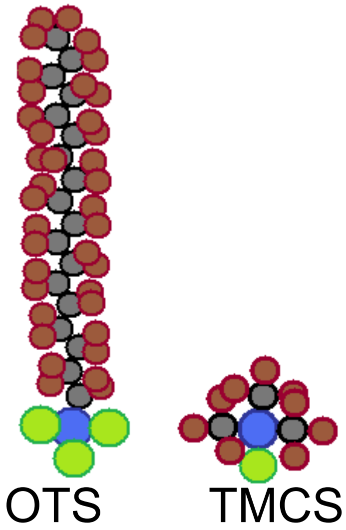
Eliminates high-K and metal etching step

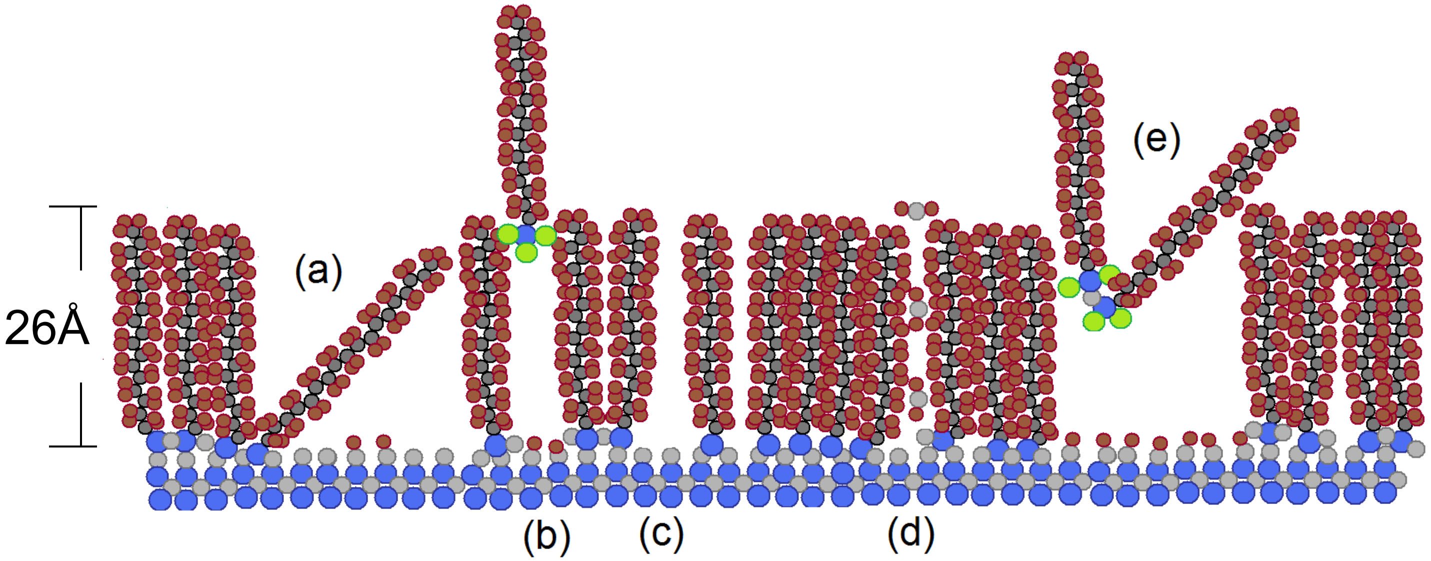
Both high-K and metal layers deposited in same reactor

Reduced material use and waste with selective ALD growth

- Additional benefits of hydrophobic surface
  - SAM coating prevents aqueous solutions from interacting with surfaces
    - Coating metal parts or work surfaces which are exposed to water-based solution reduces the need for cleaning such tools/equipment
    - Coat ALD reactor walls with SAM to extend up-time, reduce cleaning, and improve throughput

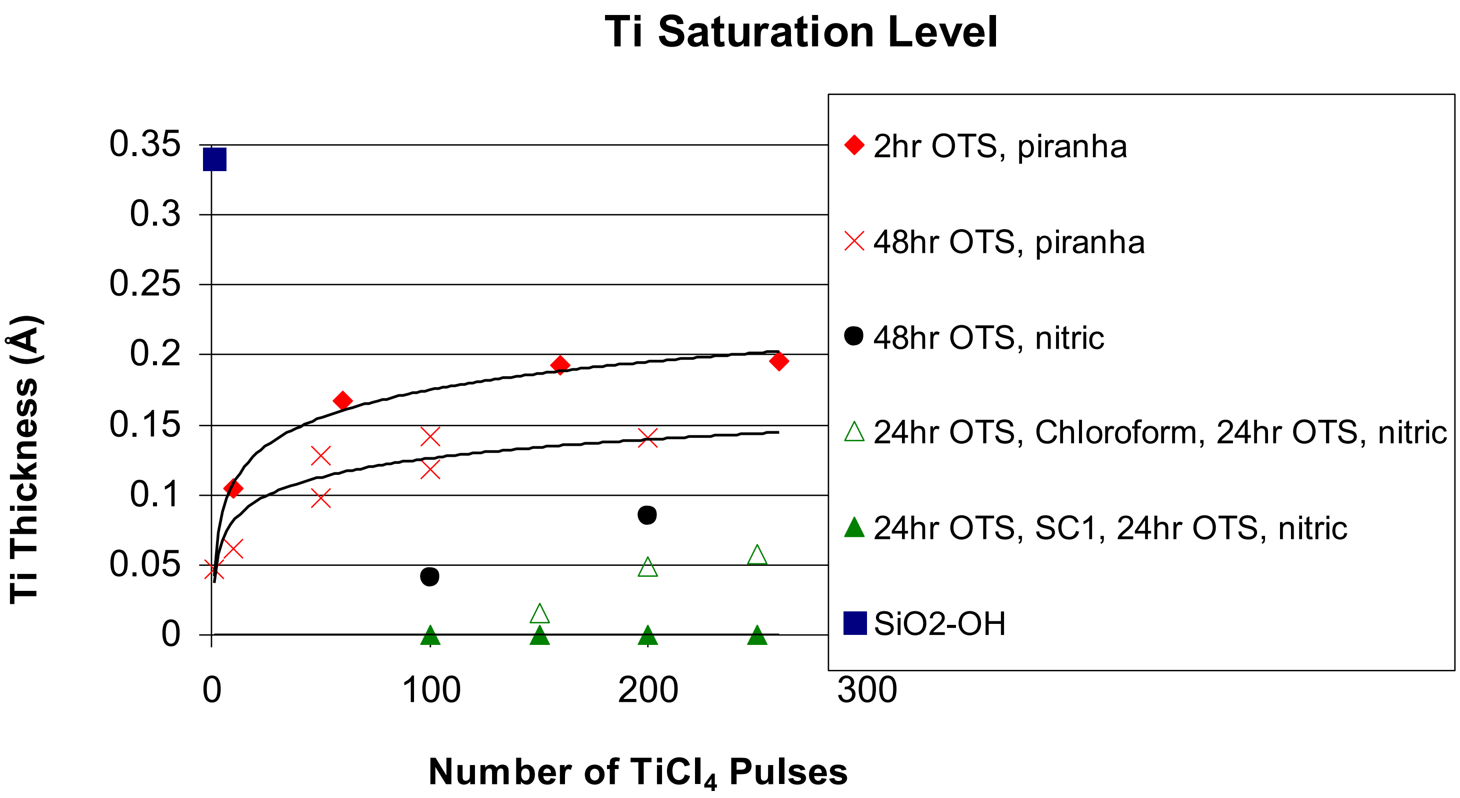
SAM Defects

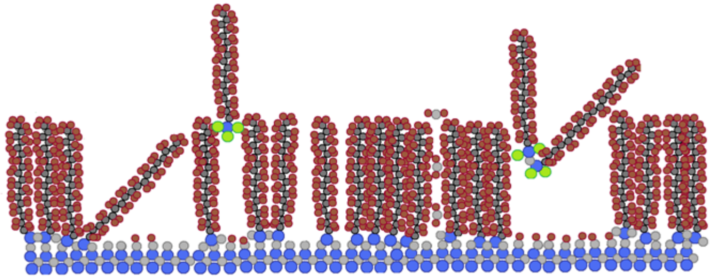




- (A) Poor alignment at island boundaries block surface sites (poor uniformity)
- (B,C) Gaps in SAM too small for primary SAM molecule
- (D) Water absorbed/adsorbed in SAM layer
  - Either during SAM formation or during ALD process
- (E) Polymerized SAM molecules on surface
  - Block surface sites
 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

Defect monitoring using $TiCl_4$ pulses



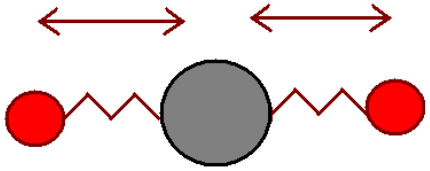


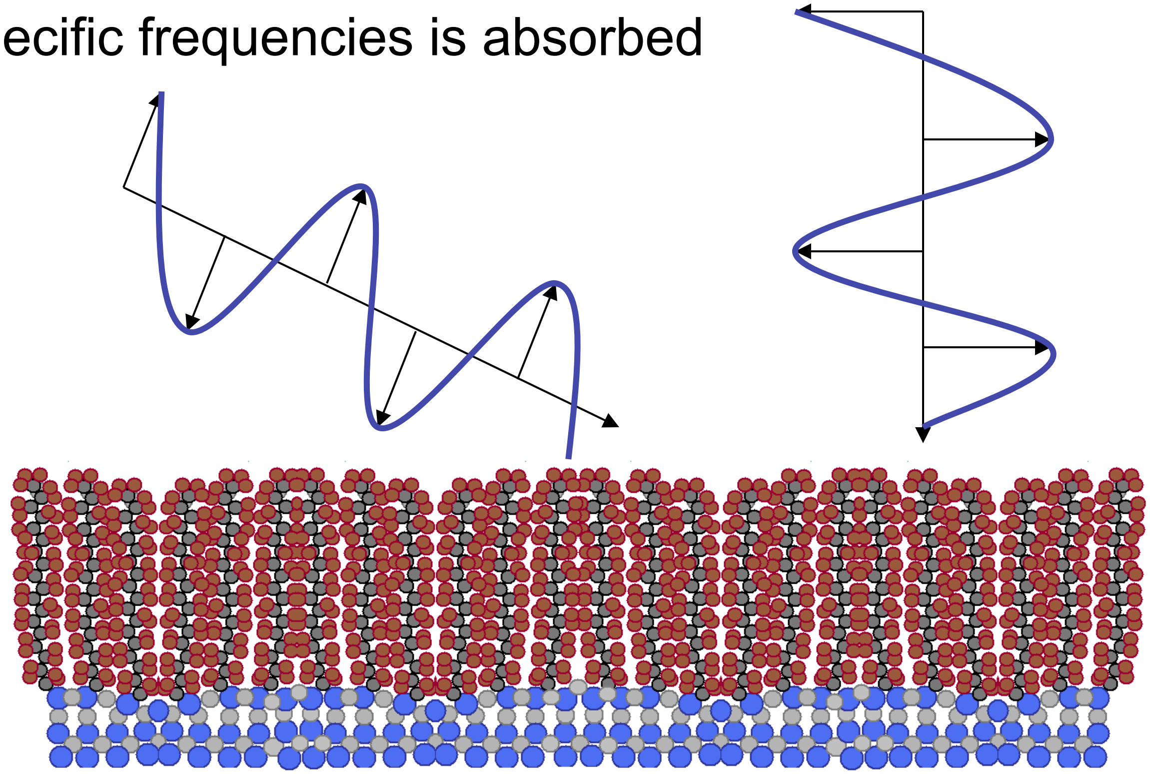
- Defect level in SC1 re-hydroxylated samples was below XPS limit for up to 250 seconds of $TiCl_4$ exposure

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}

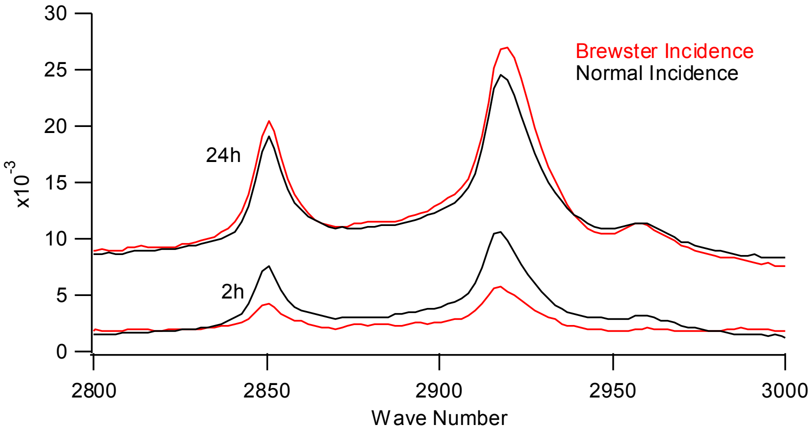




Analysis of CH_2 peaks Nitric acid/piranha

- At 2h the OTS layer formed on piranha and nitric are similar for both normal and Brewster incidence
- At 24h the CH_2 peak areas from the piranha prepared sample were double the peak area of nitric etched samples for normal incidence and nearly five times the area for the Brewster angle
  - This suggests that after 24h the piranha prepped sample has far more polymerization and misaligned molecules
- After extraction or SC1 re-hydroxylation the samples are similar again

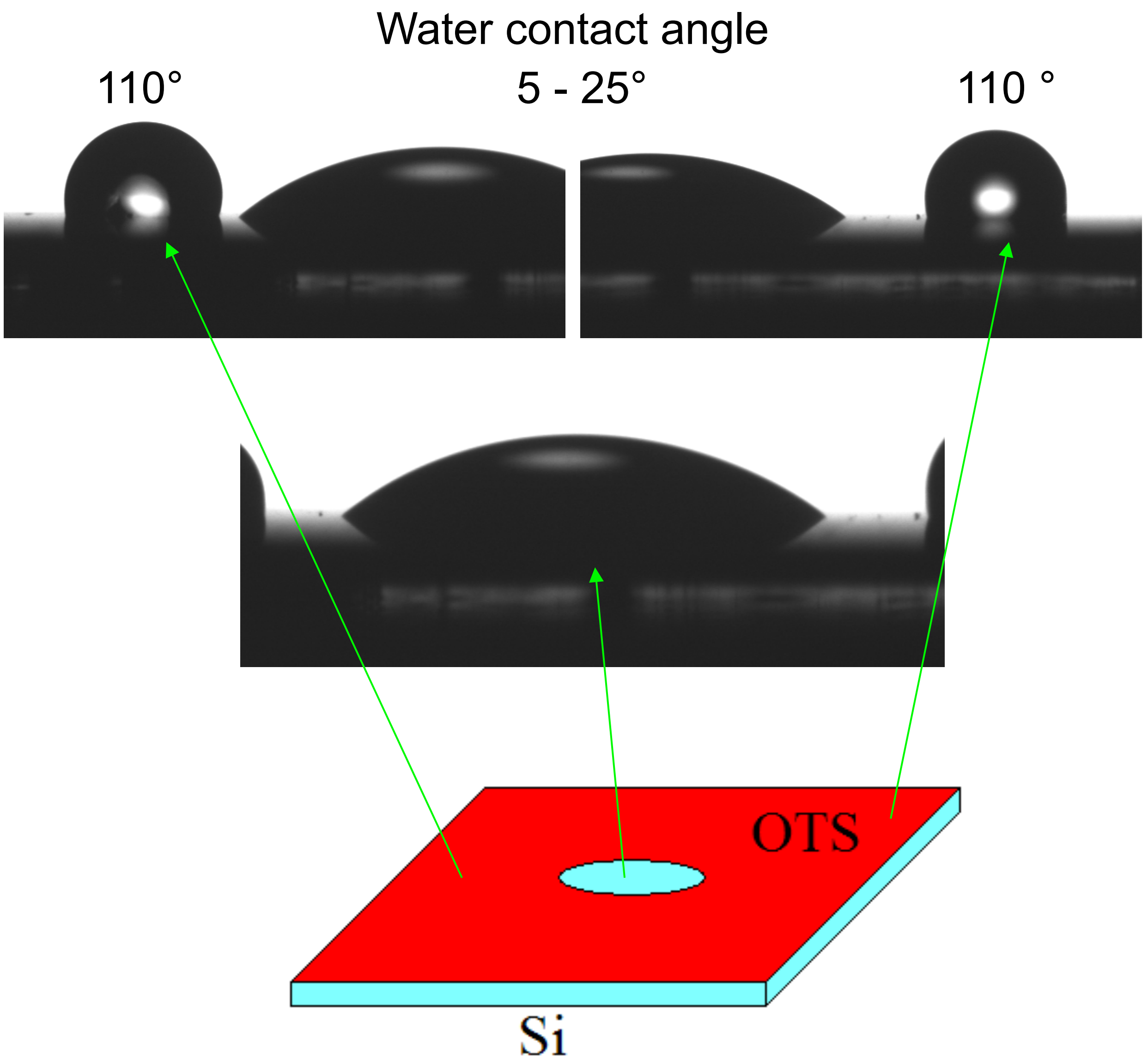
	2h	24h	24h ext	24h sc1	24h ext 24h	24h sc1 24h
NORMAL incidence						
Symmetric 2850cm^{-1}	0.8453	**0.5169**	0.7403	0.6584	0.7953	0.8700
Antisymmetric 2919cm^{-1}	0.9553	**0.5501**	0.8403	0.7036	0.8836	1.0046
BREWSTER incidence						
Symmetric 2850cm^{-1}	0.6389	**0.2193**	0.9715	0.8973	1.1104	1.0415
Antisymmetric 2919cm^{-1}	0.8632	**0.2819**	1.0876	0.9818	0.9906	1.1663



Analysis of CH_2 peaks Brewster angle/Normal Incidence

2850cm^{-1}	10min	2h	**24h**	24h ext	24h sc1	24h ext 24h	24h sc1 24h
nitric	1.1662	0.2919	**0.5202**	3.4516	3.1325	4.3249	3.2451
piranha	1.4577	0.3555	**1.2263**	2.6300	2.2984	2.6947	2.7108
2919cm^{-1}							
nitric	1.5863	0.3555	**0.6270**	3.3091	3.1431	3.8493	3.3328
piranha	1.7846	0.3934	**1.2236**	2.5567	2.2524	2.6113	2.8707

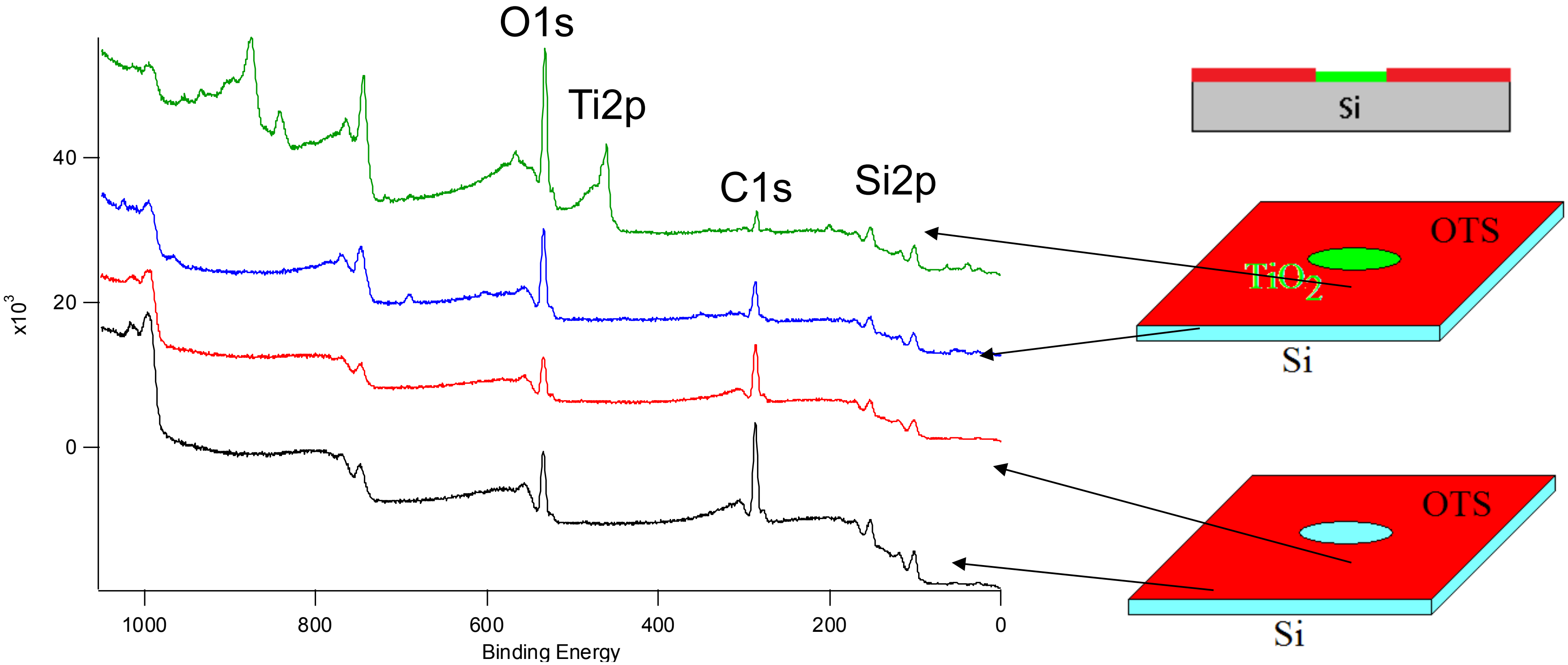
Selective high-k deposition



- 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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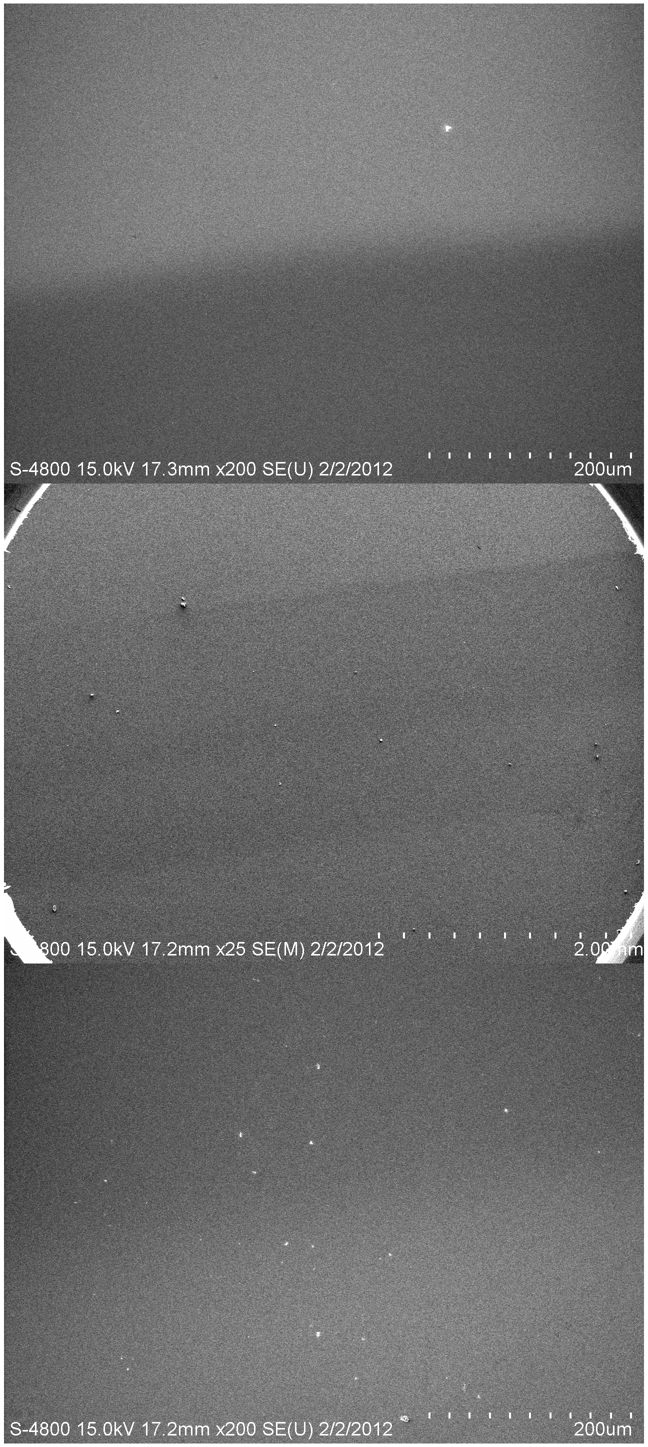
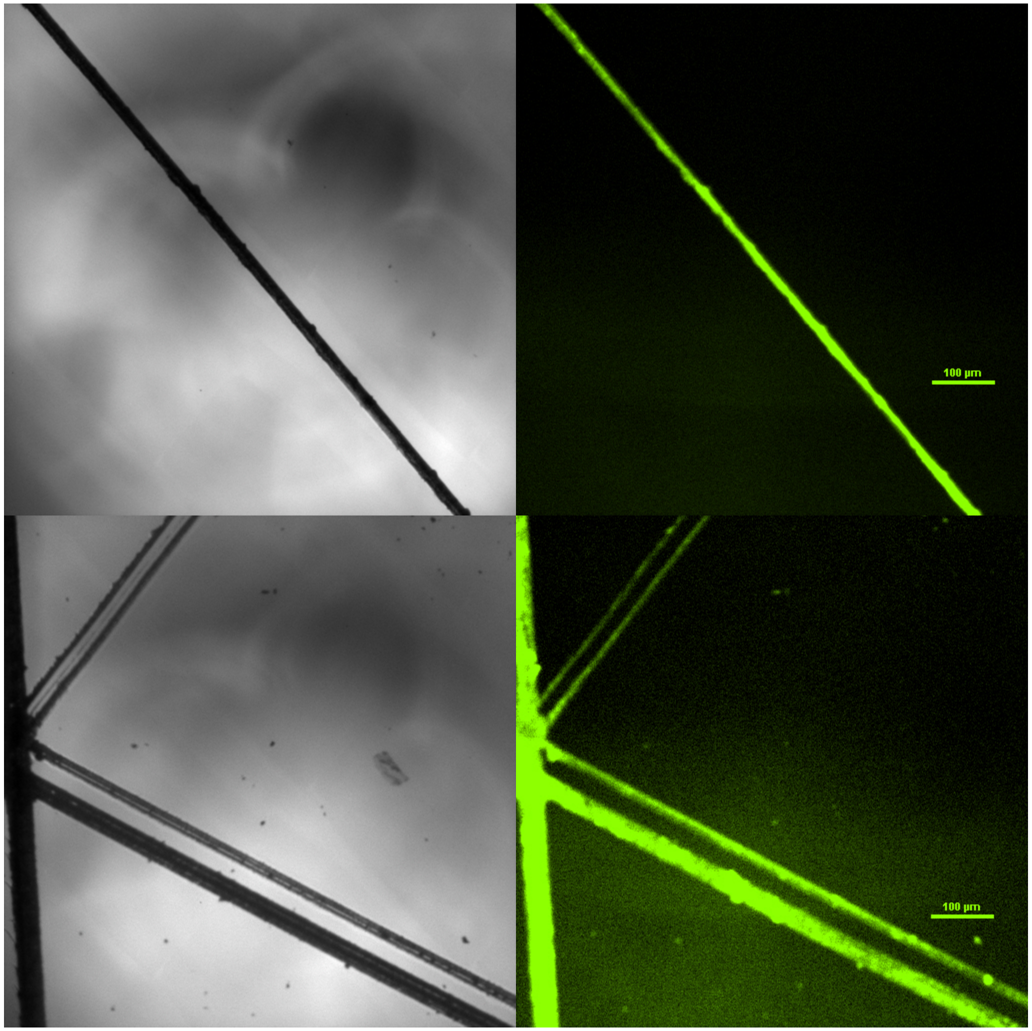
SEM images



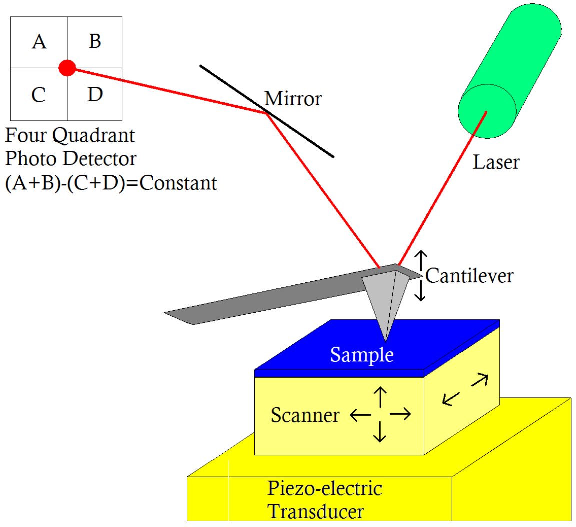
- UV light shown through an electro polished stainless steel mask
- Ozone generated at surface etches the OTS layer
  - One edge of the mask was lifted 200 µm off the surface
  - Effect of mask undercutting is visible in SEM

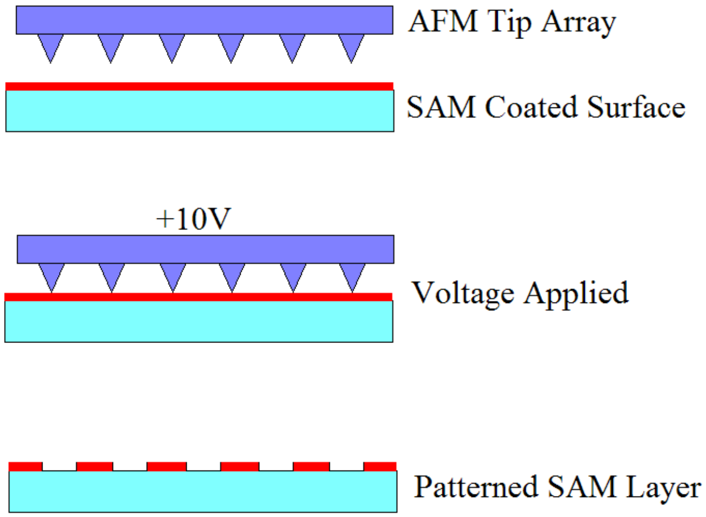
QD selective deposition



- 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

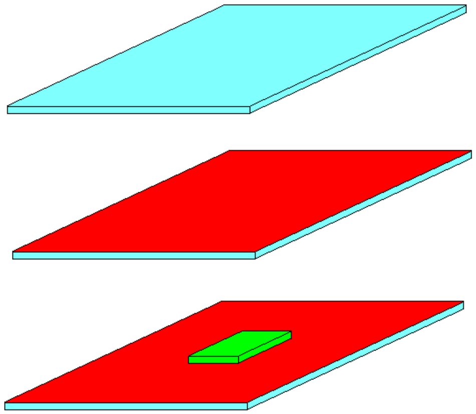
Alternate patterning approaches



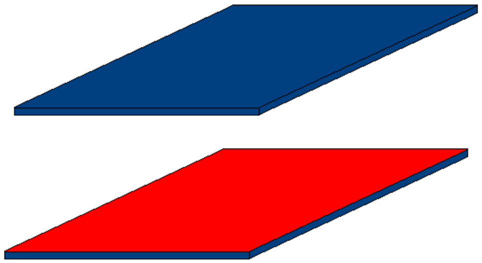


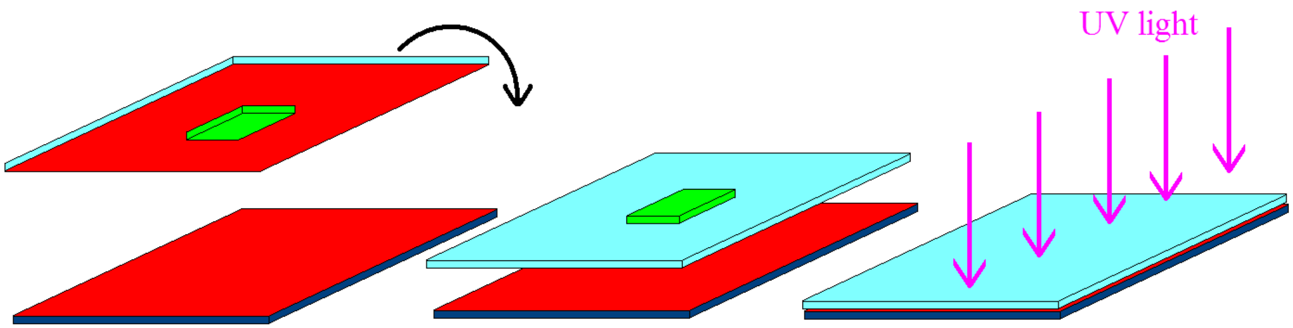
- Conductive atomic force microscopy (AFM) removes SAM
  - Multiple tip arrays can be used to make detailed nm scale pattern
- Electron beam patterning has also demonstrated nm scale patterning ability
- No need for photoresist

Repeat patterning approach

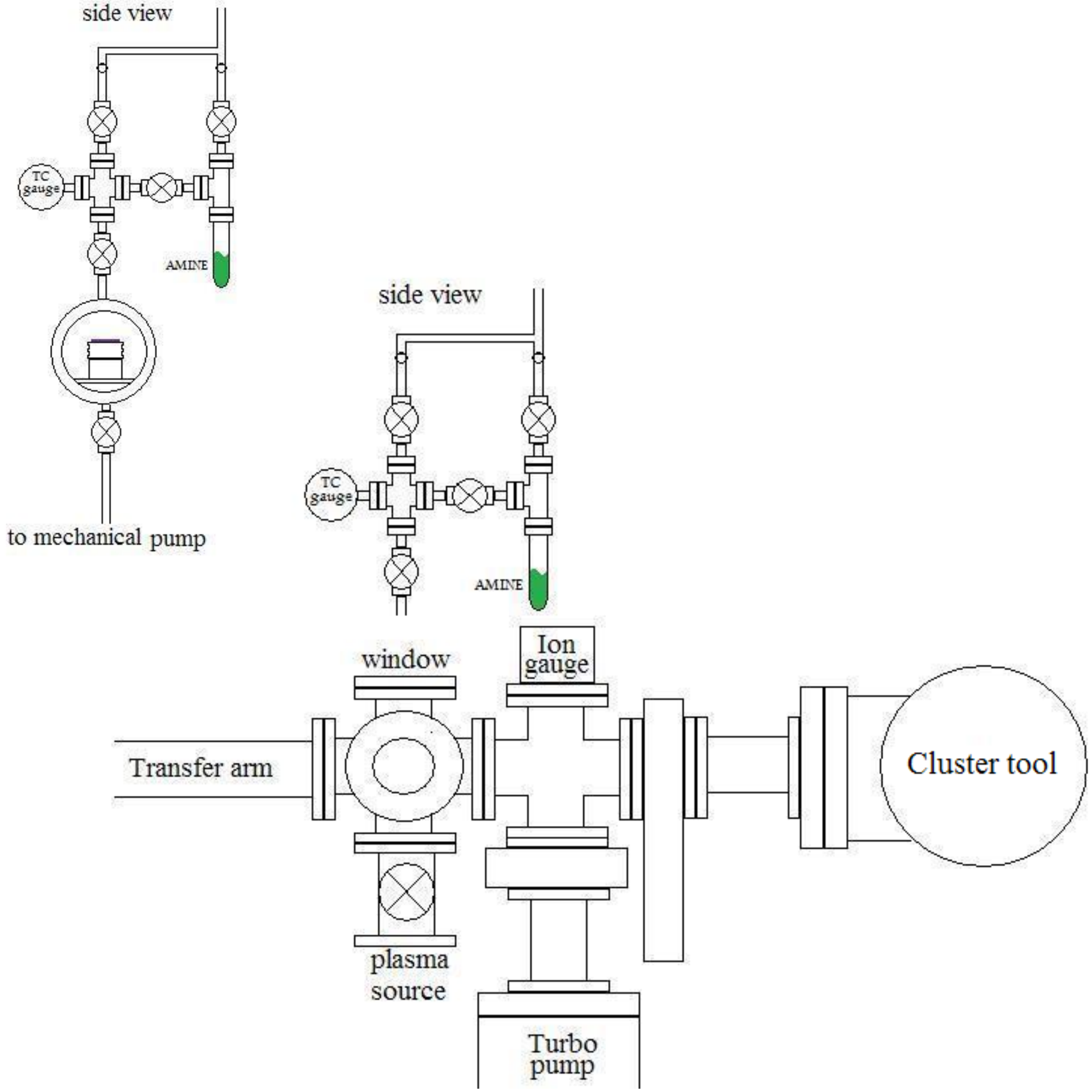


- Form high resolution master OTS pattern on glass and deposit TiO_2 selectively
  - Form OTS on Si surface
  - Copy TiO_2 master pattern to the OTS/Si wafer using UV/TiO_2 catalytic effect





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
  - Reduced SAM defects (200+ ALD 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
  - Improve 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