Surface Modification for Selective Atomic Layer Deposition of High-κ Dielectric Materials

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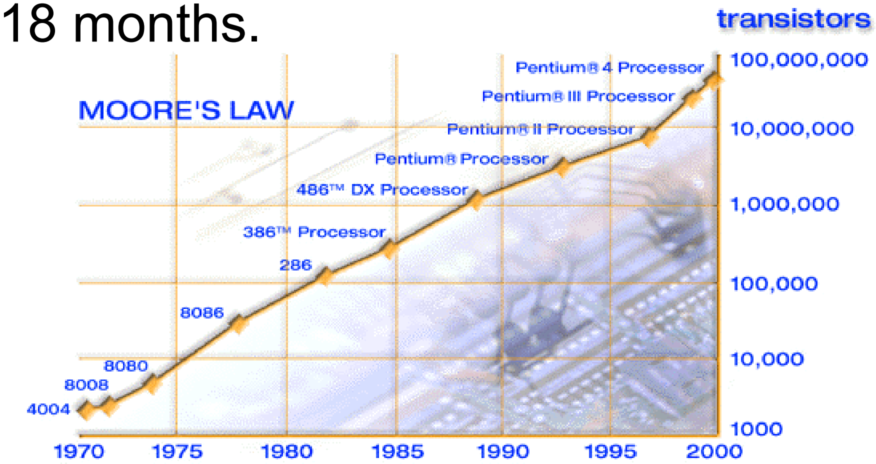
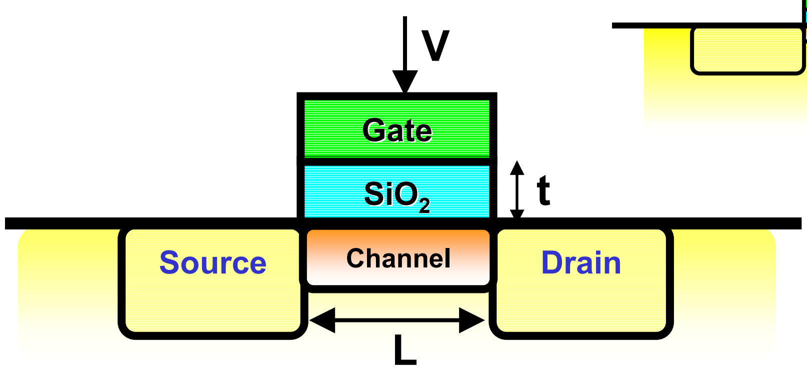
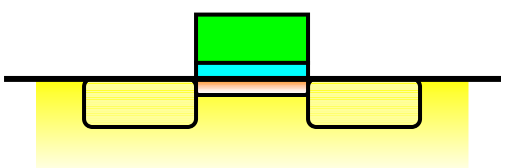
1. Moore's Law and Transistor Scaling

Moore's Law: The number of transistors in integrated circuits doubles every 18 months.



Transistor Scaling: Decrease dimensions to maintain constant electric field in the device, including the gate oxide thickness.





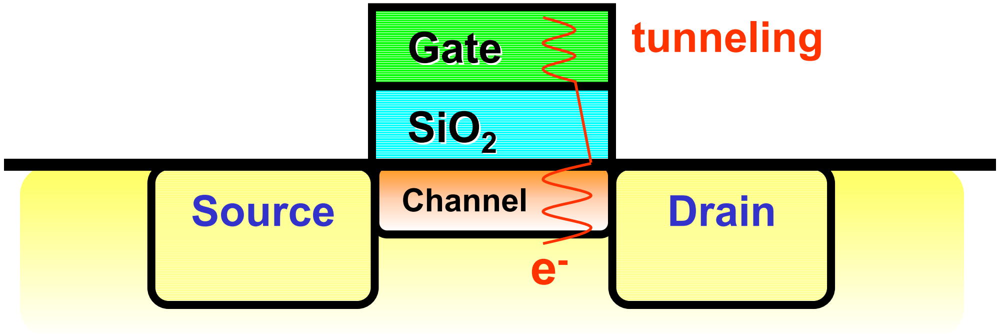
$$\text{Frequency Response} \propto \frac{1}{L}$$

$$\text{Dimensions (L, t)} \propto \frac{1}{K}$$

$$\text{Gate Capacitance} \propto \frac{1}{K}$$

2. The Need for High-κ Dielectric Materials

Leakage current through electron tunneling increases exponentially when the **dielectric film thickness is decreased**.



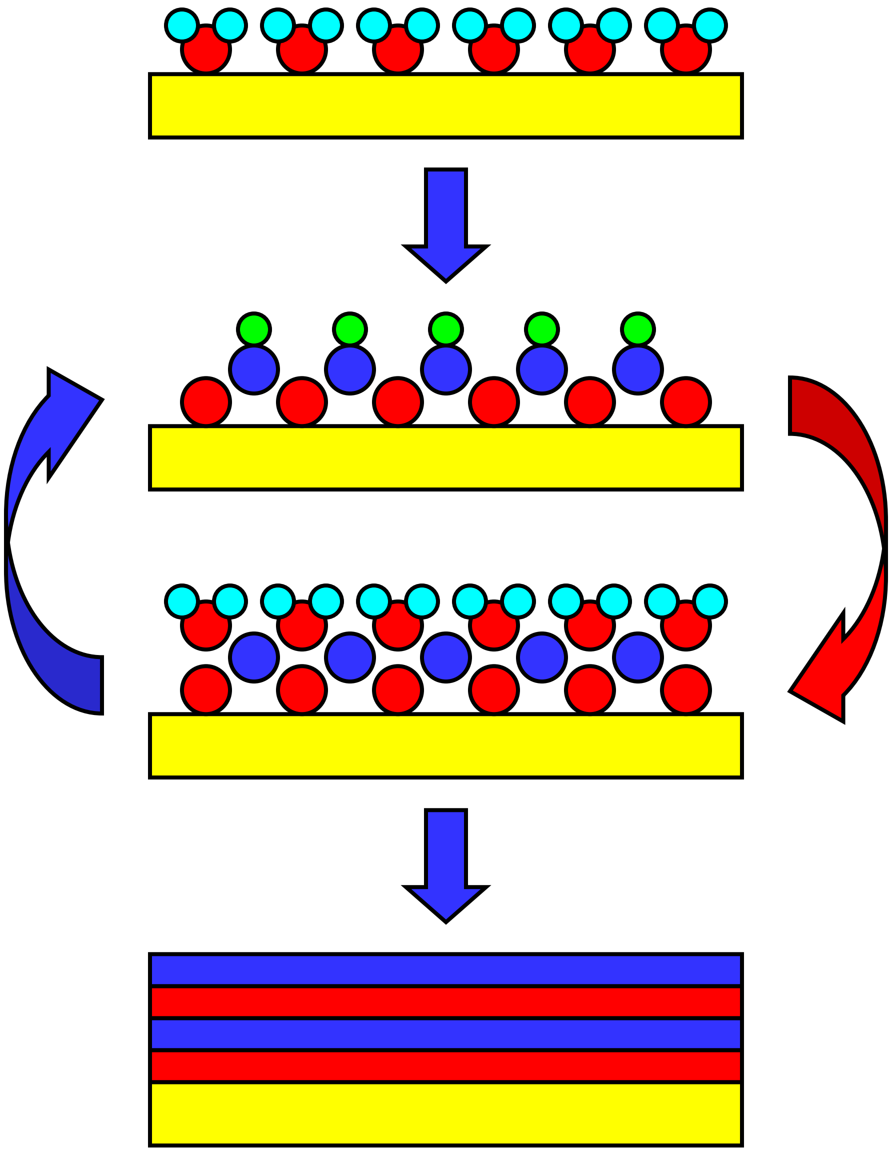
Replacing SiO_2 with **high-κ dielectric materials** allows thicker gate dielectrics and hence **reduces leakage currents**.

Dielectric Materials		κ
silicon oxide	SiO_2	3.5
silicon nitride	Si_3N_4	7
aluminum oxide	Al_2O_3	9
hafnium oxide	HfO_2	30 - 40
zirconium oxide	ZrO_2	25

$$\text{Capacitance} \propto \frac{\kappa}{t}$$

- How to deposit high-κ materials?
- How to deposit high-κ materials in an environmentally benign manner?

3. Atomic Layer Deposition (ALD)



- ALD occurs through a binary sequence of **self-limiting** surface reaction steps.
- Each step deposits an **atomic layer** of thin film material.

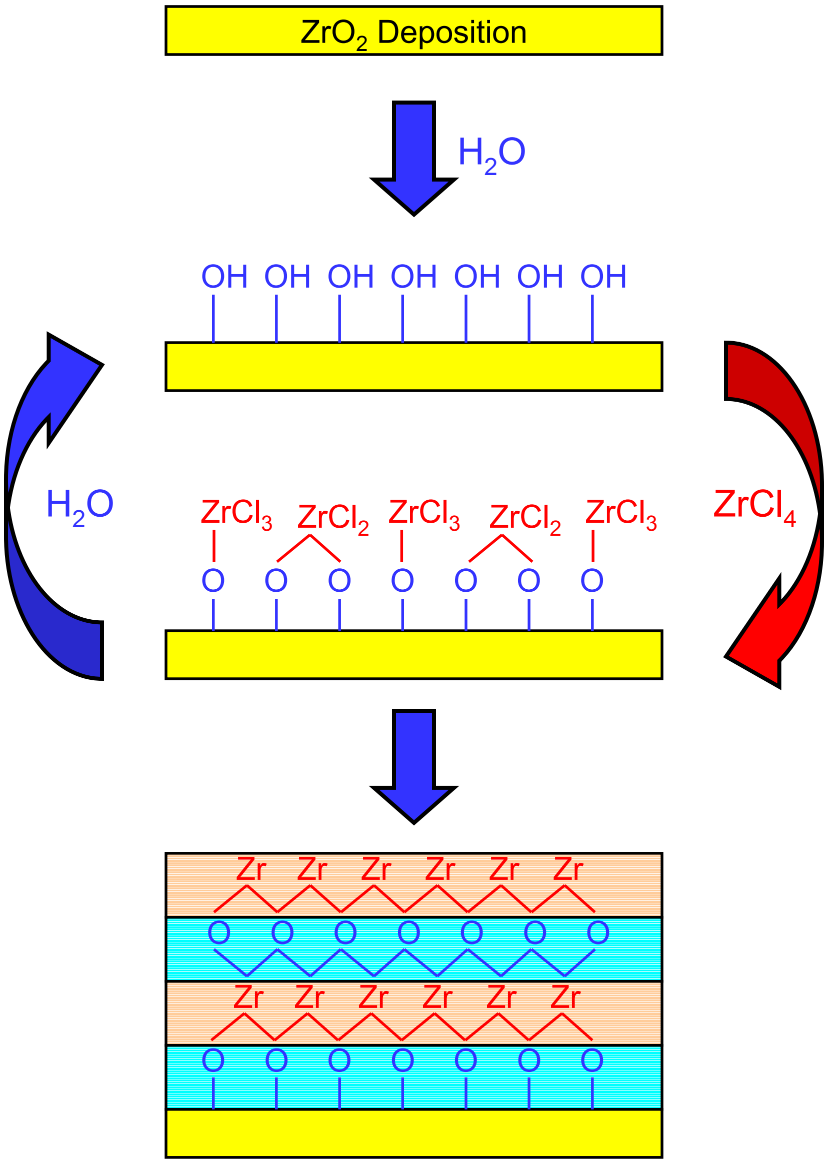
Advantages of ALD

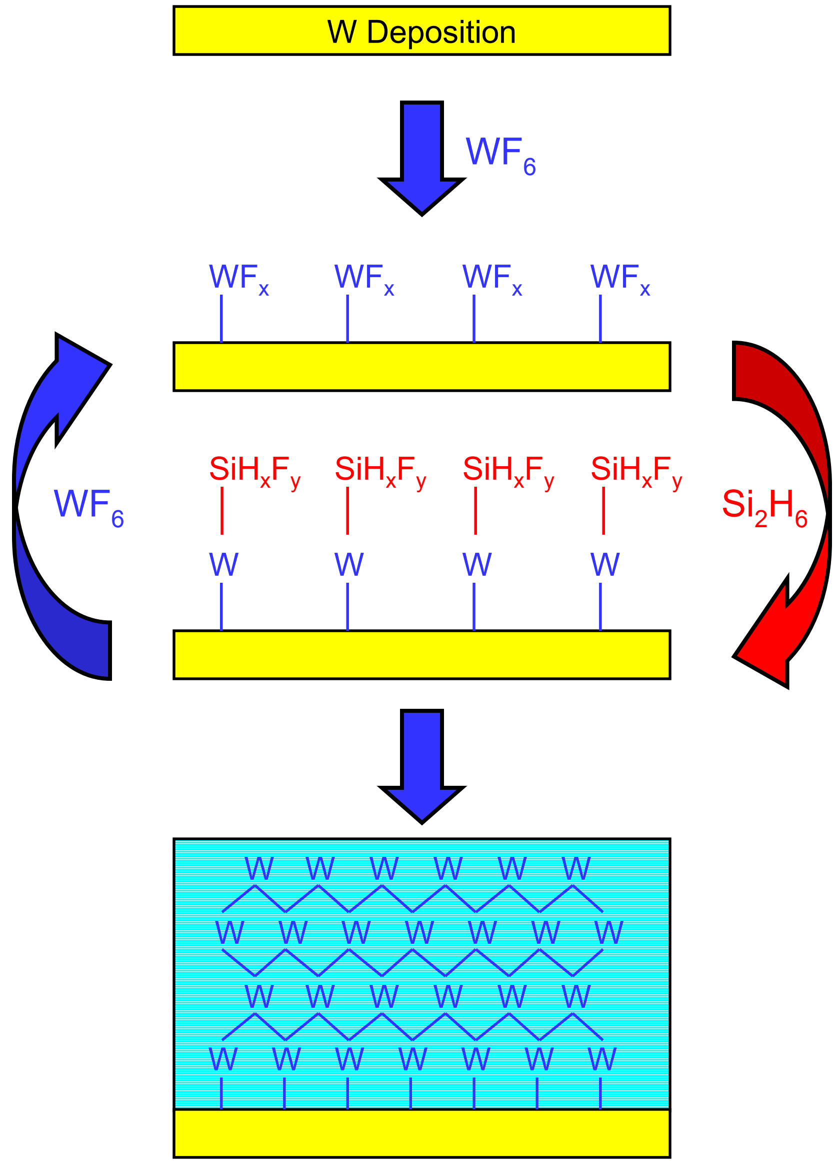
- Accurate and simple thickness control
- Excellent conformality and reproducibility
- High quality materials
- Possibility for interface modification

Applications of ALD

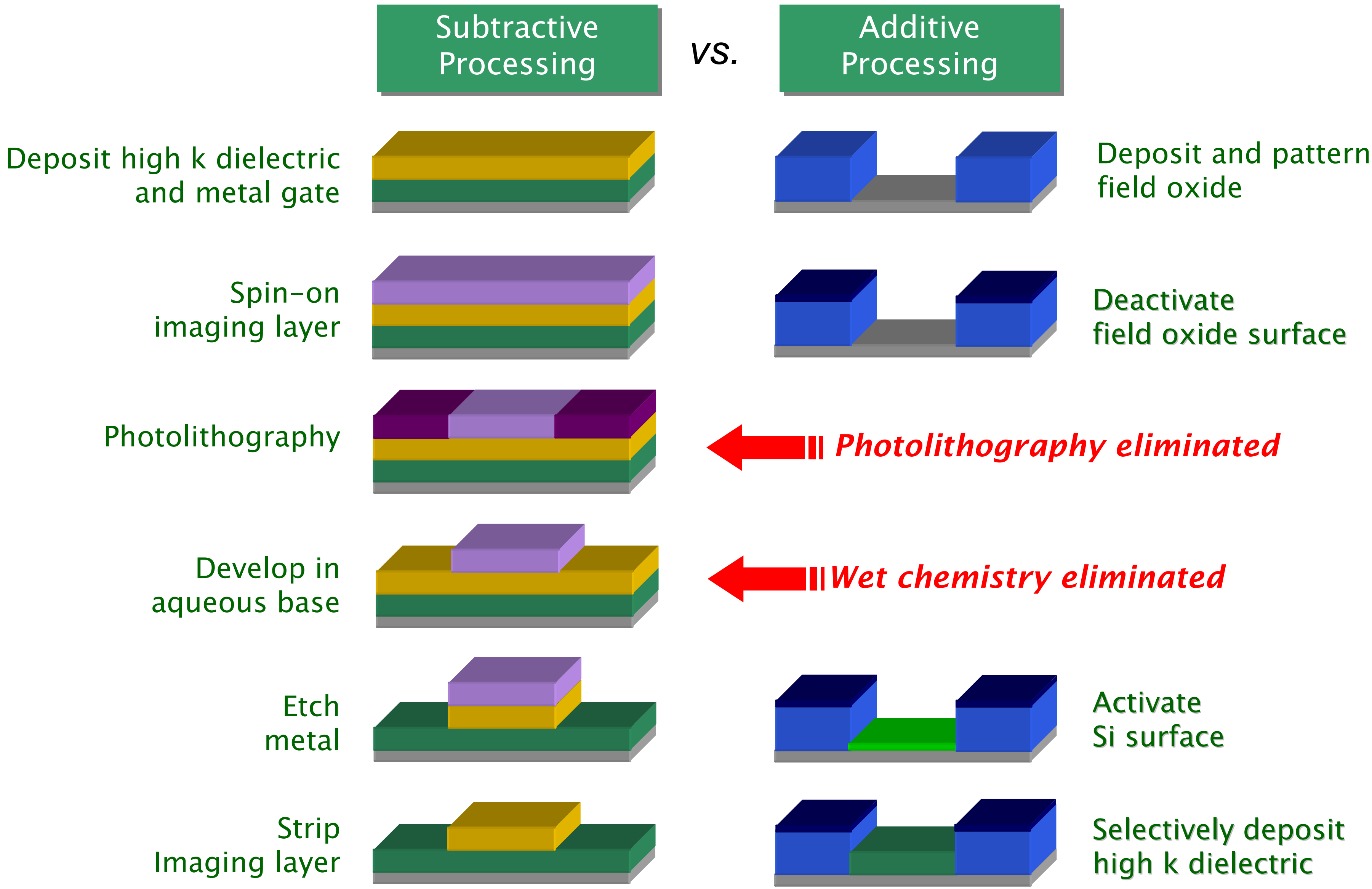
- High-κ dielectrics for gate stacks
- Metallic lines for interconnects
- Diffusion barriers

4. Examples of ALD Surface Chemistry



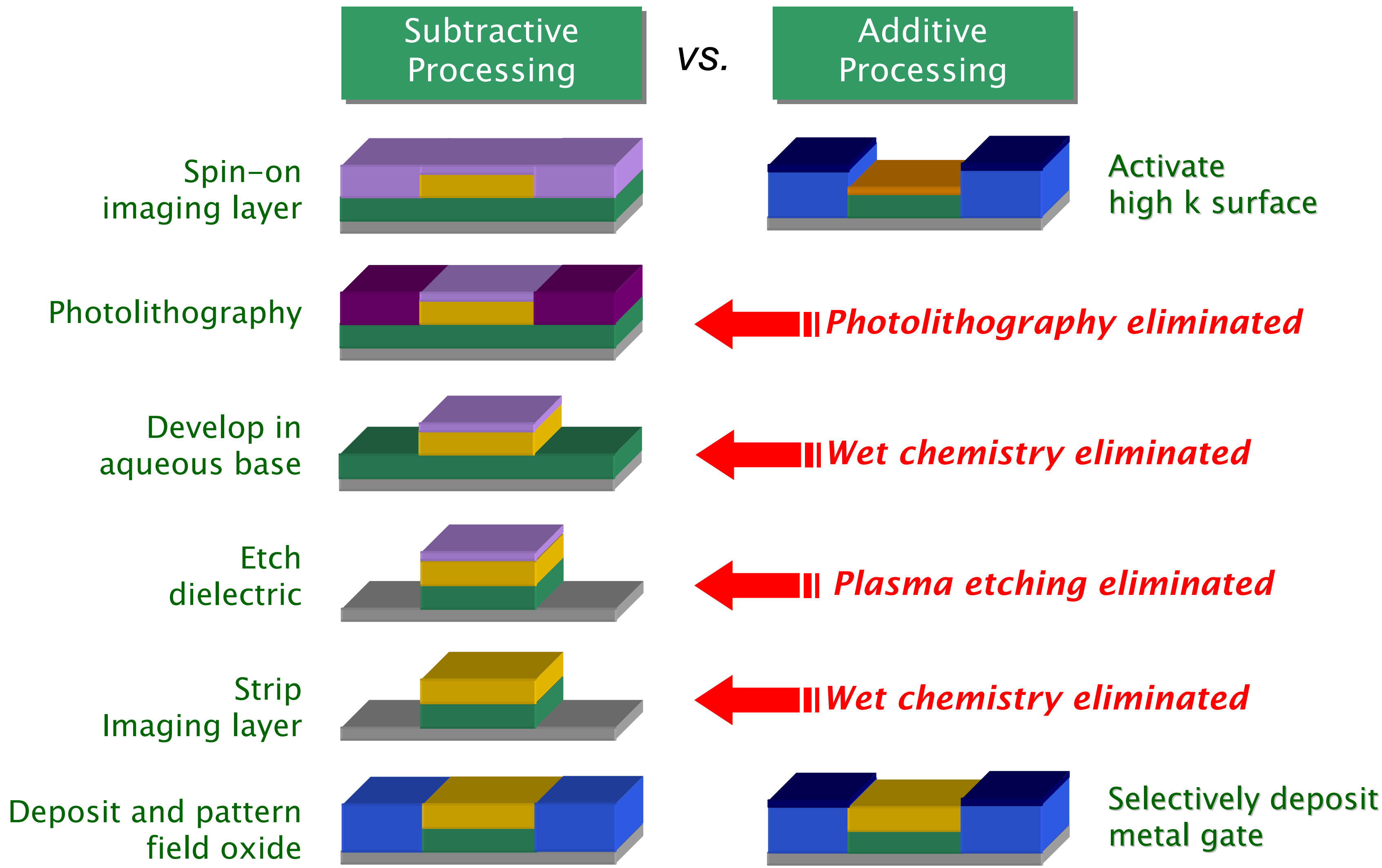


5. Environmentally Benign Selective ALD



Courtesy: Dr. Muscat

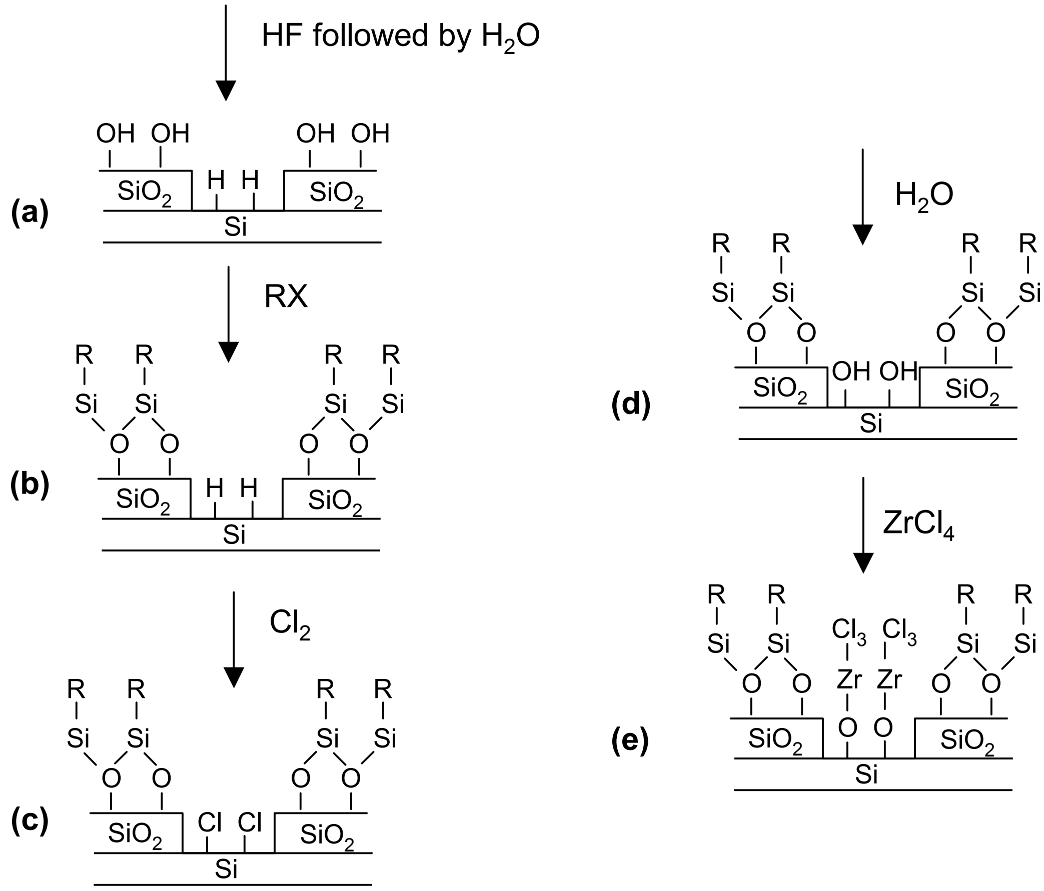
6. Process Flow for Selective ALD (con't)



Reduce processing steps & Minimize ESH impact

Courtesy: Dr. Muscat

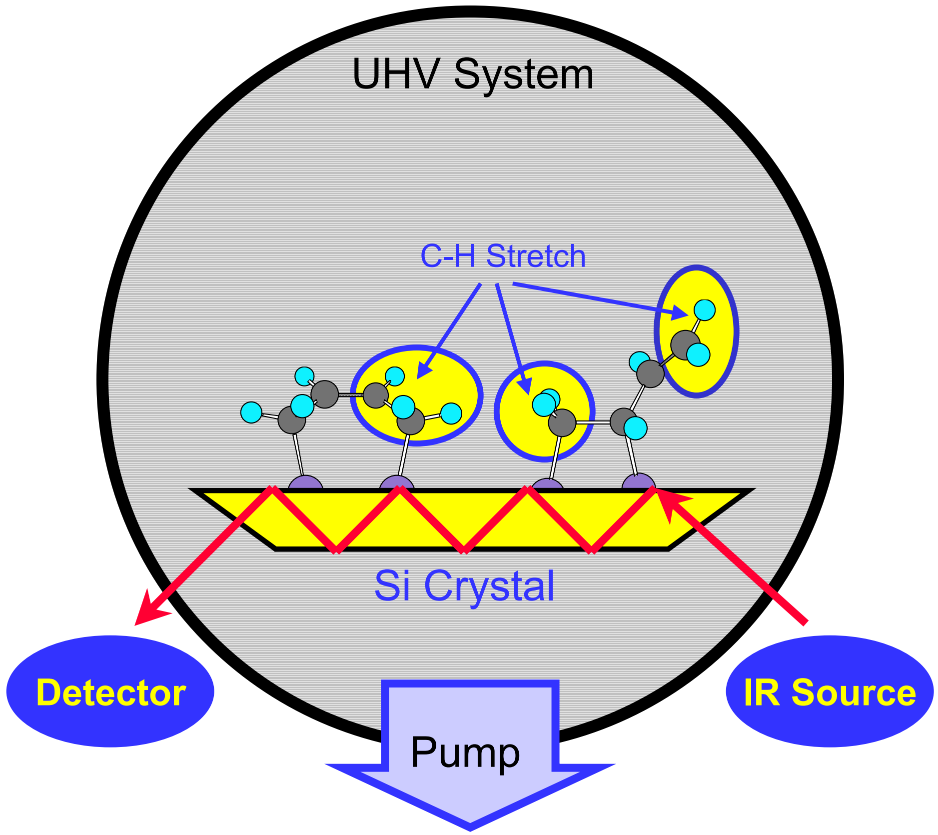
7. Selective ALD of High-κ Dielectric



Cleaned and patterned Si → Protect oxide → Si surface activation → Maskless, selective ALD

8. Combination of Experiment and Theory

Multiple Internal Reflection Fourier Transform Infrared Spectroscopy



Quantum Chemistry Calculations

Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

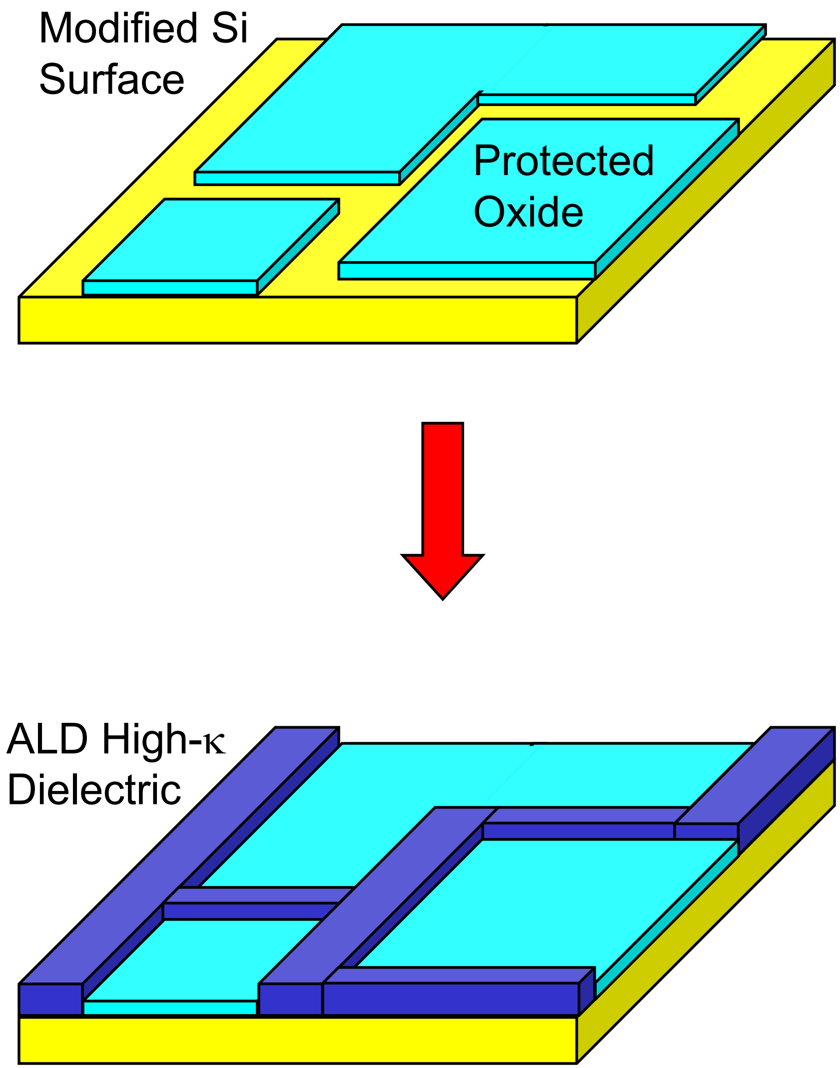
Density functional theory

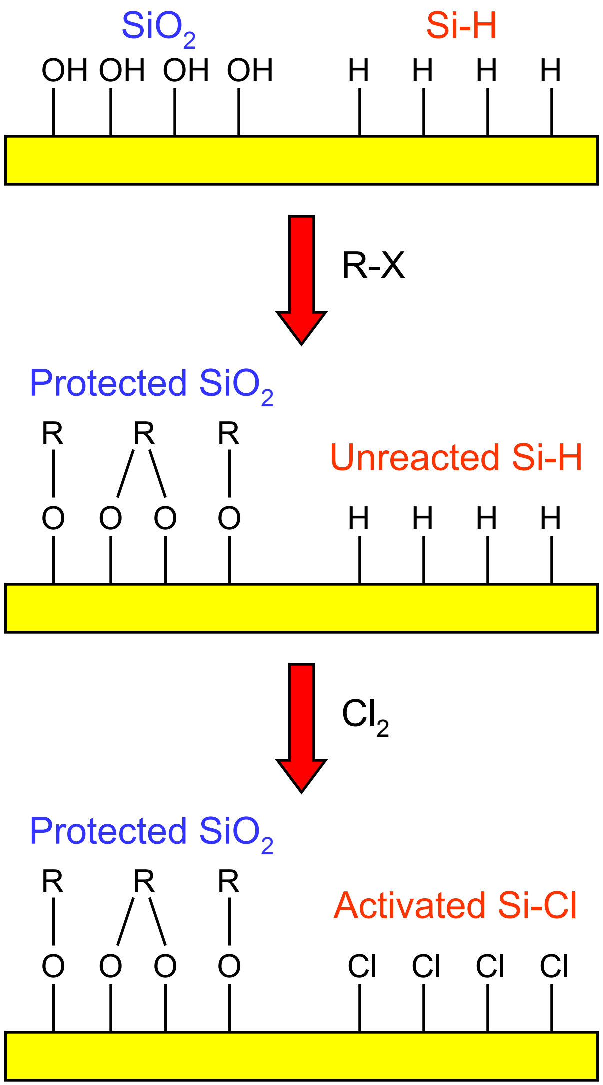
Energy E

Geometry $\frac{\partial E}{\partial R_\alpha}$

Frequency $\frac{\partial^2 E}{\partial R_\alpha^2}$

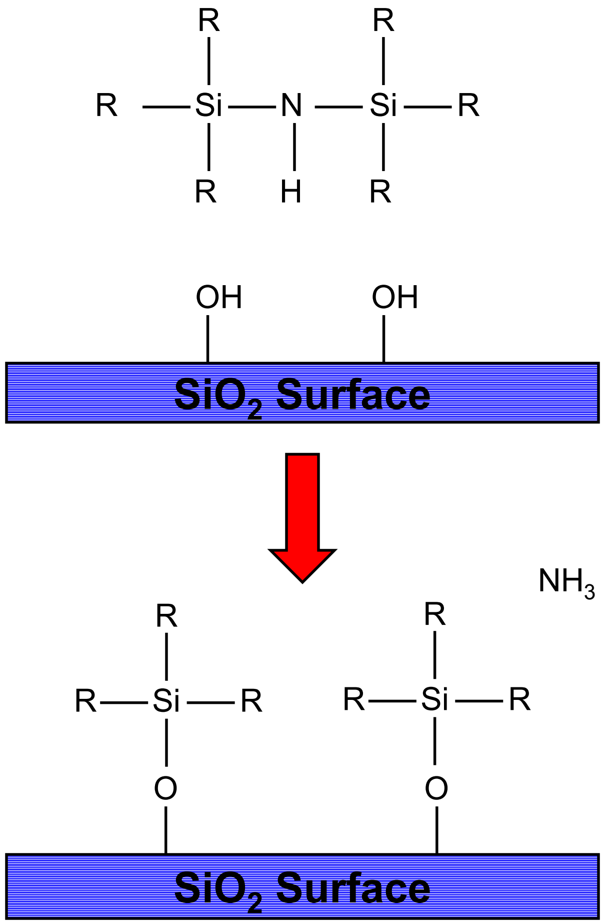
9. Surface Modification for Selective ALD



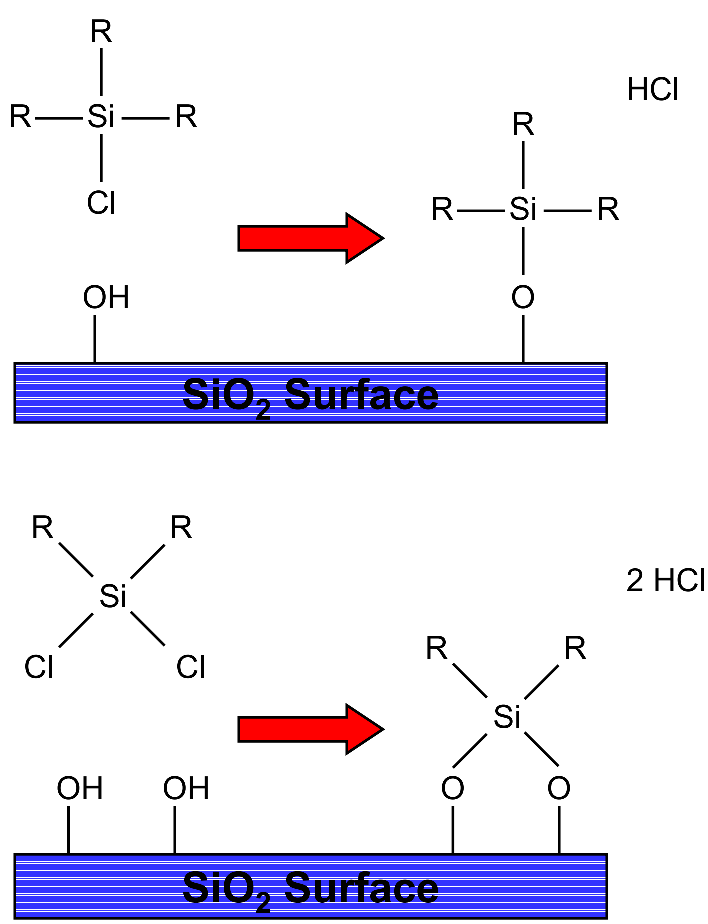


10. Strategies for Protecting SiO_2

Hexaalkyldisilazane

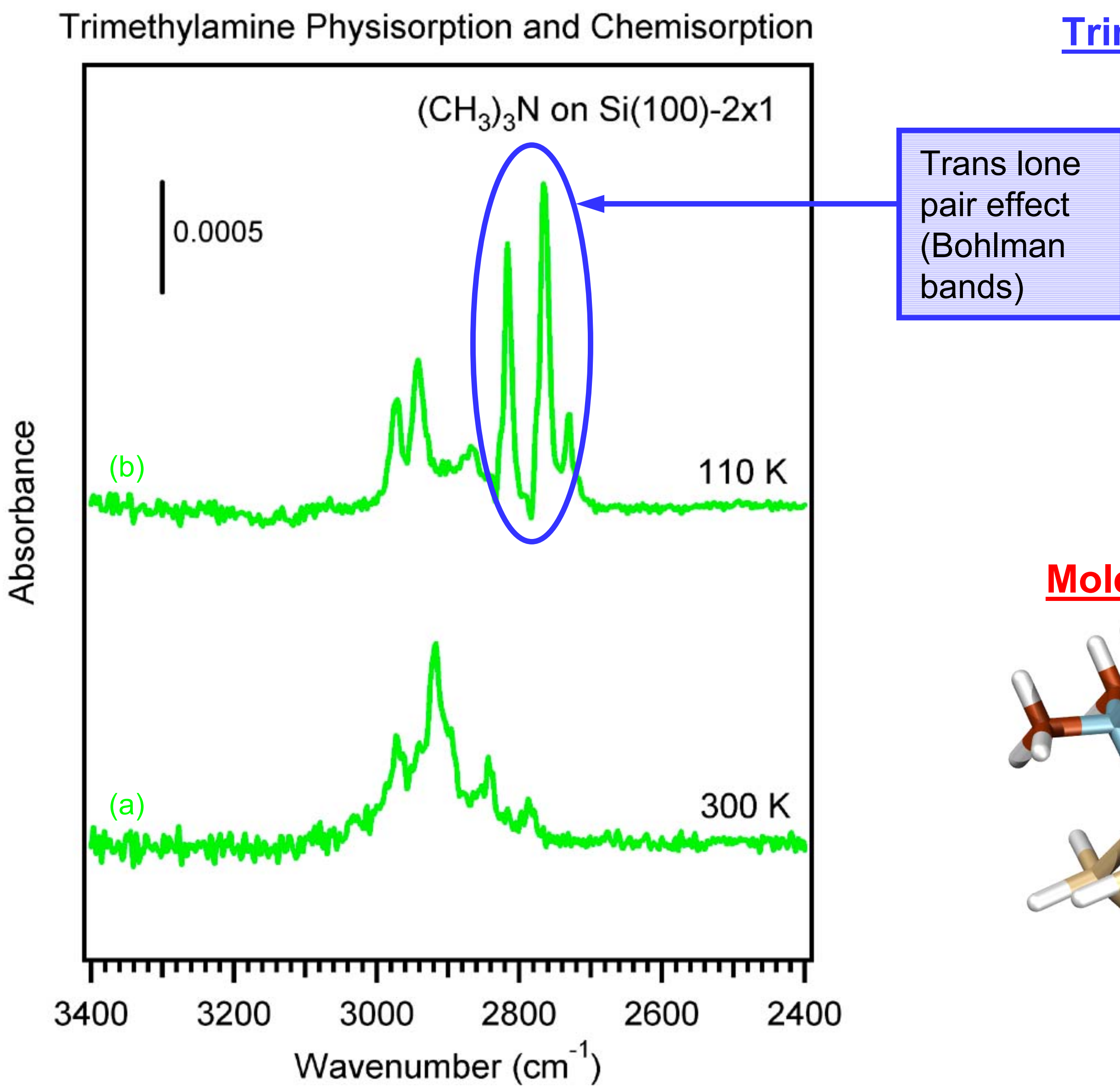


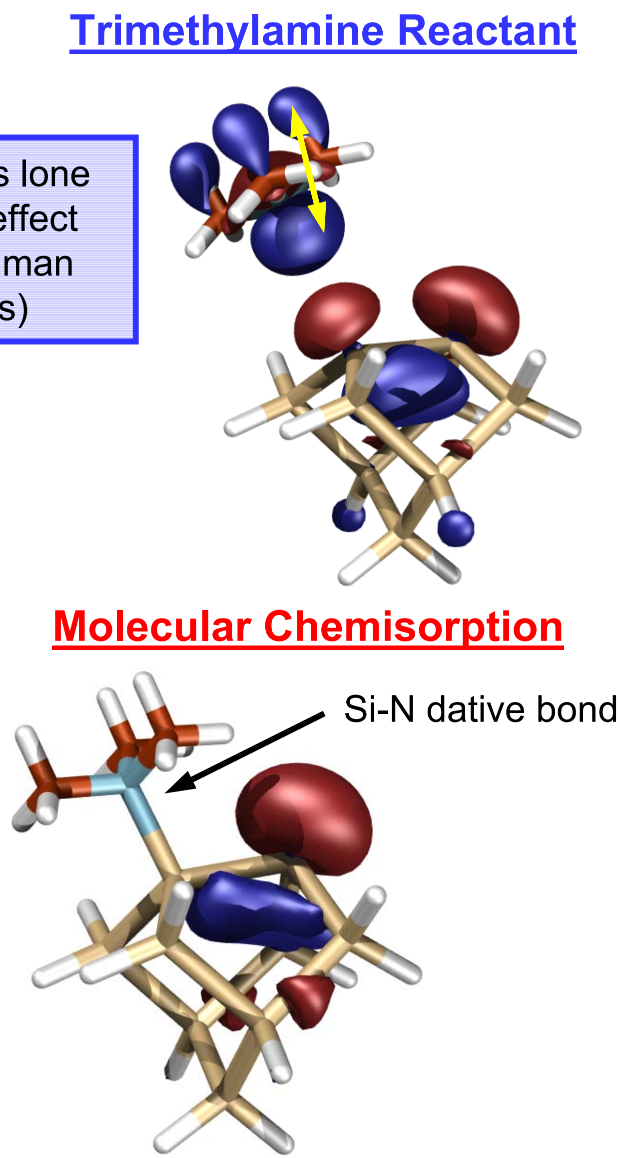
Alkylchlorosilanes



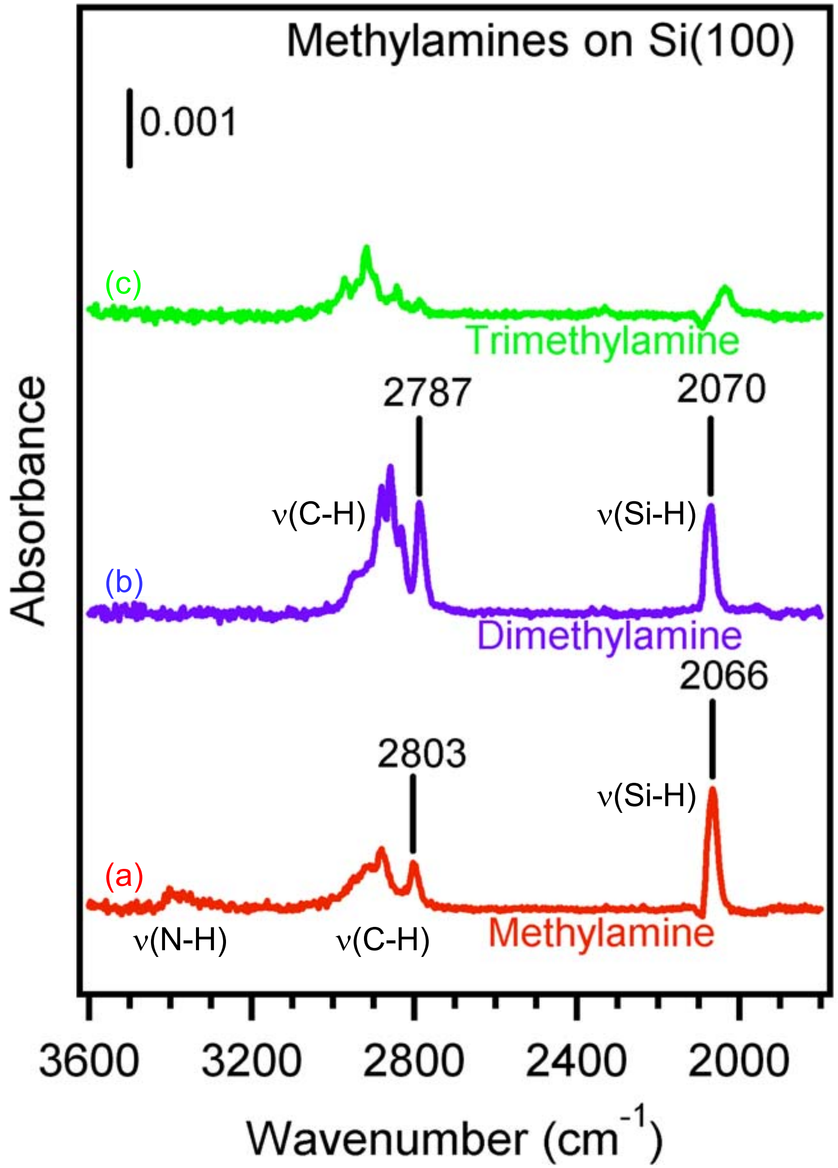
Formation of self-assembled monolayers on SiO_2 in vacuum?

11. Reactivity of N Lone Pair on Si(100)





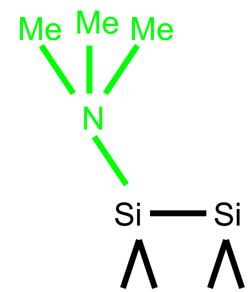
12. Chemistry of Amines on Si(100)



Trimethylamine

No N-H bonds, $N\text{-}CH_3$ cleavage unfavorable.

Molecular chemisorption through lone pair.

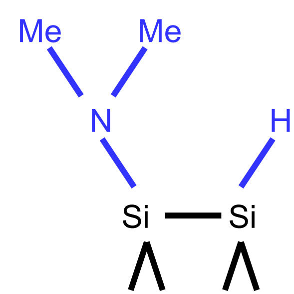


Dimethylamine

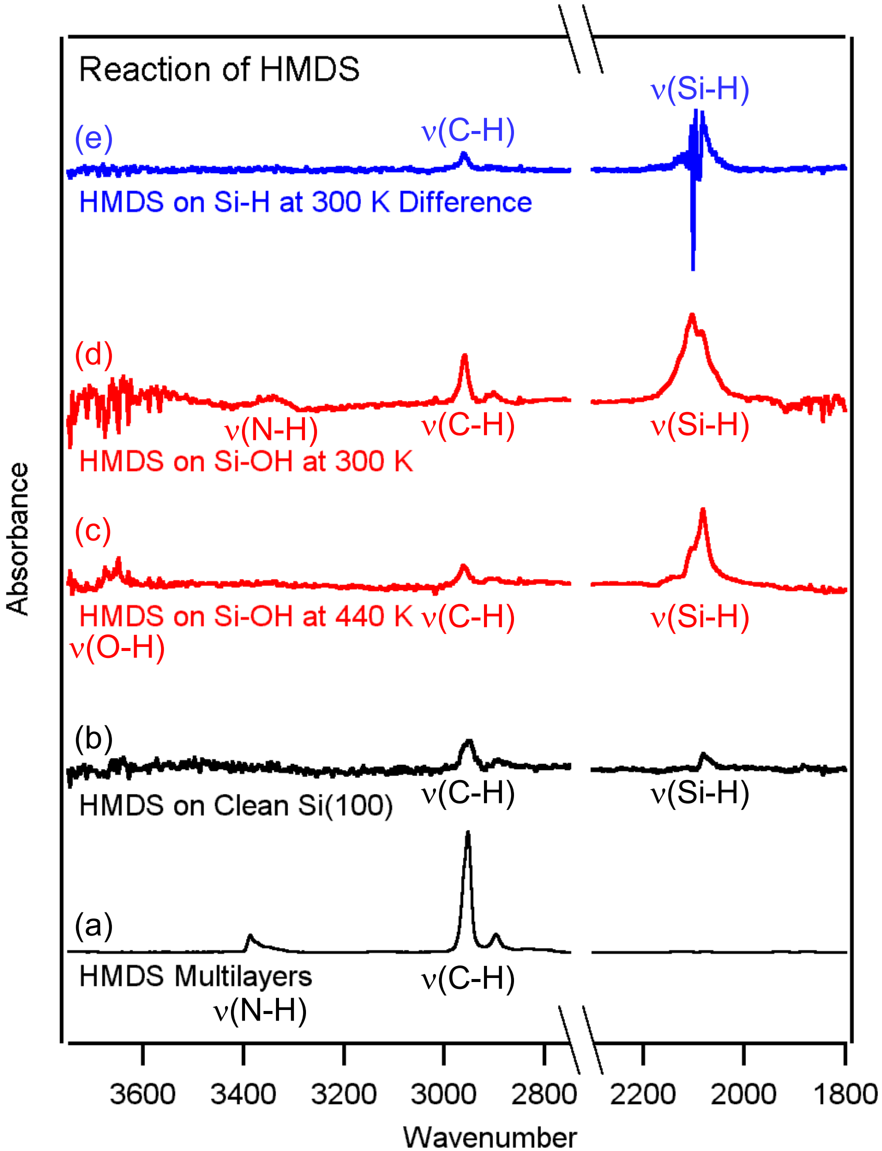
Similar to HMDS, has N-H functionality.

N-H dissociation on Si(100).

Methylamine behaves the same.



13. Reaction of Hexamethyldisilazane

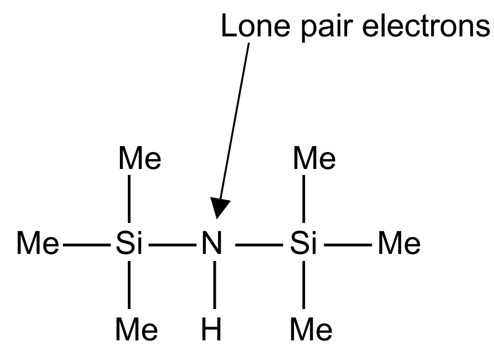


Reaction Conditions

- Reaction of H_2O at 300 K generates Si-H and Si-OH surface groups.
- Expose 0.1 mtorr HMDS to Si-OH covered surface at 300 or 440 K for 30 min.
- Record IR spectra at 300 K.

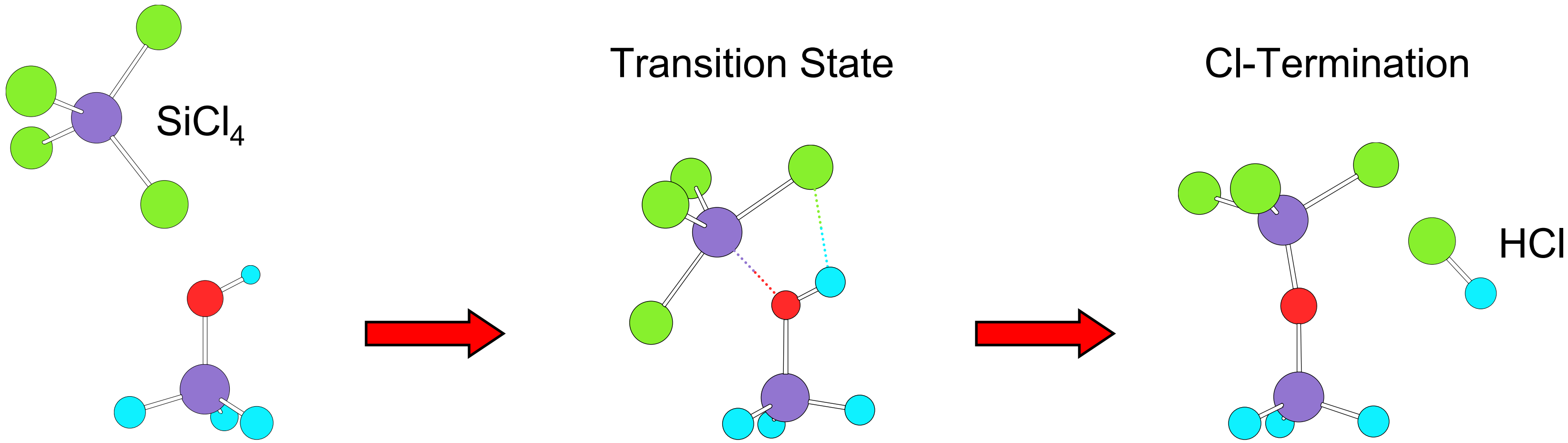
Experimental observations

- Reacts on clean Si(100).
- Reacts with Si-OH even at 300 K.
- Some selectivity for Si-OH over Si-H.



14. Modeling SiO_2 Surface and Si-OH Groups

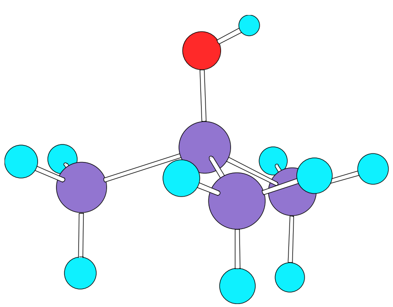
Example: Surface chemistry for silicon oxide ALD



SiH_3-OH Model

E_A = 21.9 kcal/mol

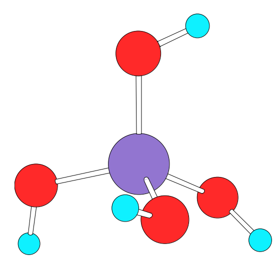
ΔE = -7.8 kcal/mol



$Si(SiH_3)_3$-OH Model

E_A = 21.4 kcal/mol

ΔE = -7.7 kcal/mol



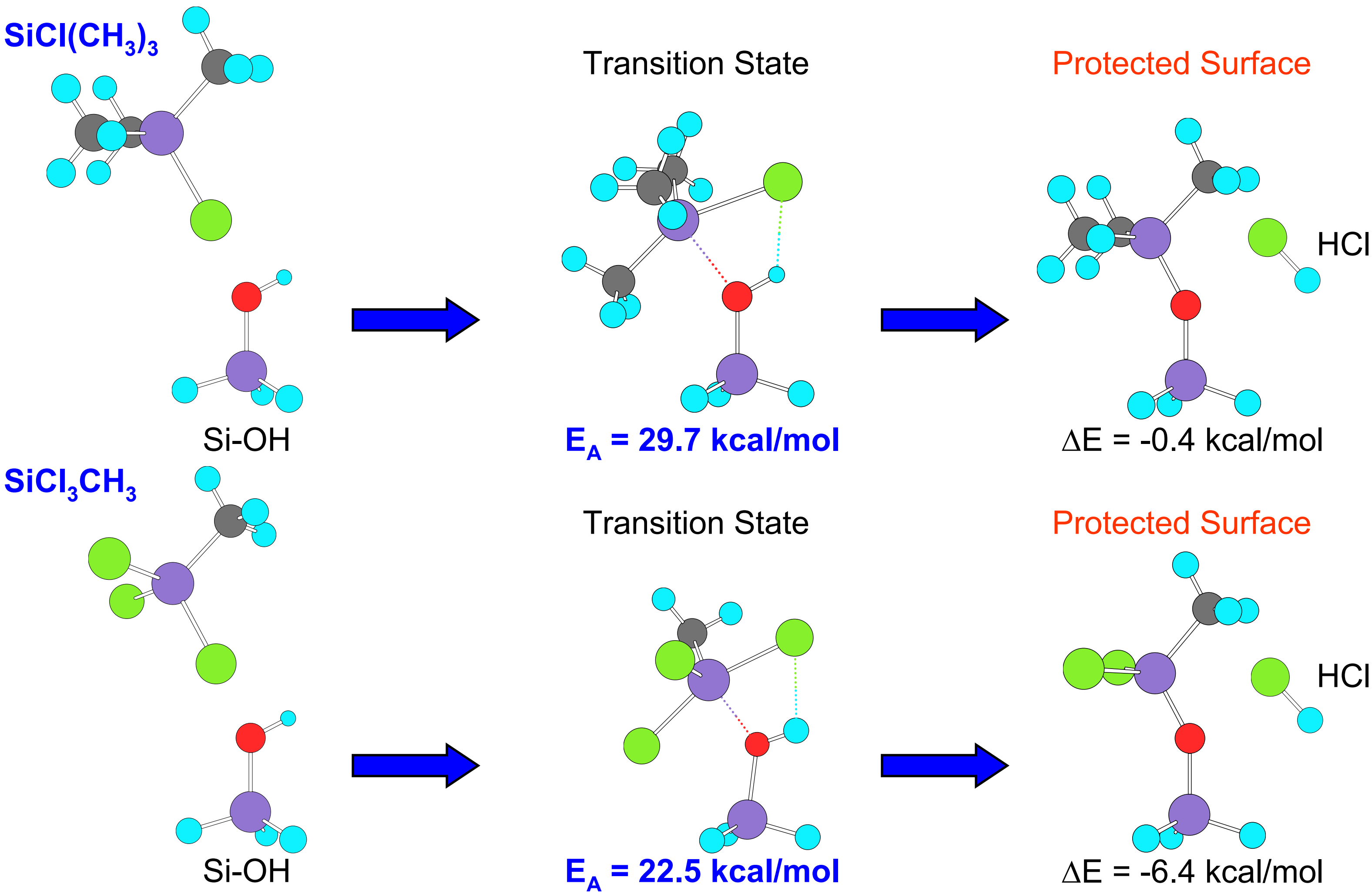
$Si(OH)_3$-OH Model

E_A = 19.8 kcal/mol

ΔE = -8.2 kcal/mol

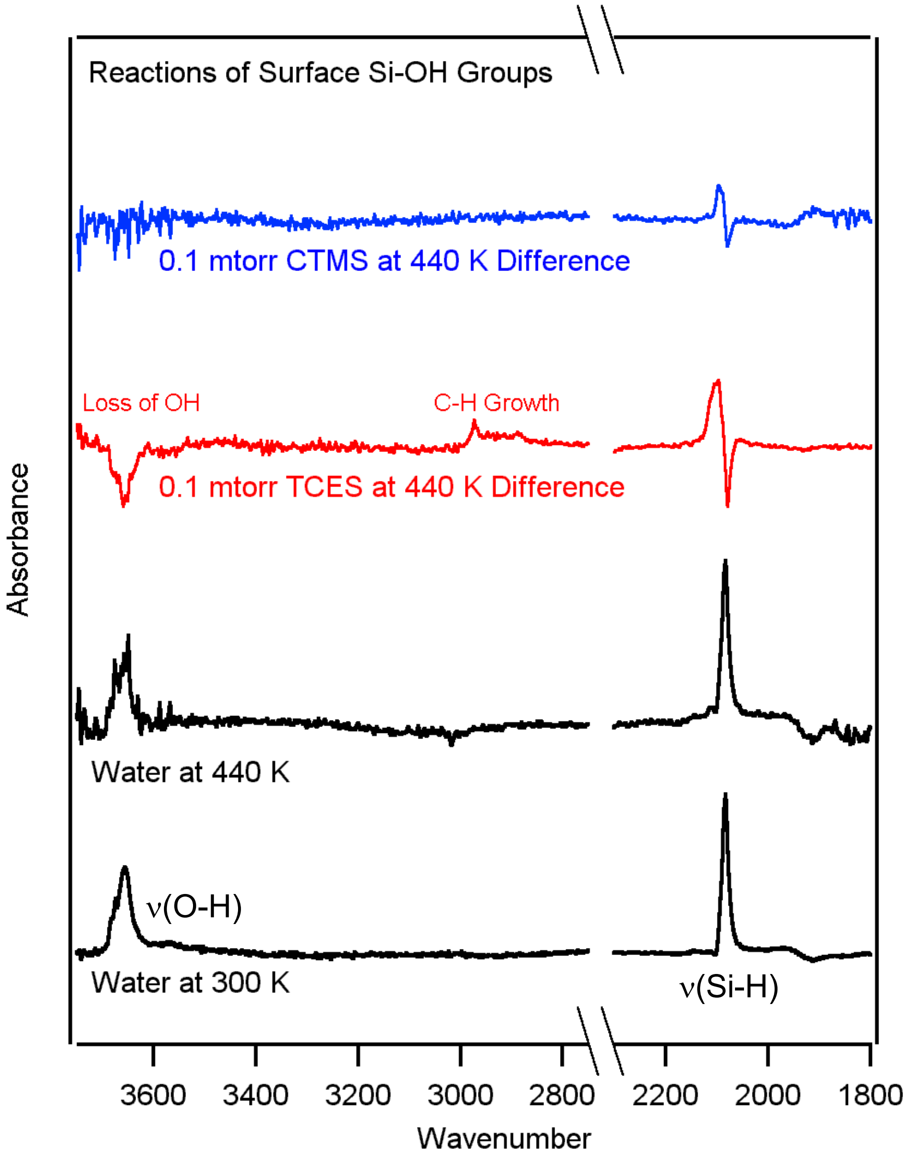
Attachment chemisty is localized at the surface functional group.

15. Reaction of Alkylchlorosilanes (Theory)



Cl substitution reduces activation barriers of surface reactions.

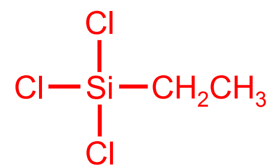
16. Reaction of Alkylchlorosilanes (Experiments)



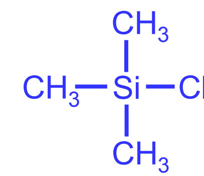
Alkylchlorosilanes

- Contain Si-Cl functional group.
- Commonly used to form siloxane bonds.
- Forms SAMs on SiO_2 surfaces.

TCES



CTMS



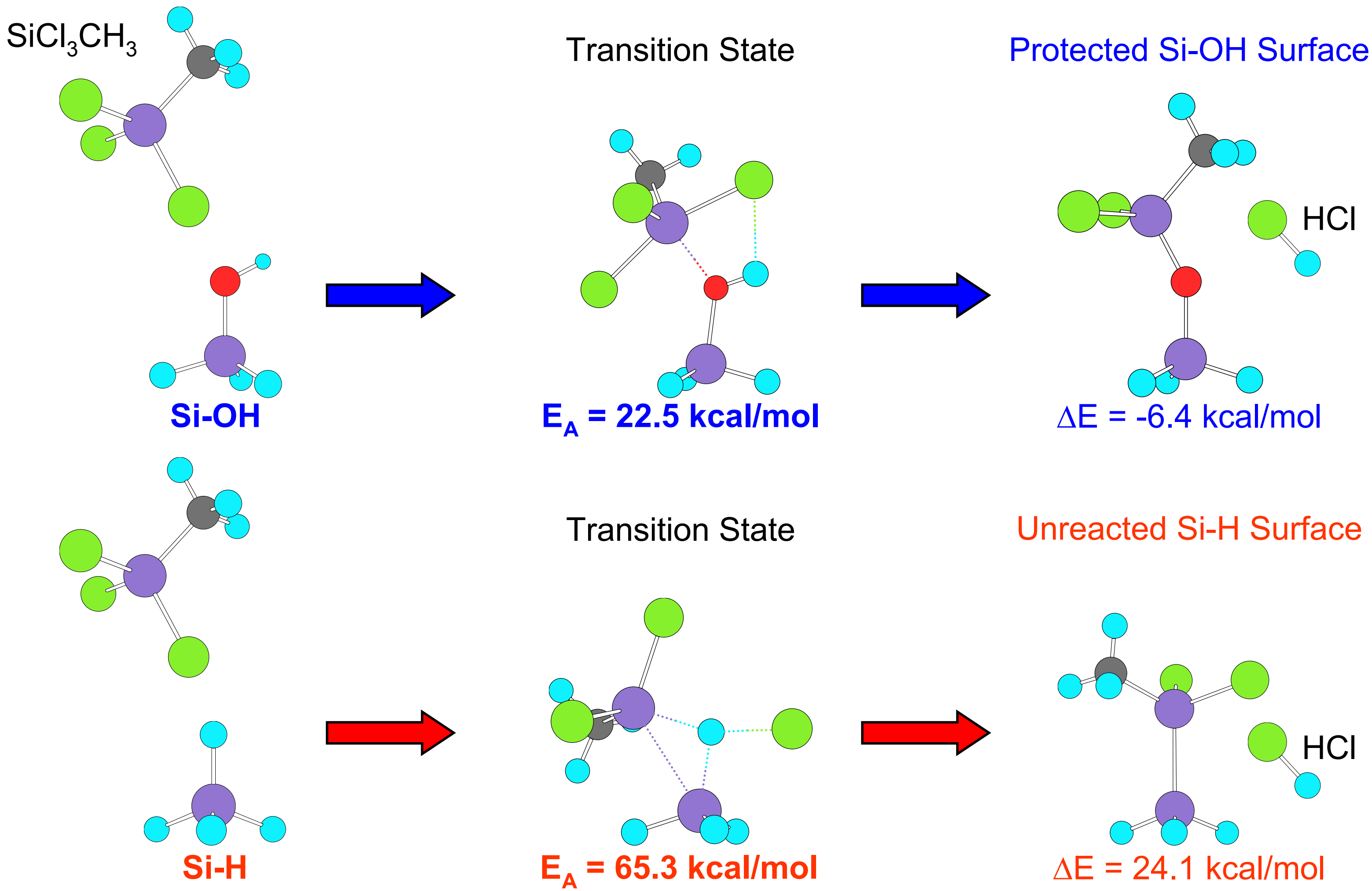
Experimental Results

- TCES spectrum shows loss of Si-OH stretch and growth of C-H stretch.
- CTMS spectrum shows no reaction.

Future Work

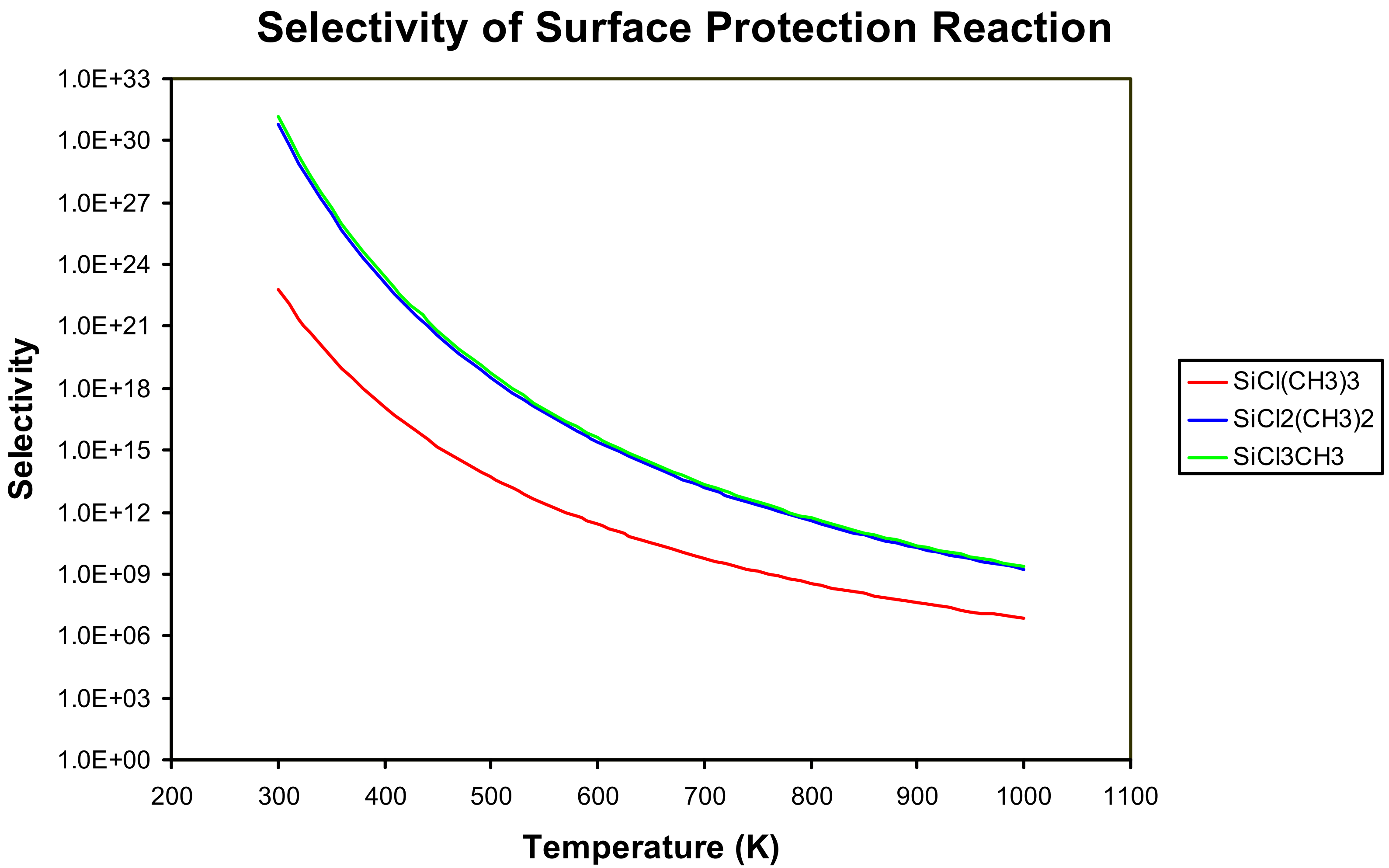
- Verify selectivity on Si-H covered surface.
- Try other functional groups ($SiCl_2R_2$).
- Reactivity toward subsequent steps.

17. Selectivity of Si-OH Over Si-H Surface



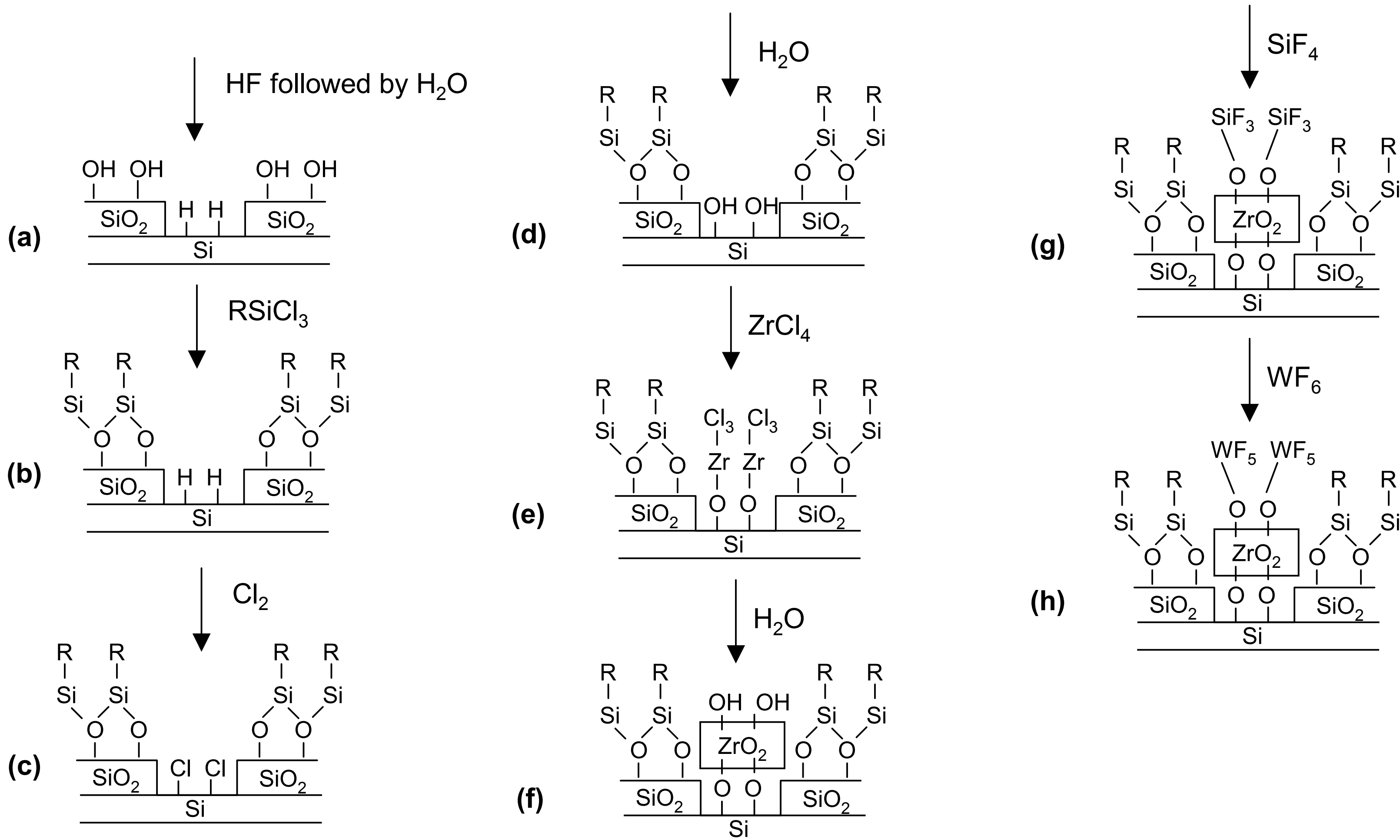
Passivation reaction is unfavorable on Si-H terminated surface.

18. Effect of Cl Substitution and Selectivity



Extremely high selectivity for Si-OH over Si-H terminated surfaces.

19. Where Can This Go in the Future?



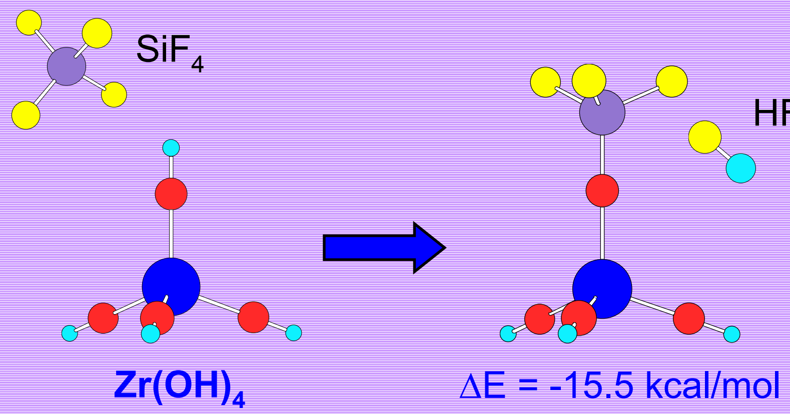
Protect oxide → Si surface activation → Selective ALD of ZrO_2 → ALD of W metal gate

20. Conclusions and Future Work

Conclusions

- Selective ALD is an environmentally benign method to deposit high-κ dielectric materials.
- Hexamethyldisilazane, which contains N-H bonds, reacts on both clean and Si-OH covered Si(100).
- We have shown successful attachment of alkylchlorosilane to surface Si-OH groups.
- DFT calculations show high selectivity of alkylchlorosilane on surface Si-OH over Si-H groups.
- Selective ALD of metal gate on high-κ dielectric in the future!

Selective Priming of ZrO_2



ALD of W Metal Gate