Surface Activation and Deactivation for ALD

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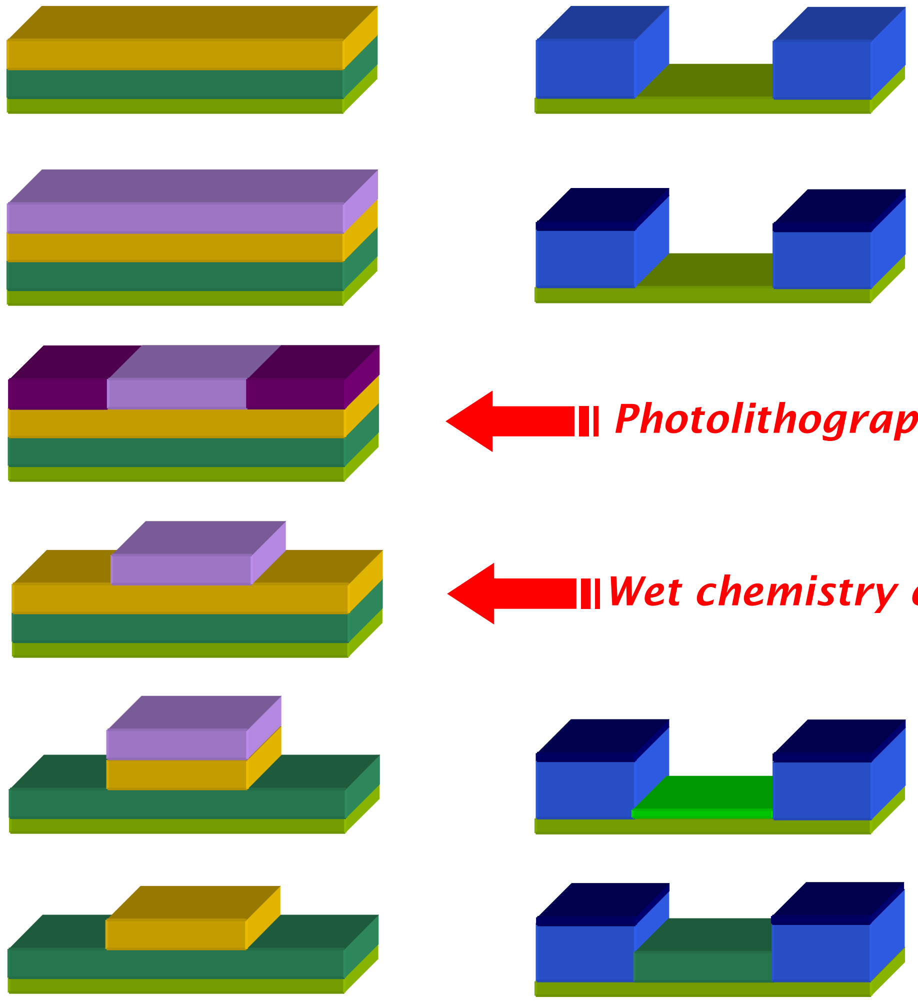
SRC/Sematech, ERC Task ID 425.026
Project Update / Teleseminar
June 25, 2009

Overall goals

- **Simplify the multistep subtractive processing used in microelectronic device manufacturing**
  - Develop an additive processing approach
  - Minimize water, energy, chemical and materials consumption
  - Reduce processing cost
    - Sematech process model

- **Focus on high-k gate stack**
  - Fabricate low defect high-k/substrate

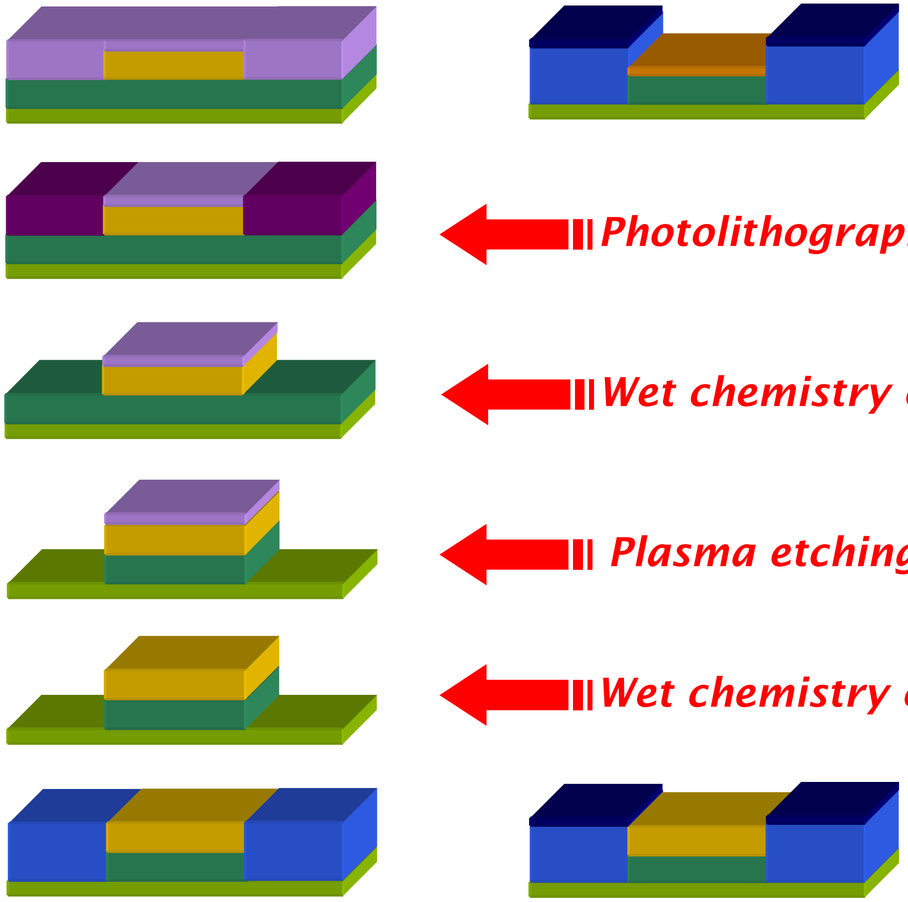
Self-aligned Gate Stack



Subtractive Processing	vs.	Additive Processing
Deposit high k dielectric and metal gate		Deposit and pattern field oxide
Spin-on imaging layer		Deactivate field oxide surface
Photolithography		*Photolithography eliminated*
Develop in aqueous base		*Wet chemistry eliminated*
Etch metal		Activate Si surface
Strip Imaging layer		Selectively deposit high k dielectric

Self-aligned Gate Stack

Subtractive Processing *vs.* **Additive Processing**



Spin–on imaging layer

Activate high k surface

Photolithography

Photolithography eliminated

Develop in aqueous base

Wet chemistry eliminated

Etch dielectric

Plasma etching eliminated

Strip Imaging layer

Wet chemistry eliminated

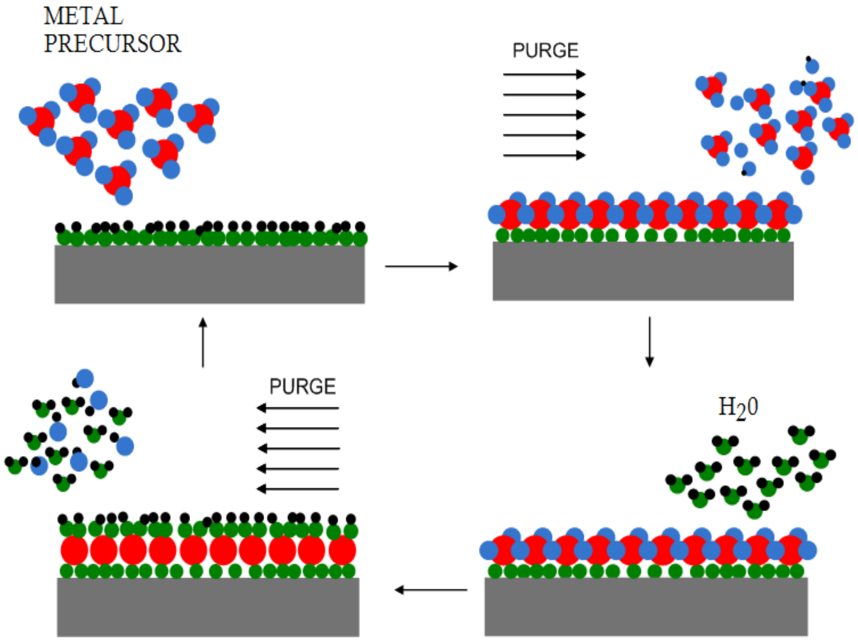
Deposit and pattern field oxide

Selectively deposit metal gate

Reduce processing steps & Minimize ESH impact

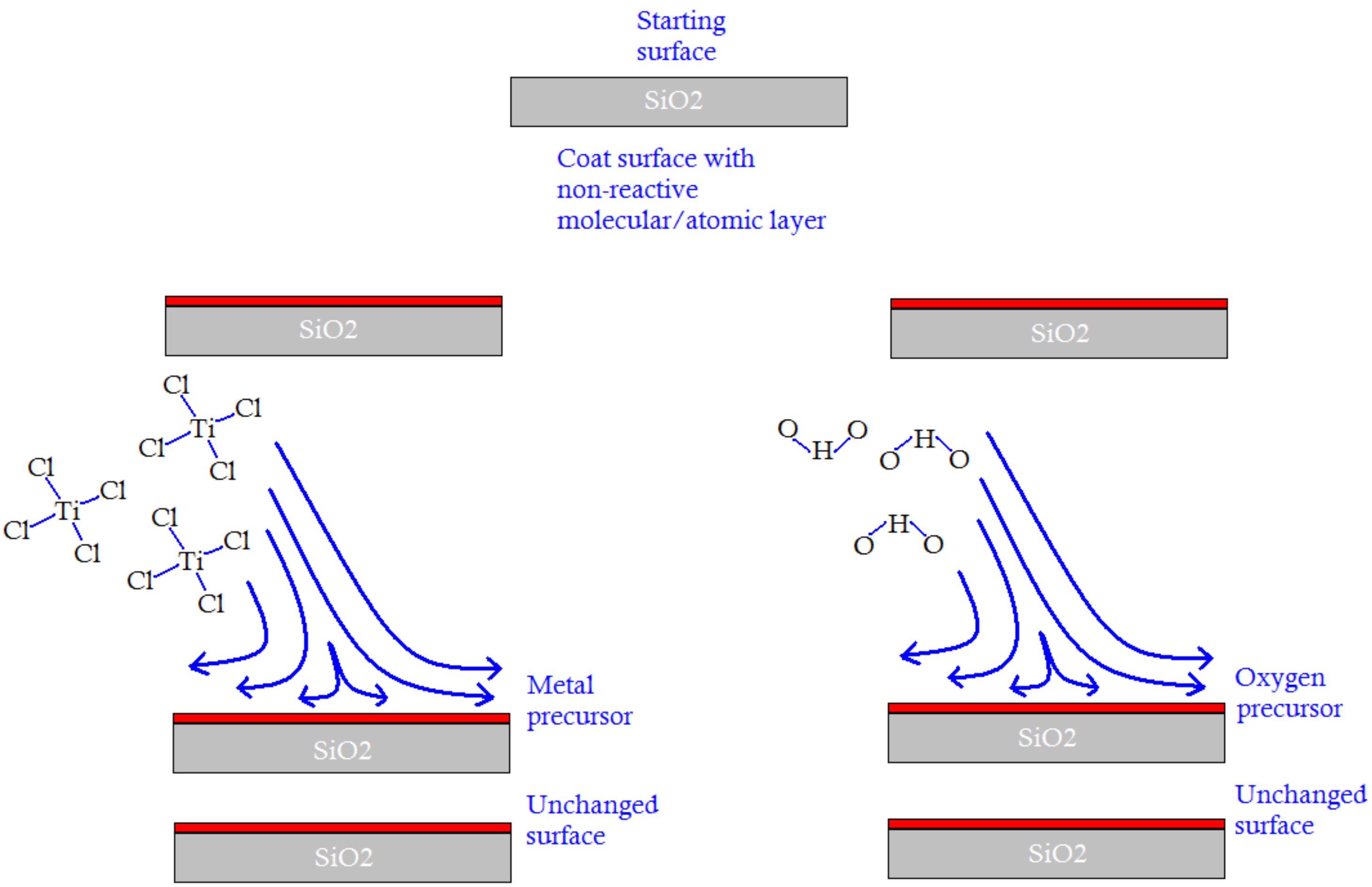
Atomic layer deposition of high-k films

- Break overall reaction into two half reactions and run one at a time to achieve self-limiting growth
  - Surface exposed to sequential pulses of metal and oxygen precursors to deposit oxide



- Two step chemical reaction
  - $TiCl_4$ + **OH** = **$TiCl_3$-O** + HCl
  - $2(H_2O)$ + **$TiCl_3$-O** = **OH-Ti-O** + $3(HCl)$

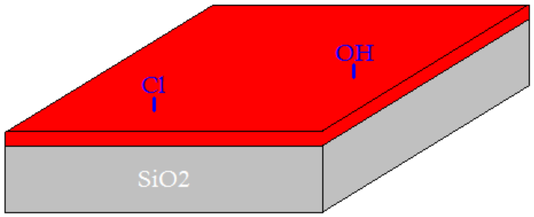
Deactivating ALD



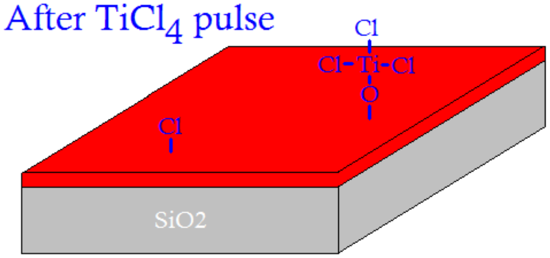
- Coat surfaces with molecules/atoms which do not react with precursors
  - Stable surface is required; no change in surface chemistry after precursor exposure, no adsorbed water, and no thermal breakdown

Deactivating ALD

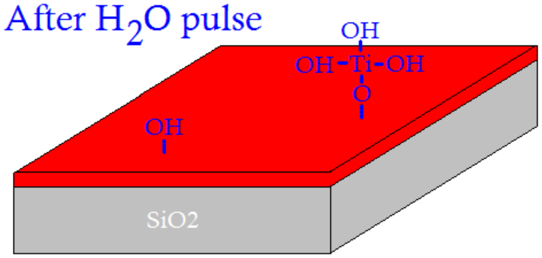
Defects in non-reactive layer



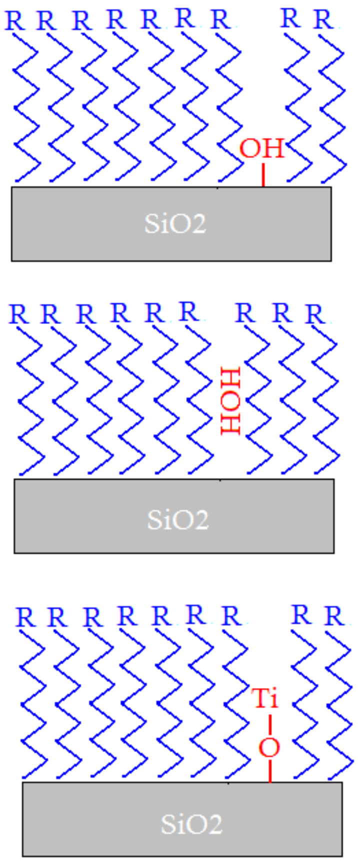
After $TiCl_4$ pulse



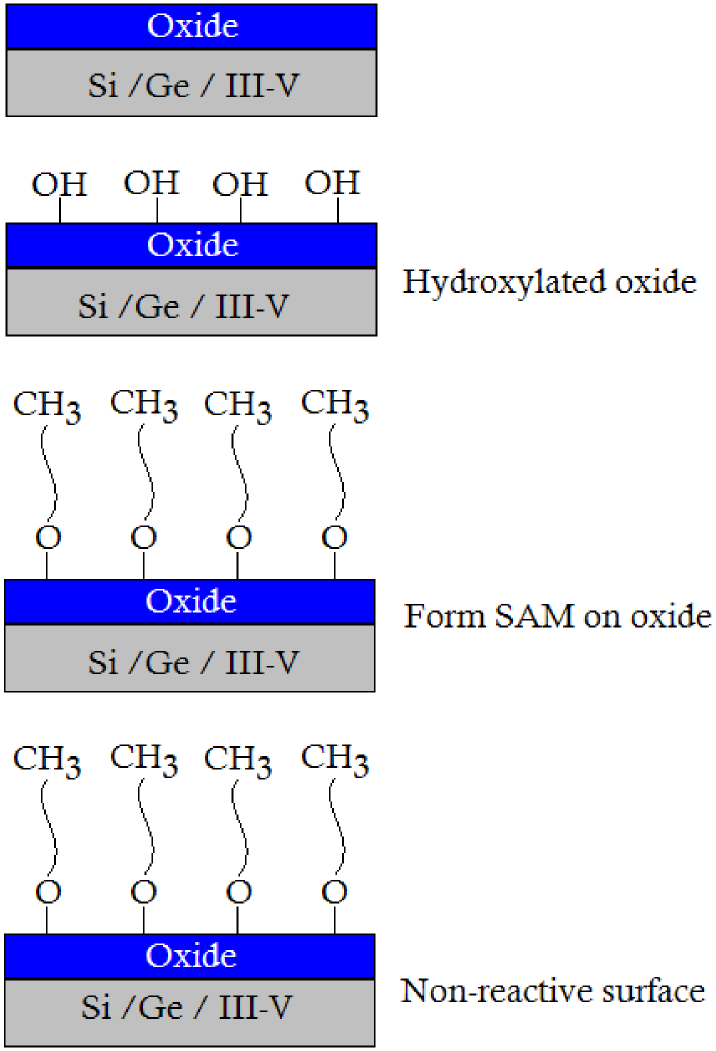
After H_2O pulse



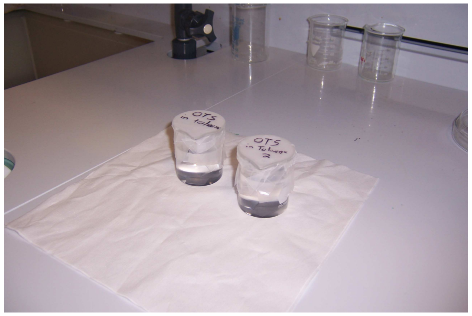
- Stopping ALD requires complete surface coverage
  - – Defects will start ALD deposition
    - Unblocked hydroxyl groups
    - Adsorbed water
    - Other chemical defects or binding sites on surface



Deactivating with SAMs



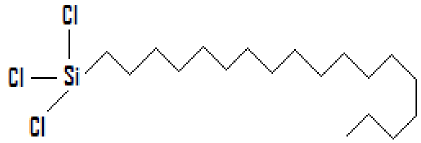
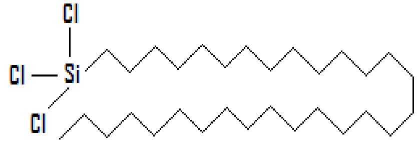
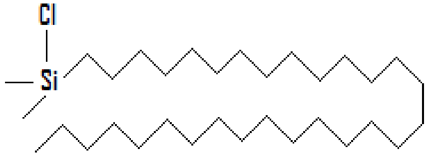
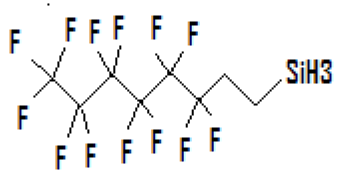
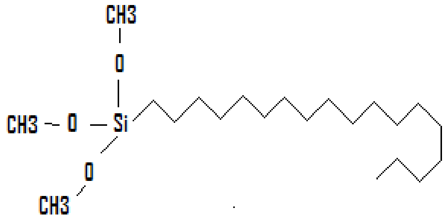
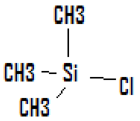
- Self assembled monolayer
  - Reacts with the surface to form a single layer
    - Unreacted SAM molecules can act as defect sites
  - Binds to all potential ALD nucleation sites
  - Prevents H_2O from absorbing during ALD
    - Water in SAM can act as a defect site
- Deposited with either liquid or vapor phase methods



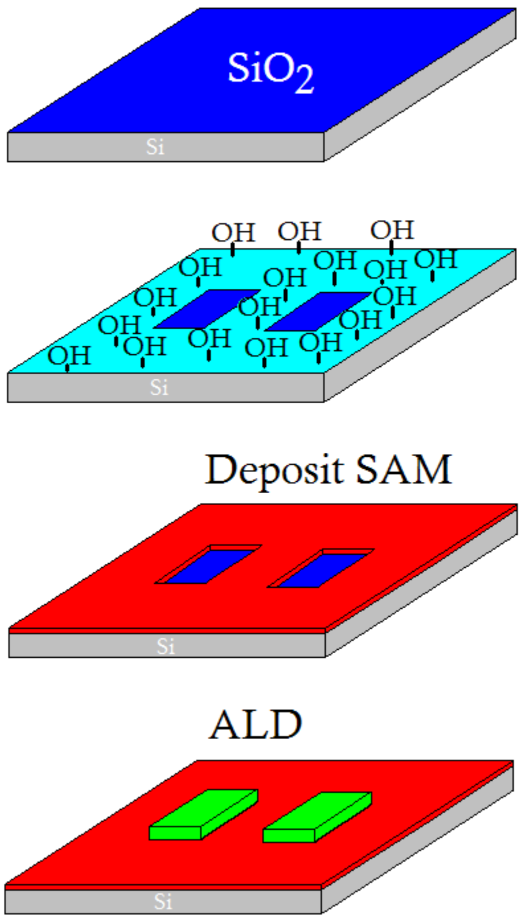
Liquid Phase

Vapor phase

SAM Molecules

SAM molecules	Formula	Structure
Octadecyltrichlorosilane OTS	$C_{18}H_{37}Cl_3Si$	 26Å
Triacontyltrichlorosilane TTS	$C_{30}H_{61}Cl_3Si$	 33Å
Triacontyldimethylchlorosilane TDCS	$C_{32}H_{67}ClSi$	 33Å
Tridecafluoro-1,1,2,2-tetrahydrooctylsilane FOTS	$C_8H_7F_{13}Si$	 12Å
Octadecyldimethoxysilane ODS	$C_{21}H_{43}O_3Si$	 26Å
Trimethylchlorosilane TMCS	C_3H_9ClSi	 4Å

Selective Area ALD



- Many ways to pattern surface
  - – Photolithography of oxide, followed by piranha etch and HF etch
    - Shown in schematic
  - – Contact / liftoff printing of SAM using pre-formed stamp
  - – Hard mask of pattern used to expose desired areas to chemical treatment
- Cover surface with selectively reactive molecules
  - – Bind SAM molecules only where deactivation is desired
- Deposit high-K layer via ALD only where desired

Literature review

- SAM density, thickness, and water contact angle determine the quality and effectiveness of the SAM [1]
- Required 2hrs for the water contact angle to plateau at 110° for an octadecytrichlorosilane (OTS) SAM [4]
  - Commonly used SAM molecule, high water contact angle
- Larger precursors are easier to deactivate than smaller or more volatile precursors [2,3,4,6]
  - Lower probability that the precursor will find a binding site
  - "Ru nucleation is not as sensitive to quality of the monolayer surface as observed for Hf or Zr oxide and Ti based film deposition" [4]

1) J. Hong, D. Porter, R Sreenivasan, P. McIntyre, S. Bent. *Langmuir*, 23, 1160-1165, (2007)
2) X. Jiang, S. Bent. *Journal of the Electrochemical Society*, 154 (12), D648-D656, (2007)
3) X. Jiang, R. Chen, S. Bent. *Surface & Coatings Technology,* 201, 799-8807, (2007)
4) R. Chen, H. Kim, P. McIntyre, D. Porter, S. Bent. *Applied Physics Letters,* 86, 191910, (2005)
5) R. Chen, H. Kim, P. McIntyre, S. Bent. *Chem. Mater.*, 17, 536-544, (2005)
6) K. Park, J. Doub, T.Gougousi, G. Parsons. *Applied Physics Letters,* 86, 051903, (2005)
7) E. Färm, M. Kemell, M. Ritala, M. Leskelä. Chem. Vap. Deposition, 12, 415-417, (2006)

Literature review

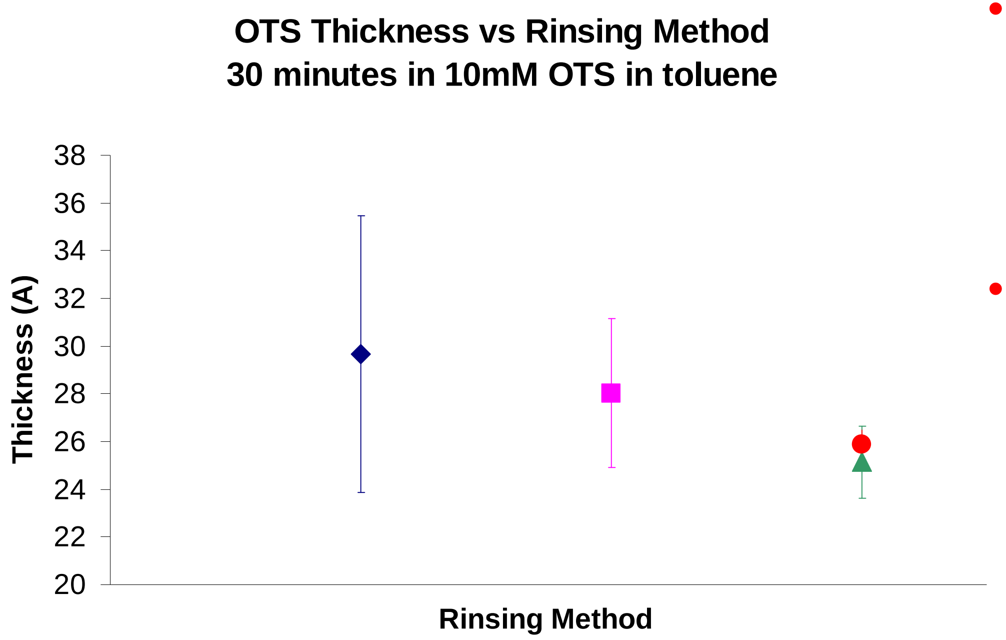
	Material deposited	Precursors	SAM	SAM formation	Time scale	Cycles of complete deactivated
1	Pt	$CH_3C_5H_4Pt(CH_3)_3$ Air	OTS	Liquid phase 10mM in toluene	48 hours	400 [2]
2	HfO2	$Hf[N(CH_3)_2]_4$ H_2O	OTS	Liquid phase 10mM in toluene	48 hours	50 [2,3,4]
3	HfO2	$HfCl_4$ H_2O	Several	Liquid phase 10mM in toluene	48 hours	50 [5]
4	RuO2	$RuCp_2$ Dry Oxygen	OTS	Liquid phase 10mM in toluene	48 hours	300 [6]
5	Pt HfO2	$CH_3C_5H_4Pt(CH_3)_3$, Air $Hf[N(CH_3)_2]_4$, H_2O	OTS FOTS	Stamp contact printing	5 minutes	Pt-OTS-100 [2,3] Pt-FOTS-0 [2] HfO2-OTS-0 [3]
6	HfO2	$Hf[N(CH_3)_2]_4$ H_2O	OTS FOTS	Vapor phase SAM and H2O sealed in reactor	48 hours	OTS-50 [1] FOTS-50 [1]
7	Ir	$Ir(acac)_3$ O_2	ODS	Vapor phase Alternating SAM and H2O pulses	1 hour	1000 [7]

Objectives

- Develop processes that are feasible for industrial applications
  - Deactivate surfaces for longer
  - Form SAM faster
    - Vapor phase delivery
    - Investigate role of water
  - Extend to other surfaces
    - SiO_2, HfO_2, TiO_2, III-V’s
  - Explore untested SAM molecules

Liquid phase sample prep and rinse

- Quality OTS layer after only 30 minutes (not 2hrs)
  - 26Å
  - 110° water contact angle
  - Smaller standard deviation after 48hrs in OTS than 30min in OTS
- Chloroform rinse was more effective than IPA and Methanol for OTS and TTS

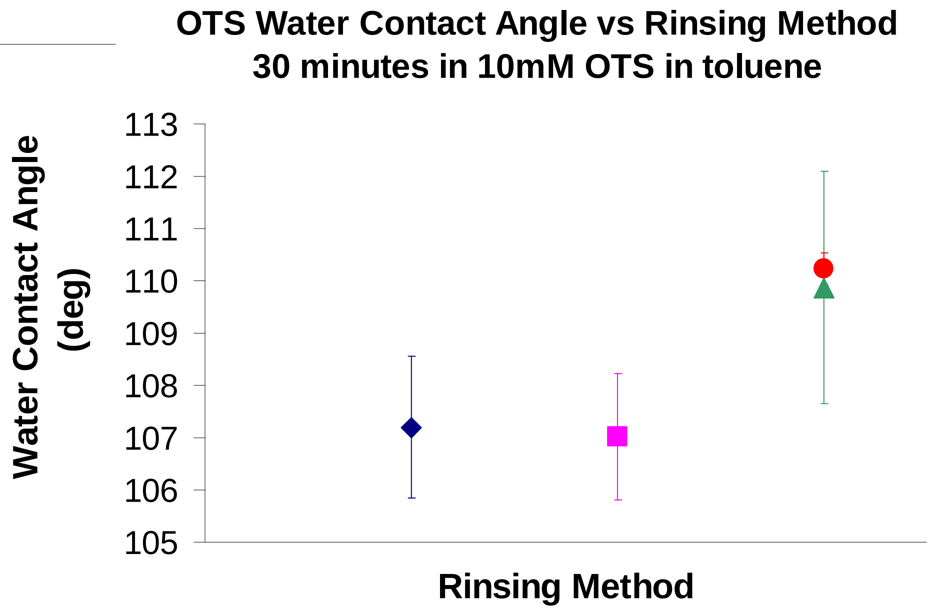


◆ IPA rinsed

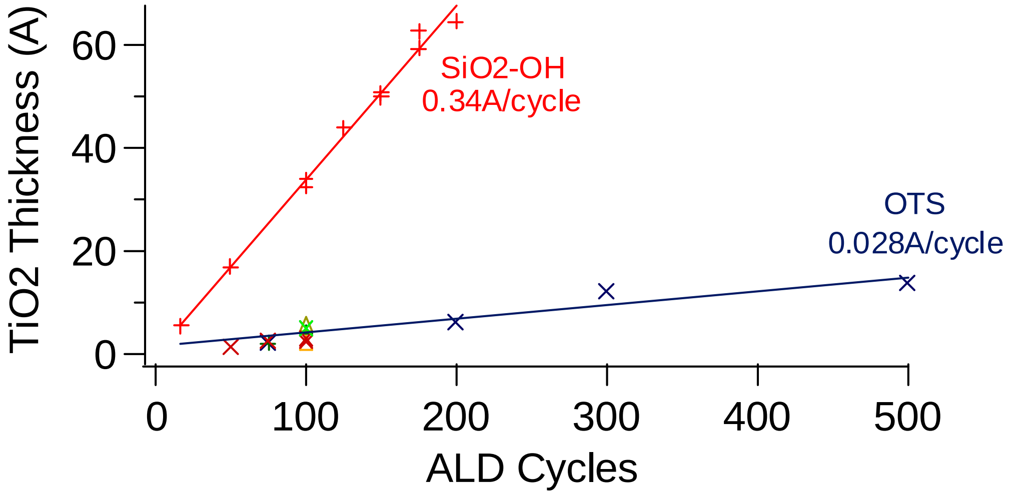
■ Methanol rinsed

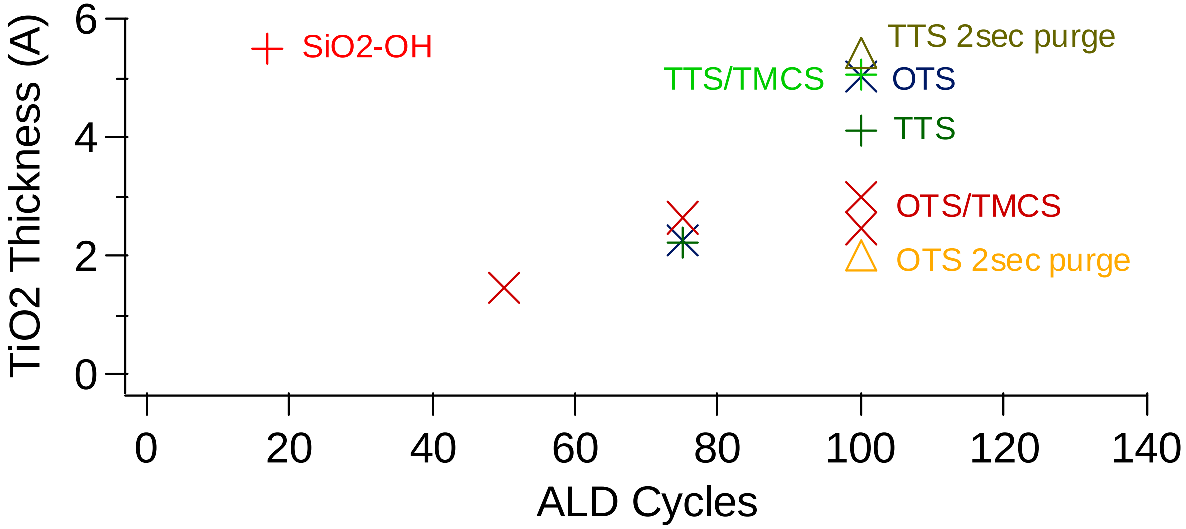
▲ Chloroform rinsed

● 48hrs OTS sample, chloroform rinsed



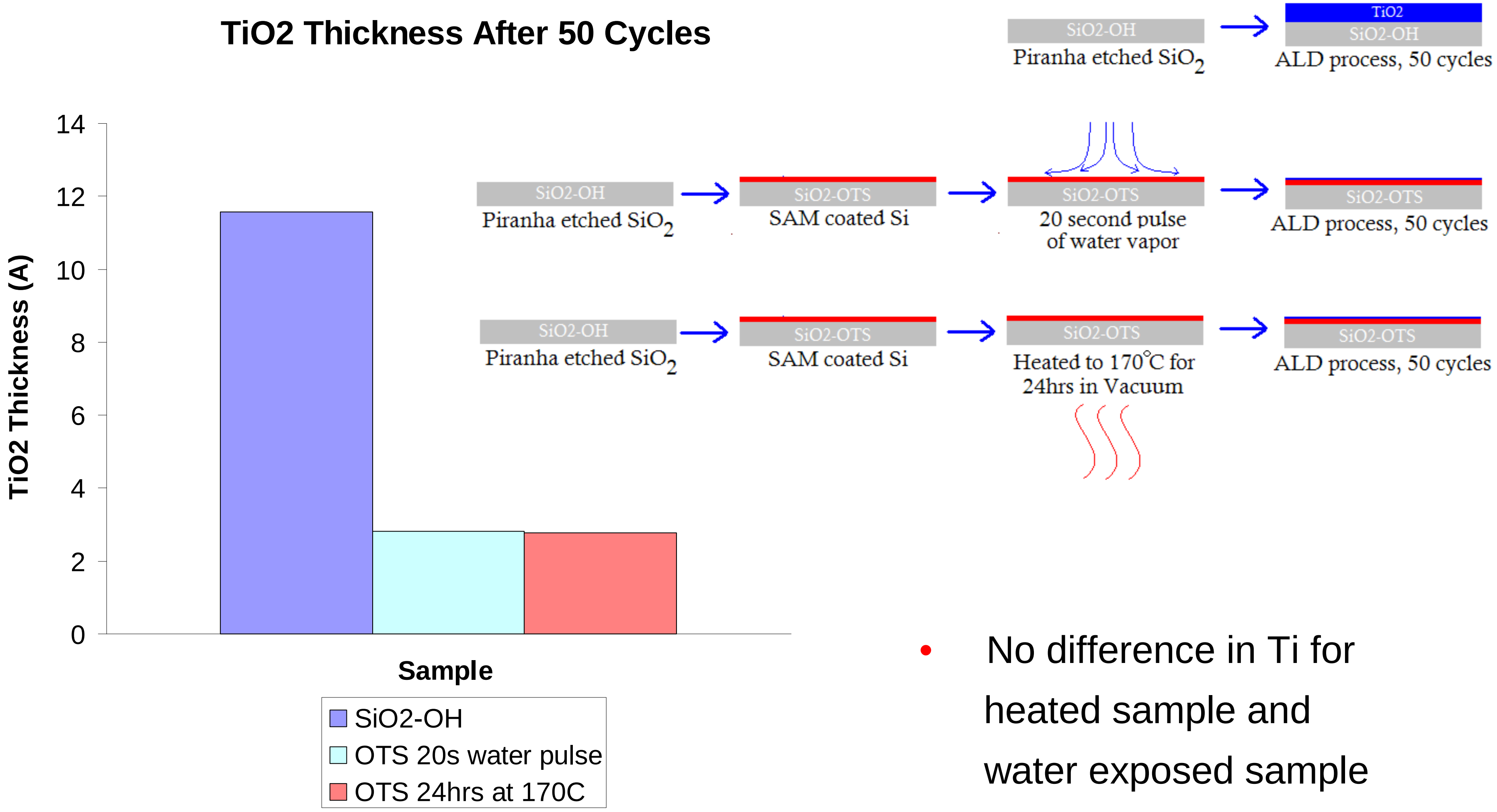
Deactivation results





- Reduced growth rate by factor of 12 for up to 500 cycles
- Potential SAM defects
  - Water in/on SAM
  - Unblocked hydroxyl groups
  - Instability to $TiCl_4$ precursor
- Data spread is primarily due to sample variation
  - OTS, OTS/TMCS, OTS w/ long purges
  - TTS, TTS/TMCS, TTS w/ long purges

Effect of water on deactivation



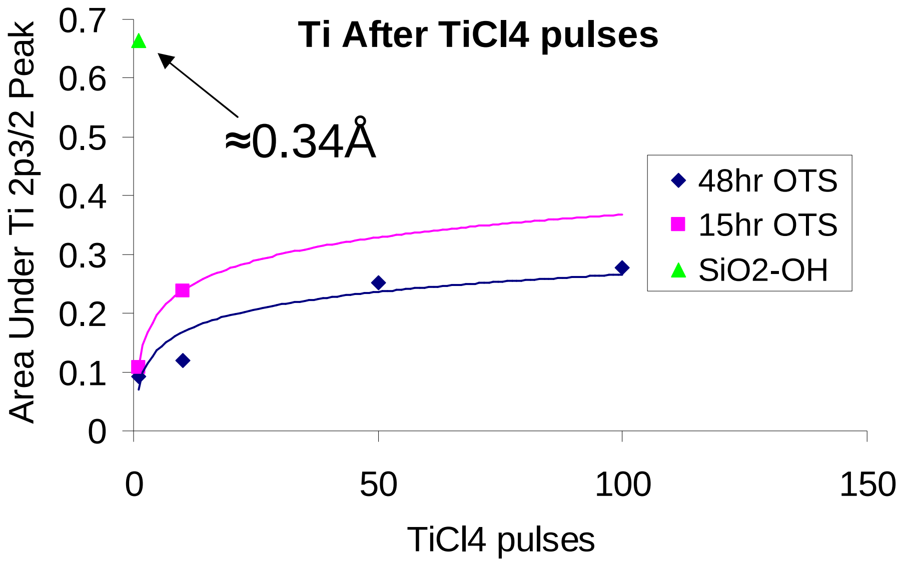
Piranha etched SiO_2 → ALD process, 50 cycles

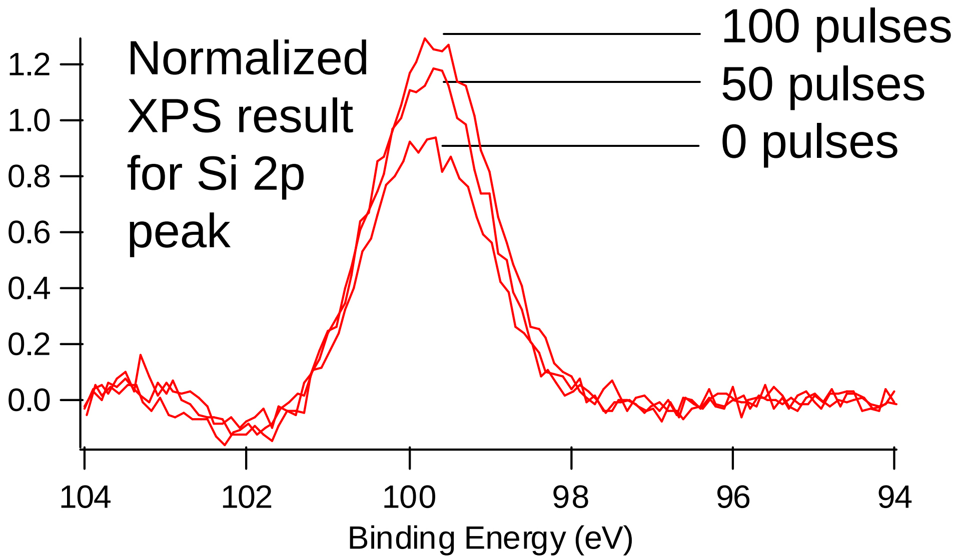
Piranha etched SiO_2 → SAM coated Si → 20 second pulse of water vapor → ALD process, 50 cycles

Piranha etched SiO_2 → SAM coated Si → Heated to 170°C for 24hrs in Vacuum → ALD process, 50 cycles

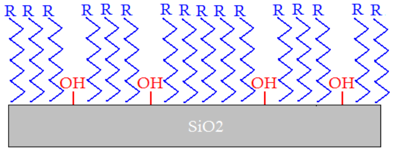
- No difference in Ti for heated sample and water exposed sample

OTS stability when exposed to $TiCl_4$

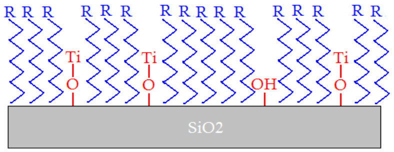




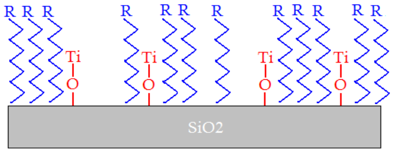
- Samples exposed to $TiCl_4$ pulses only (no H_2O)
- Si peak goes up after $TiCl_4$ pulses
  - Possible SAM degradation



- Starting SAM



- After 10 $TiCl_4$ pulses



- After 100 $TiCl_4$ pulses

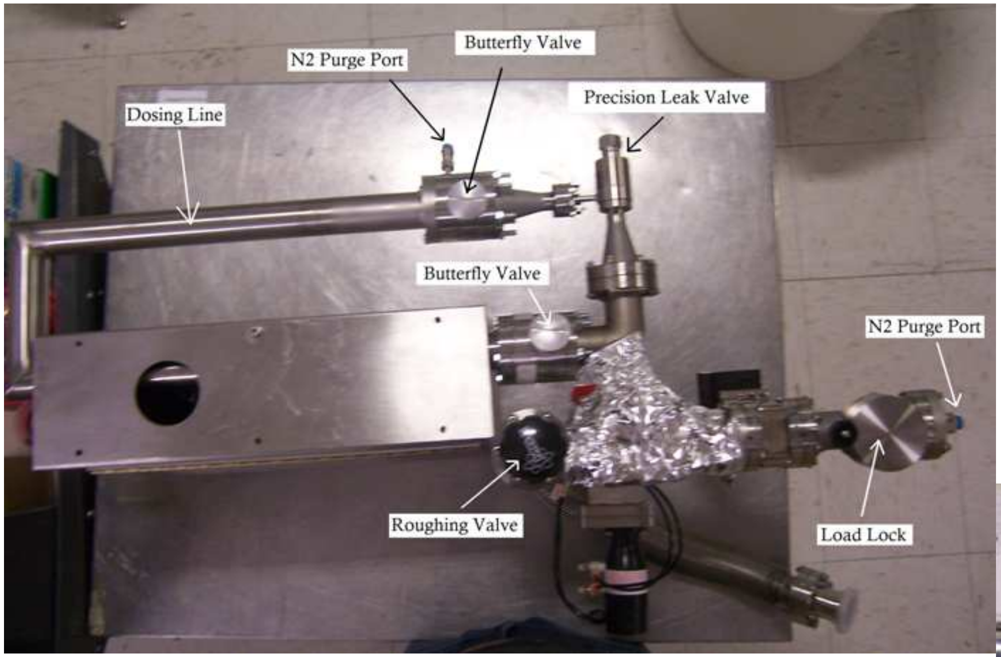
Conclusion

- Rinsing the SAMs in chloroform gave the highest water contact angle, and one monolayer thickness
- Reduced TiO_2 growth rate by a factor of 12 for up to 500 cycles
- Exposing the SAM to water before ALD and baking the SAM at 170℃ for 24hrs before ALD gave the same amount of titanium deposition after 50 cycles
- Small amount of titanium is present on SAM surfaces after a single $TiCl_4$ pulse
  - Defects in liquid formed SAMs
  - Degradation of SAM due to $TiCl_4$ is a possible problem

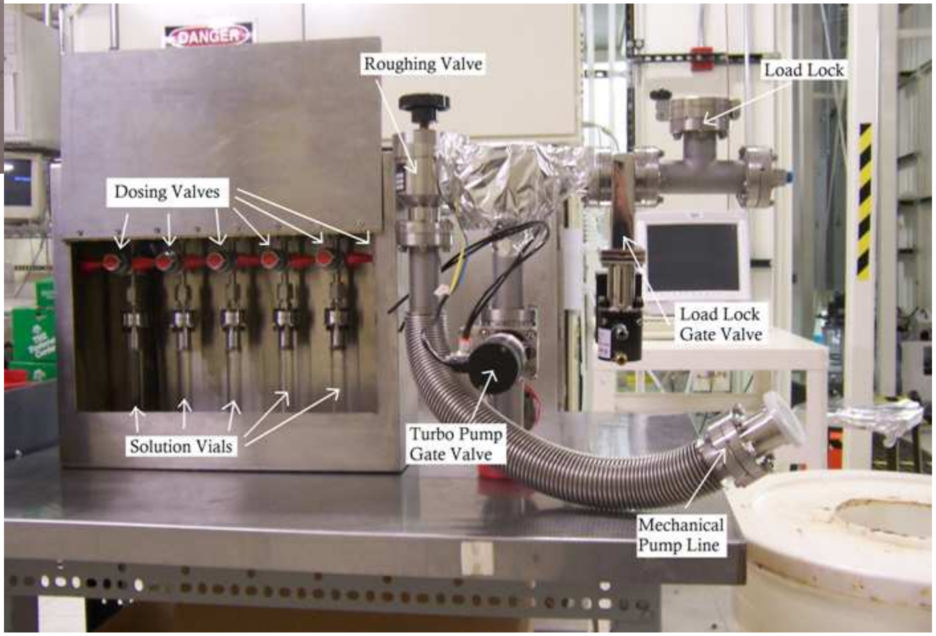
Future work

- Develop high quality SAMs using vapor deposition
  - Investigate the role of water in SAM formation
- Continue the study of SAM degradation due to $TiCl_4$ exposure during ALD
- Continue the study of water in/on the SAM during ALD

Future work



- Develop high quality SAMs using vapor deposition
  - Control pressure and exposure times precisely
    - Develop optimal pressures
  - Pulse water vapor between SAM exposures
    - Develop optimal pulse times
  - Lower SAM formation times to practical point for industry



Acknowledgements

- SRC/Sematech Engineering Research Center
- ASM
  - Eric Shero
  - Mohith Vergese
  - Steve Marcus
  - Christophe Pomarede