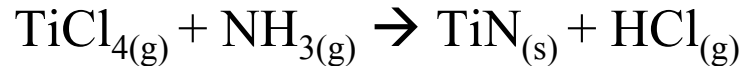


Fundamental Vacuum Beam Studies of Radical Enhanced Atomic Layer Chemical Vapor Deposition (REAL-CVD) of TiN

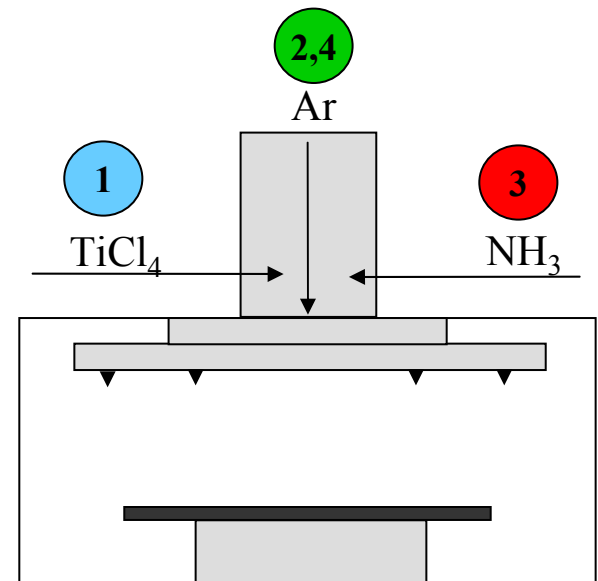
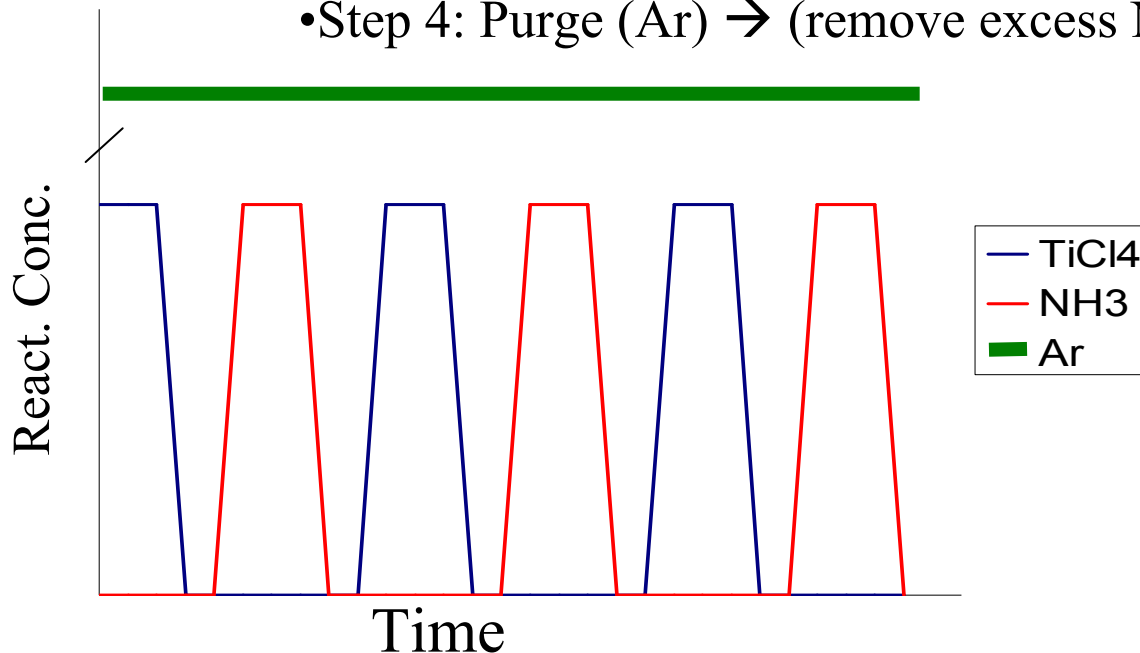
Dr. Frank Greer,
Dr. D. Fraser, Dr. J.W. Coburn, and
Professor David B. Graves
NCCA VS
December 12, 2002

What is Atomic Layer Deposition?

- Atomic Layer Deposition (ALE, ALD, ALCVD...)
 - Usually a four step, pulsed, cyclical process
 - Breaks up a CVD reaction into two half reactions

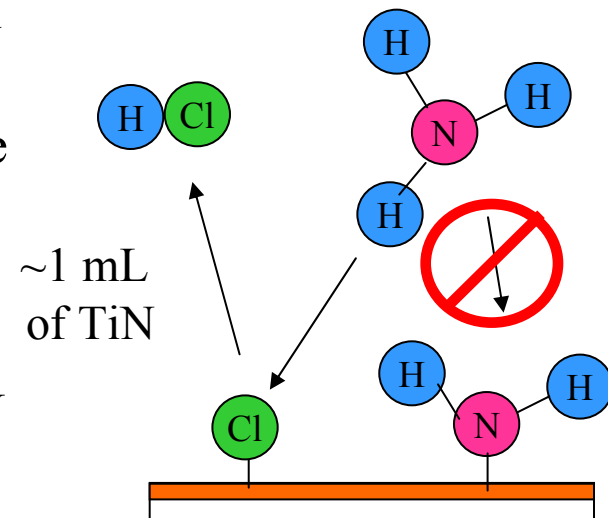
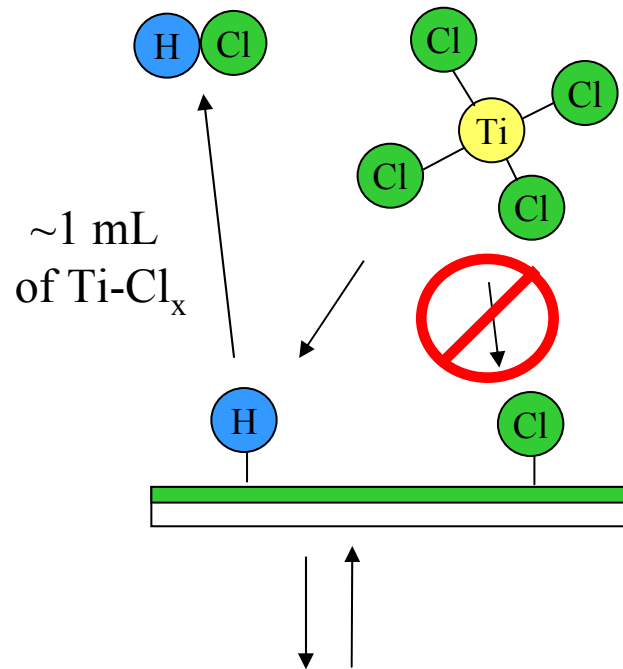
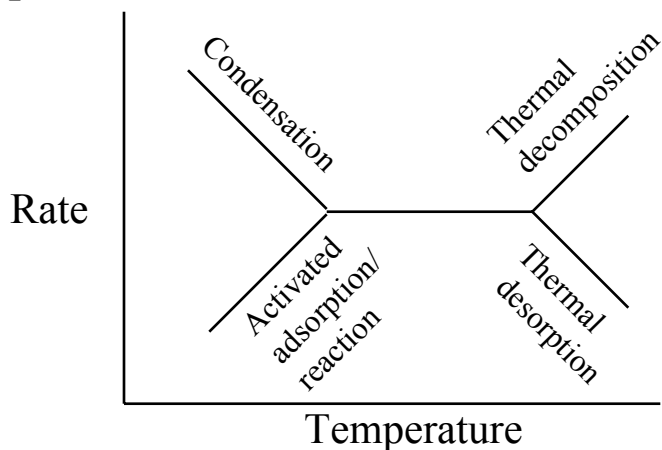


- Step 1: Metallic Precursor (TiCl_4) \rightarrow (adsorb TiCl_x , release HCl)
- Step 2: Purge (Ar) \rightarrow (remove excess TiCl_4)
- Step 3: Stripping Molecule (NH_3) \rightarrow (release HCl , add N)
- Step 4: Purge (Ar) \rightarrow (remove excess NH_3)



Distinguishing Features of ALD

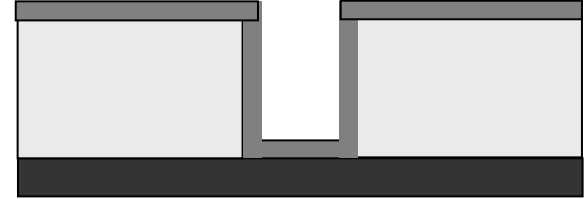
Typical Growth Rate Profile for Thermal ALD



- Each step proceeds by self-limiting surface rxns.
 - First pulse - Chemisorption of metallic precursor (*e.g.* TiCl_4)
 - Surface temp. high enough to avoid condensation and low enough to avoid decomposition
 - Second pulse - Reactive ligand stripping by reactive stable molecule (*e.g.* NH_3)
 - Surface temp. high enough to ensure high rate of dechlorination
- Reaction cycled to achieve film growth, one ML of TiN at a time

ALD for TiN Diffusion Barriers

- TiN Diffusion Barrier Requirements
 - Highly conformal
 - Low resistivity
 - Low impurity concentrations (<0.5% preferred)
- Many different approaches and films reported^{1,2}
 - $\text{TiCl}_4 + \text{NH}_3 \rightarrow \text{TiN}$
 - Good resistivity and conformality reported
 - Residual Cl% increases with decreasing substrate T during dep.
 - (0.5% at 500°C, 1.5% at 400°C, 3.0% at 350°C)
 - High Cl% may lead to corrosion of metallic films
- Substrate temperature is high
 - Other materials incompatible with substrate $T > 300^\circ\text{C}$
 - Chemical stability of organic low-k films
 - Mismatch of thermal expansion coefficients
 - Low temperature ALD desirable

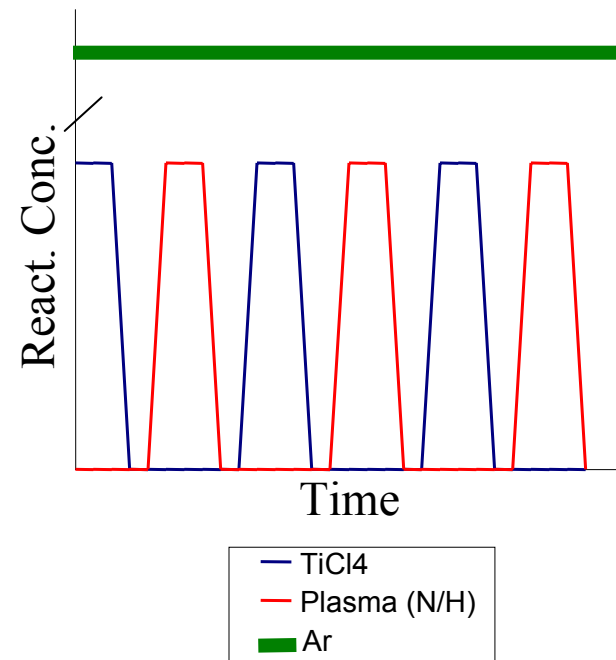
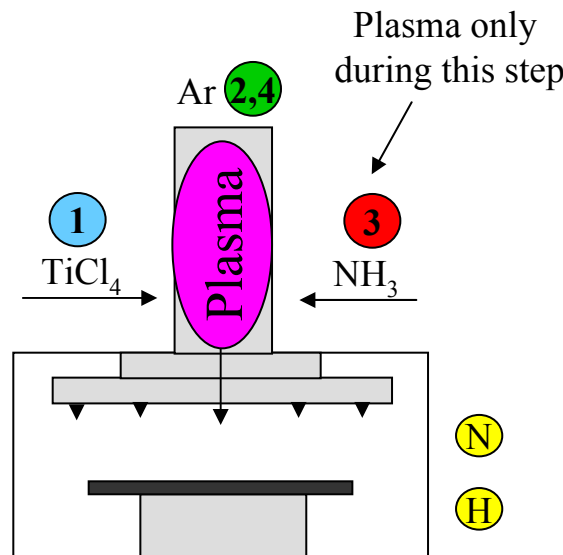
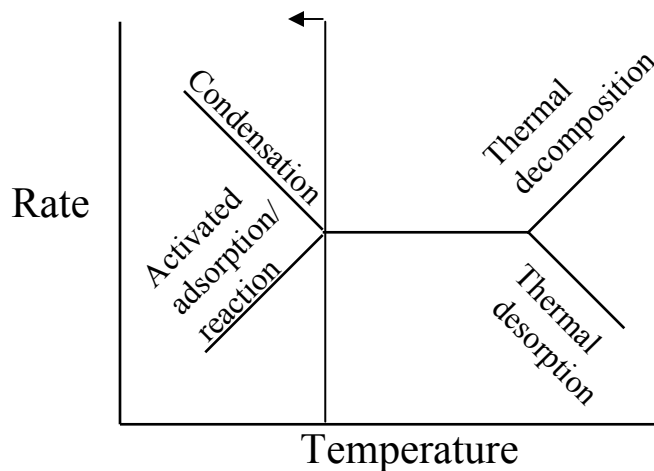


1. Satta *et al.*, *MRS 2000 Spring Mtg. (D6.5)*

2. Ritala *et al.*, *JES* 147, 2000

Radical Enhanced ALD¹

- Uses volatile metallic precursor and a **radical** source to deposit a film
- Radicals generated upstream of reactor (no ion bombardment of substrate)
- Plasma not used during precursor exposure or purge steps
- Reactants introduced in separate steps to achieve atomic layer control
- H radicals abstract Cl, N radicals nitrogenate the Ti
- Potentially access lower surface T for processing/different film properties

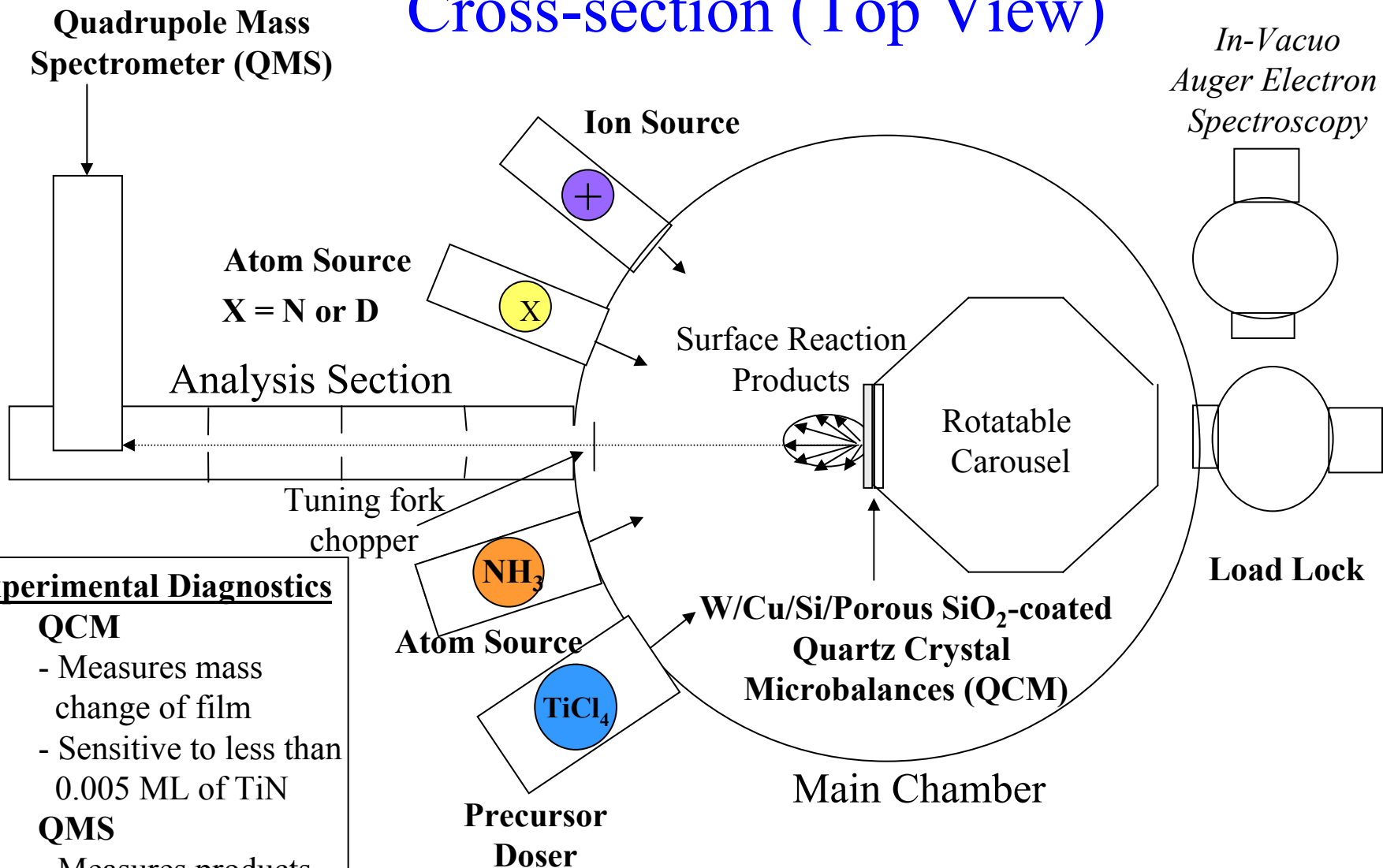


¹A. Sherman U.S. Patent 1999.

REALCVD Processing Questions

- **Answer these low temperature processing questions:**
 - TiCl_4 precursor
 - Can self-limiting adsorption be achieved without precursor condensation?
 - What are the kinetics of TiCl_4 monolayer adsorption?
 - Radicals
 - Are radicals sufficiently reactive to remove the Cl from the adsorbed TiCl_x precursor?
 - Are radicals sufficiently unreactive to stop after one ML of reaction?
 - Does recombination play an important role in radical transport in features?
- Method \rightarrow Monitor each reaction step *in-situ*, in real time

Schematic of the Beam Apparatus in Cross-section (Top View)

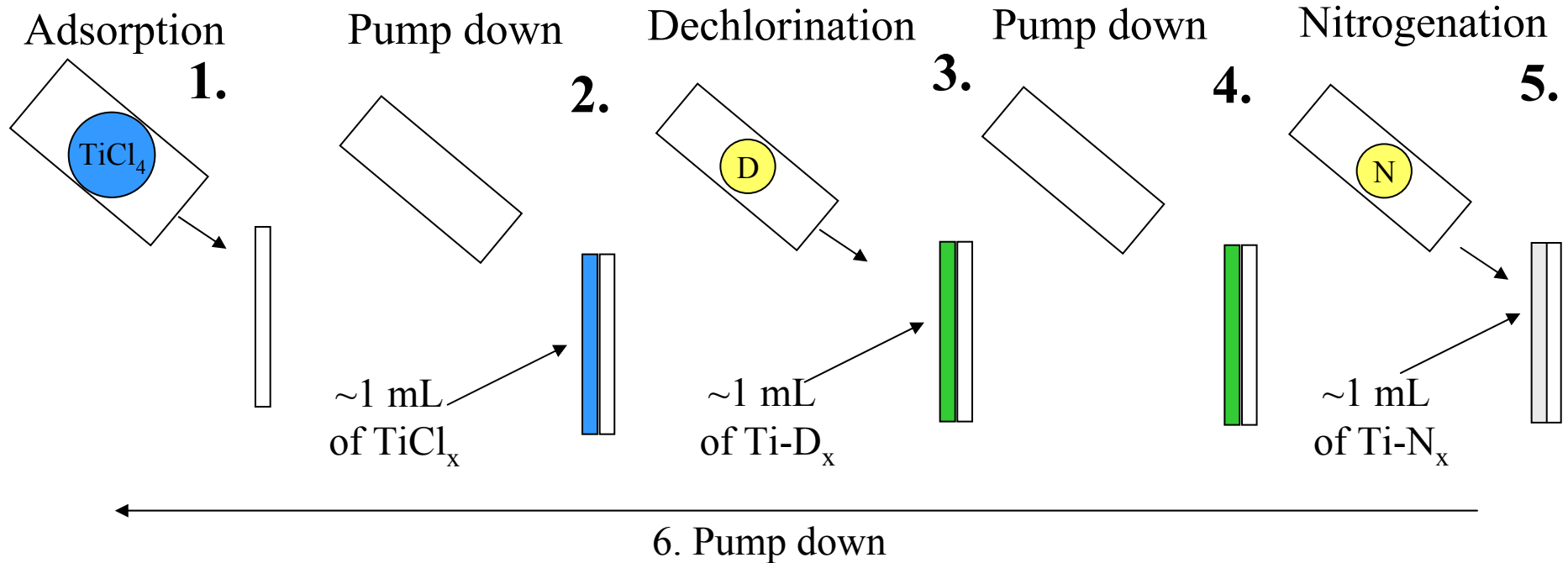


Experimental Diagnostics

1. **QCM**
 - Measures mass change of film
 - Sensitive to less than 0.005 ML of TiN
2. **QMS**
 - Measures products formed on film
 - Characterize beams

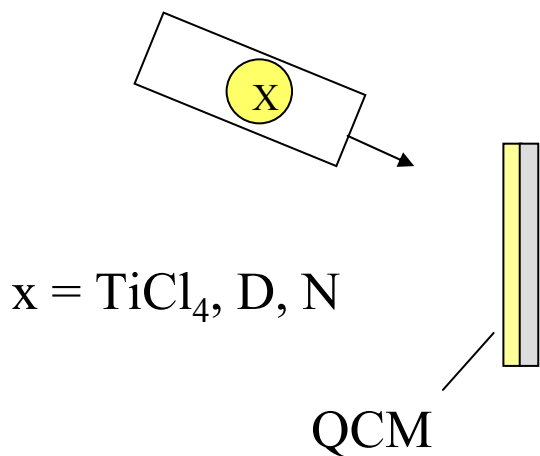
● All Molecule and Radical Sources Absolutely Calibrated

Experimental Procedure

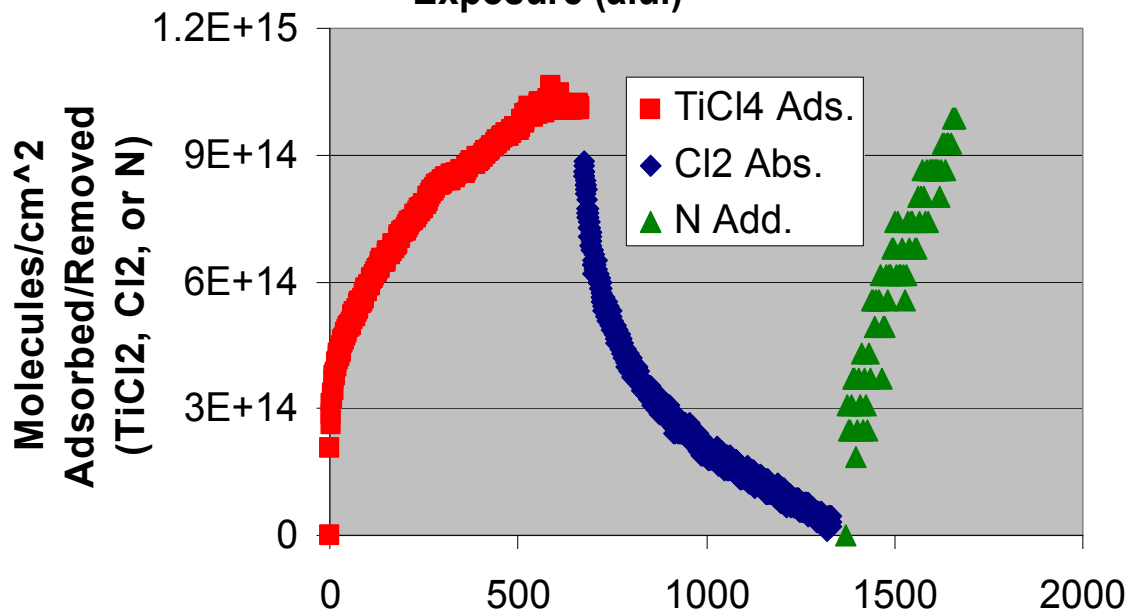
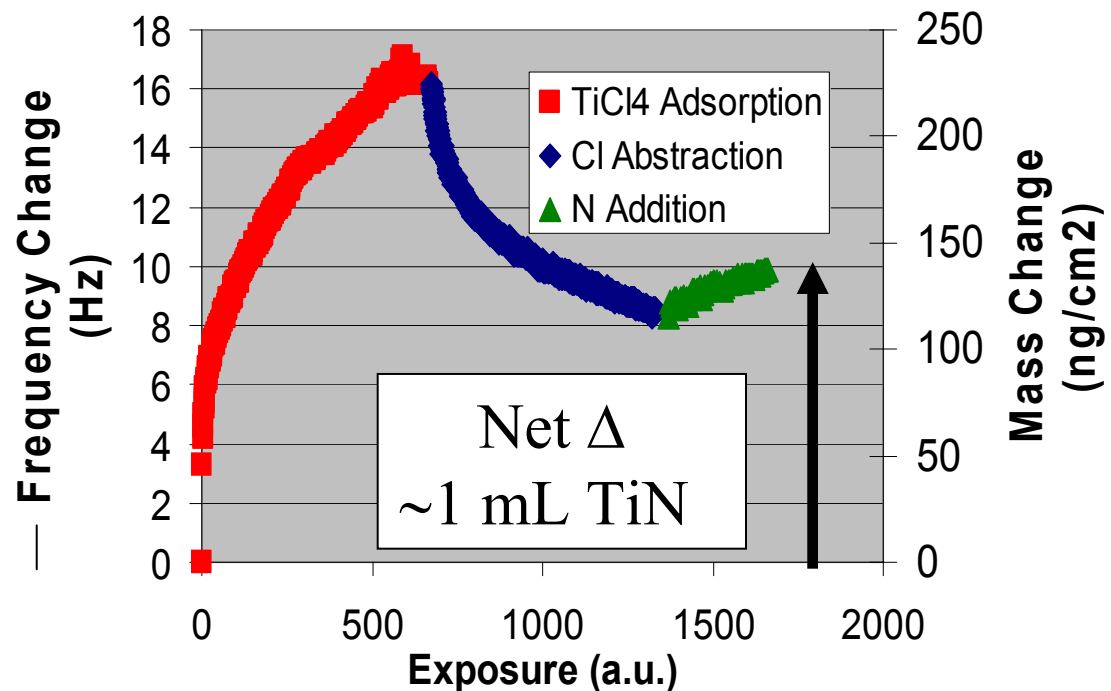


- Conventional ALD-like sequence
 - Each step in process monitored *in-situ* with QCM
 - Resulting films removed for *ex-situ* XPS analysis and sheet resistance measurements
- Surface temp varied (300K - 450K)

Monitoring TiN Deposition with QCM

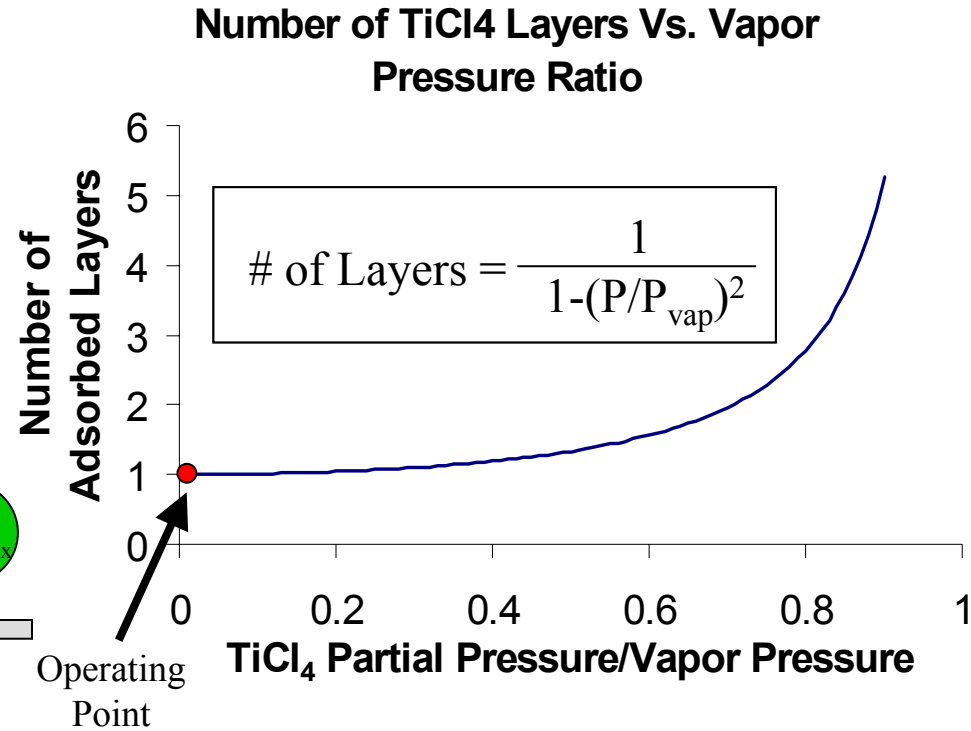
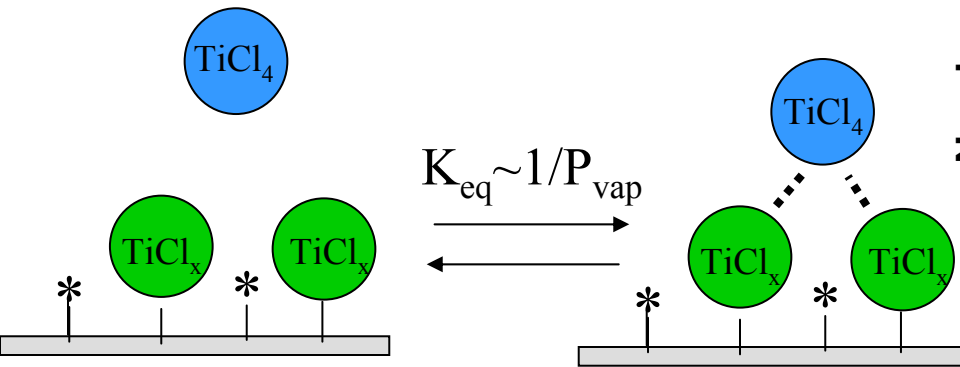


- QCM measures Δf
 - $\Delta f \propto \Delta m$
- Given Δm and assumptions
 - $\Delta m \rightarrow \Delta(\text{TiCl}_2, \text{Cl}, \text{N})$
- Given $\Gamma_{\text{TiCl}_4}, \Gamma_{\text{D}}, \Gamma_{\text{N}}$
 - $\Delta(\text{TiCl}_2, \text{Cl}, \text{N}) \rightarrow$ Reaction Prob's

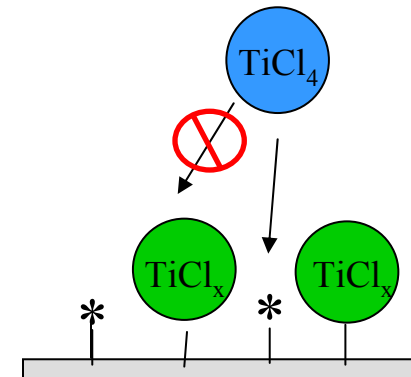


BET Isotherm - Avoiding Condensation

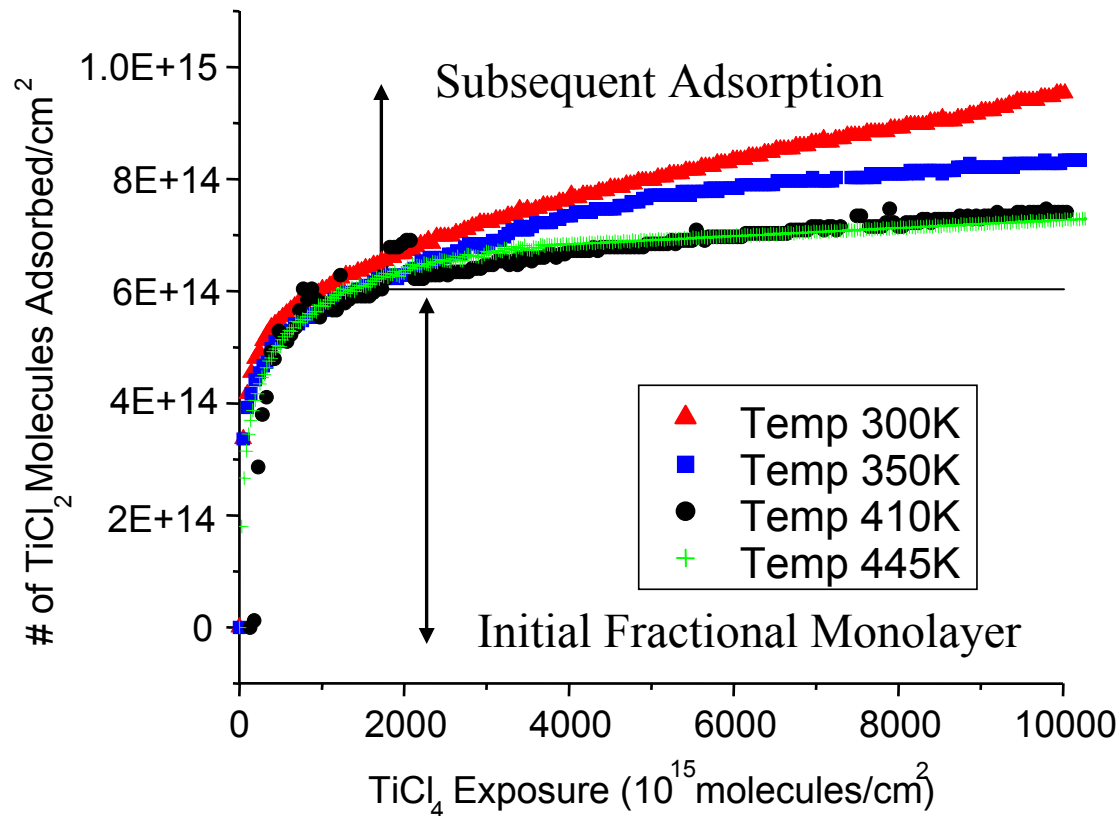
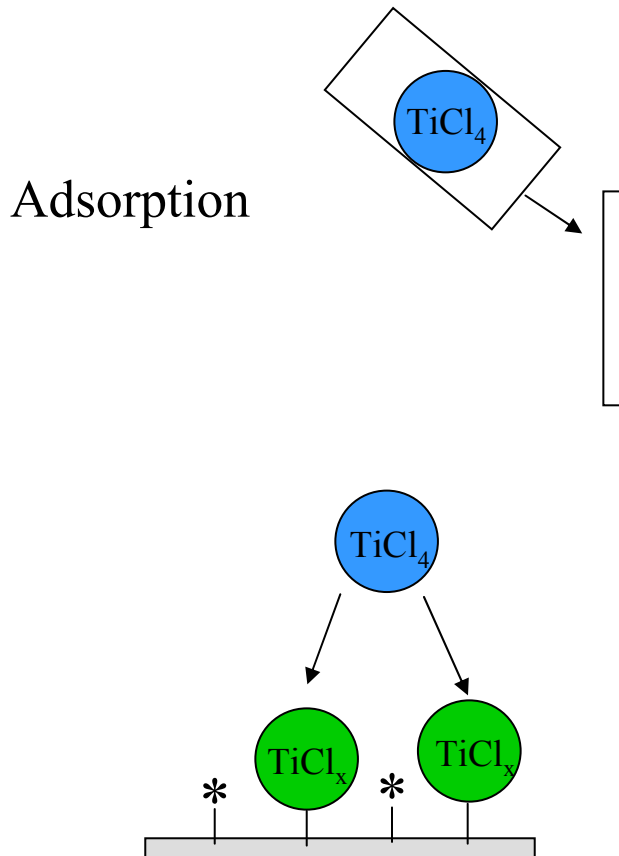
- BET Isotherm is an **equilibrium** calculation
- Assumes surface interactions of multilayers similar to liquid phase



- Adsorption inconsistent with multilayer adsorption (equilibrium)
 - $P/P_{\text{vap}} \sim 4 \times 10^{-3}$
- Suggests all measured adsorption is chemisorption on initial surface



Precursor Adsorption



- Two distinct uptake regimes
 - Initial rapid ads. followed by significantly slower ads.
- Increase in substrate temperature reduces term adsorption rate for high exposures

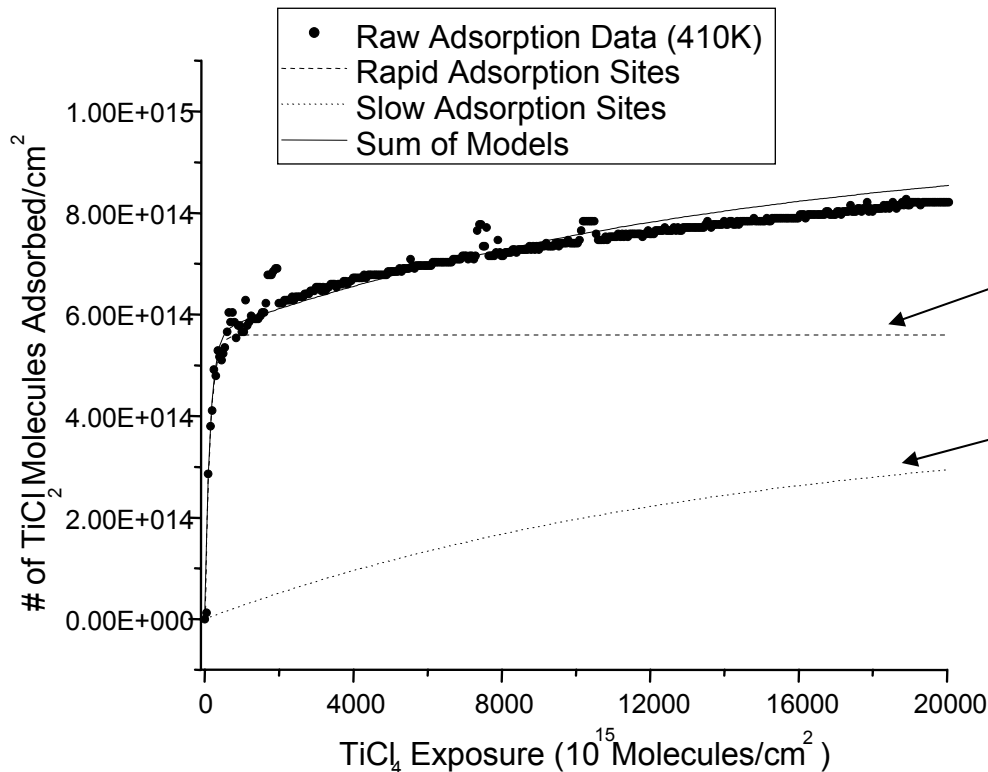
Adsorption Model

- Increase in substrate temperature increases desorption more rapidly than diffusion^{1,2}

- Two Site Model Fit to Data

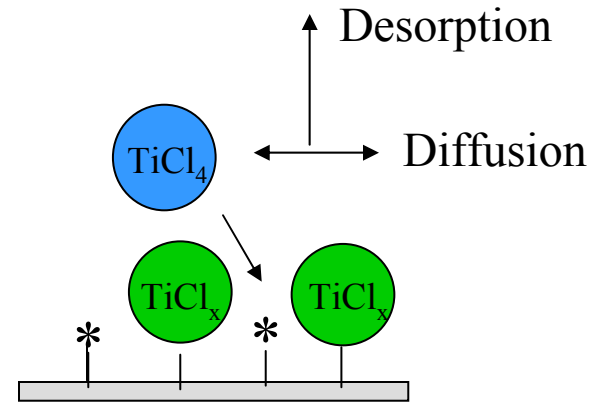
- Sticking probabilities

- Active site (*) densities



Unhindered sites rapidly filled by TiCl_4

Hindered sites slowly filled by TiCl_4
(thermally activated process)

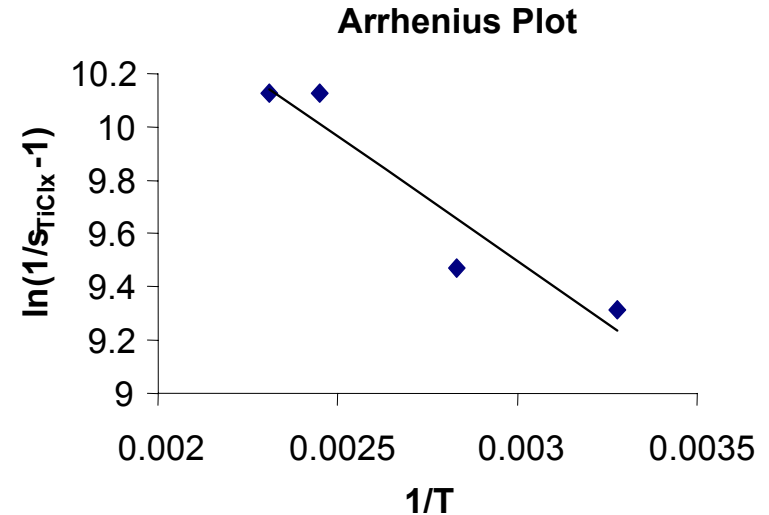


¹Widdra, W.; Yi, S.I.; Maboudian, R.; Briggs, G.A.D.; Weinberg, W.H., *Phys. Rev. Let.* **74(11)**, 1995

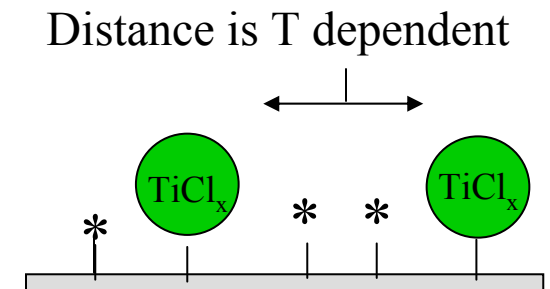
²Kota, G.P.; Coburn, J.W.; Graves, D.B., *J. Appl. Phys.* **85(1)**, 1999.

Adsorption Model Results

Temp (K)	s(TiN) initial sticking	s(TiCl _x) hindered sticking	Site Density (#/cm ²)
300	$6 \pm 2 \times 10^{-3}$	$1 \pm 0.2 \times 10^{-4}$	5×10^{14}
350	$6 \pm 2 \times 10^{-3}$	$9 \pm 2 \times 10^{-5}$	5×10^{14}
410	$6 \pm 2 \times 10^{-3}$	$6 \pm 2 \times 10^{-5}$	5×10^{14}
445	$6 \pm 2 \times 10^{-3}$	$6 \pm 2 \times 10^{-5}$	5×10^{14}

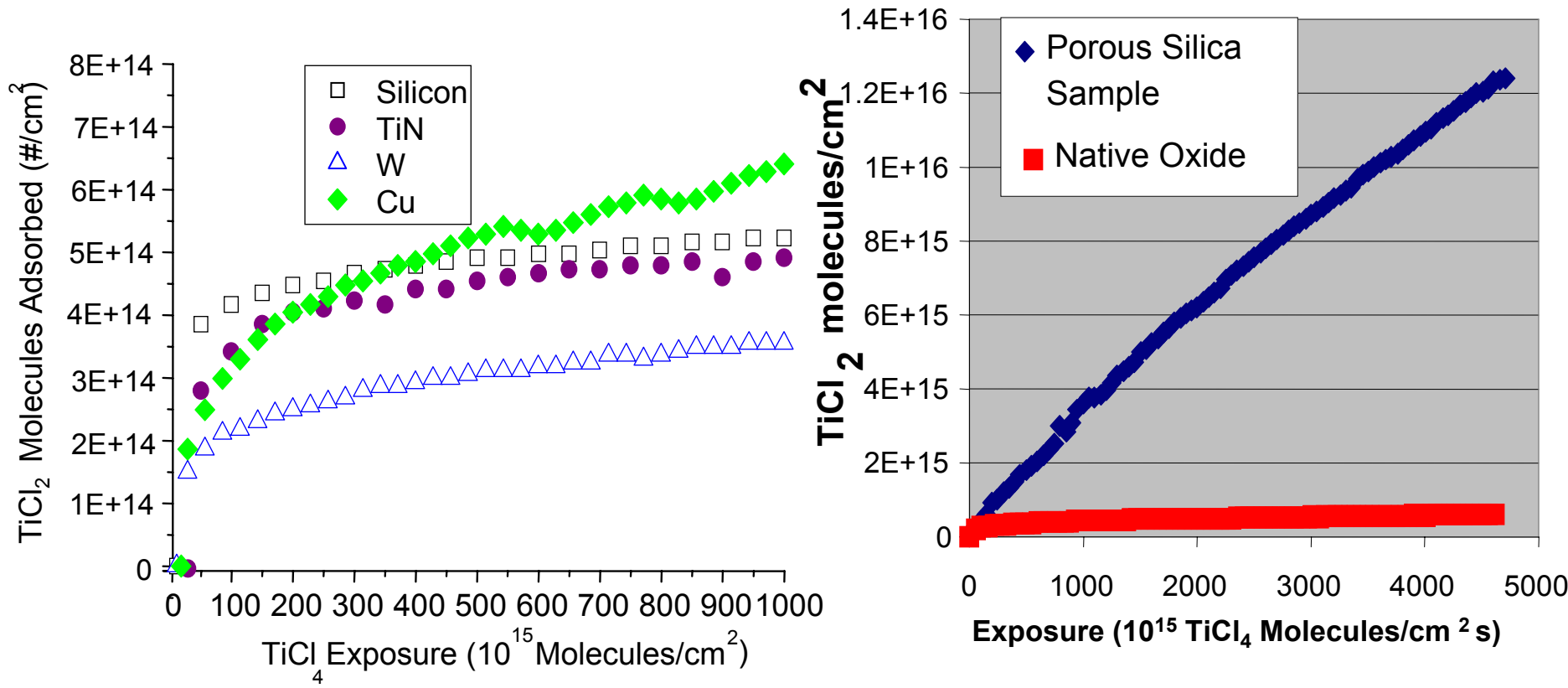


- $E_{\text{act}} = -0.08$ eV, consistent with other processes
- Initial sticking ~ 100 x hindered sticking
 - Contributes to uniformity
 - ± 3 Å for 20nm thick film
- Hindered sticking decreases with inc. T
 - Coverage appears more uniform (monolayer-like)
 - Less surface coverage achieved

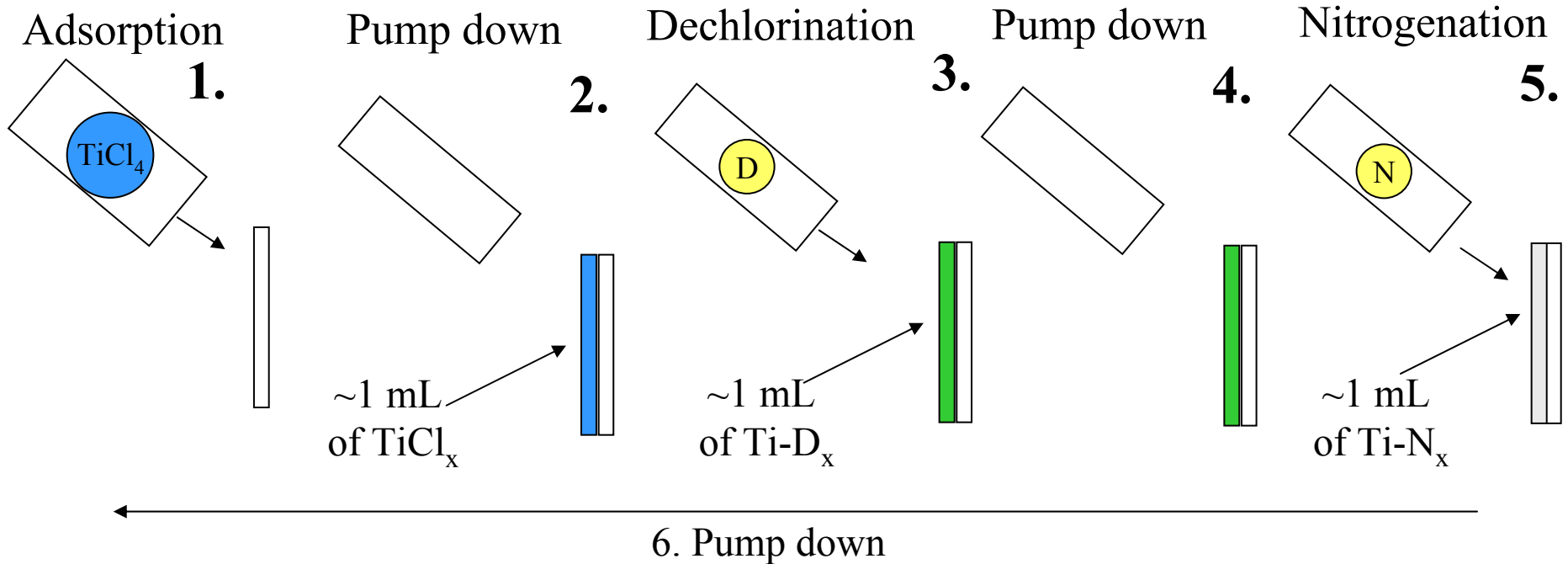


Adsorption on Different Surfaces

- Two regimes of adsorption not unique to Si surface
- Same qualitative behavior observed for TiN, W, Cu, and SiO₂
- Porous material ($\epsilon=0.5$, $d=2.5\text{nm}$) behaves much differently due to larger surface area

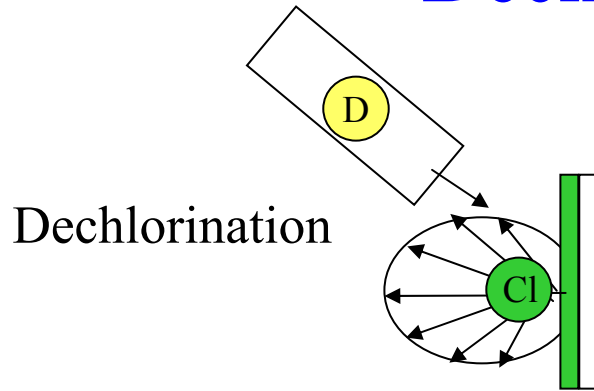


Experimental Procedure



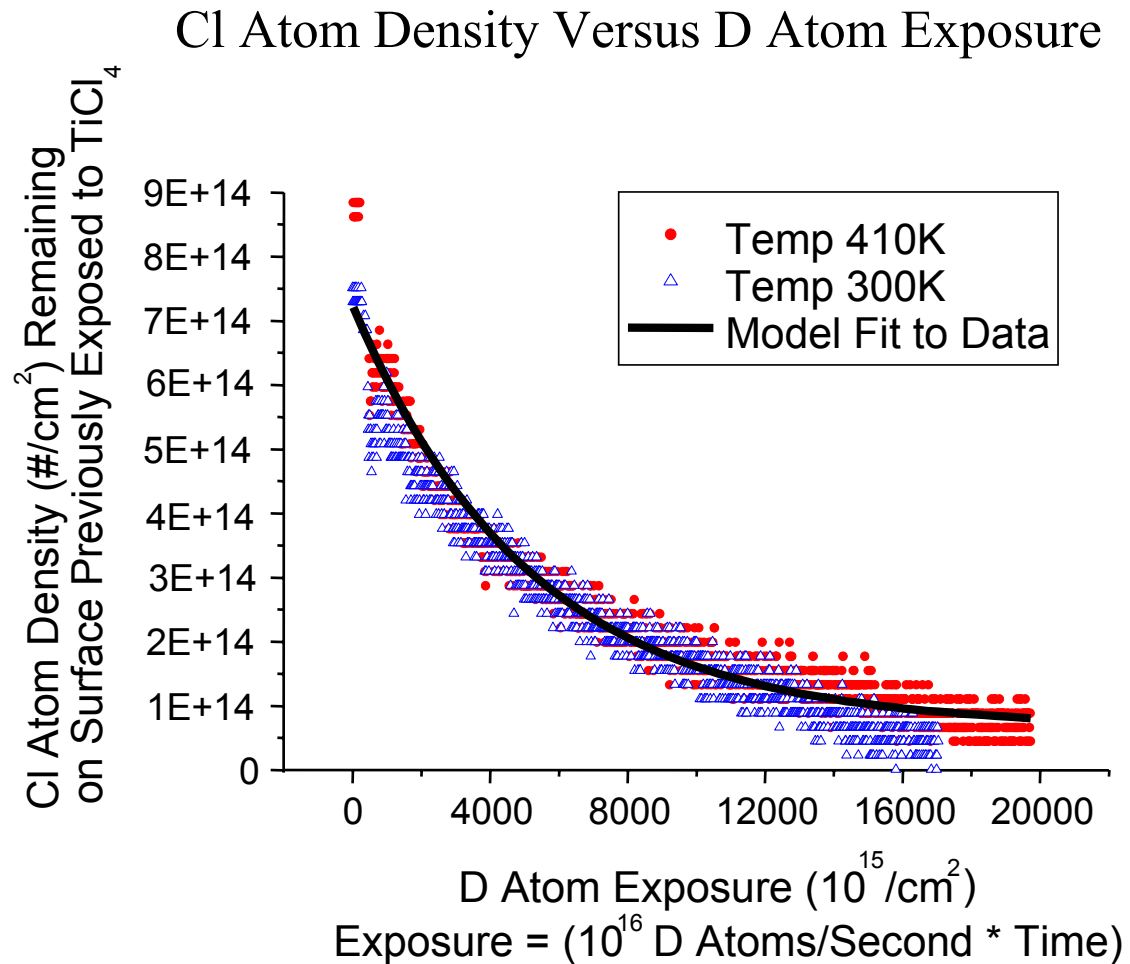
- Conventional ALD-like sequence
 - Each step in process monitored *in-situ* with QCM
 - Resulting films removed for *ex-situ* XPS analysis
- Surface temp varied (300K - 450K)

Dechlorination Results

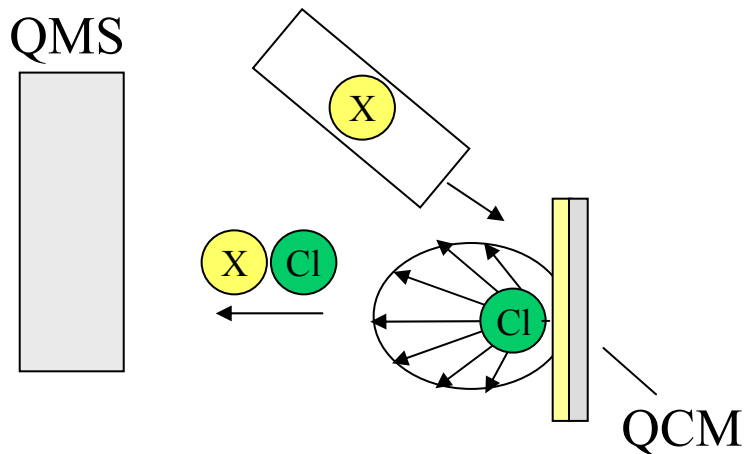


- Exp. decay in Cl surf. conc. fit assumes D abstracts and then replaces Cl

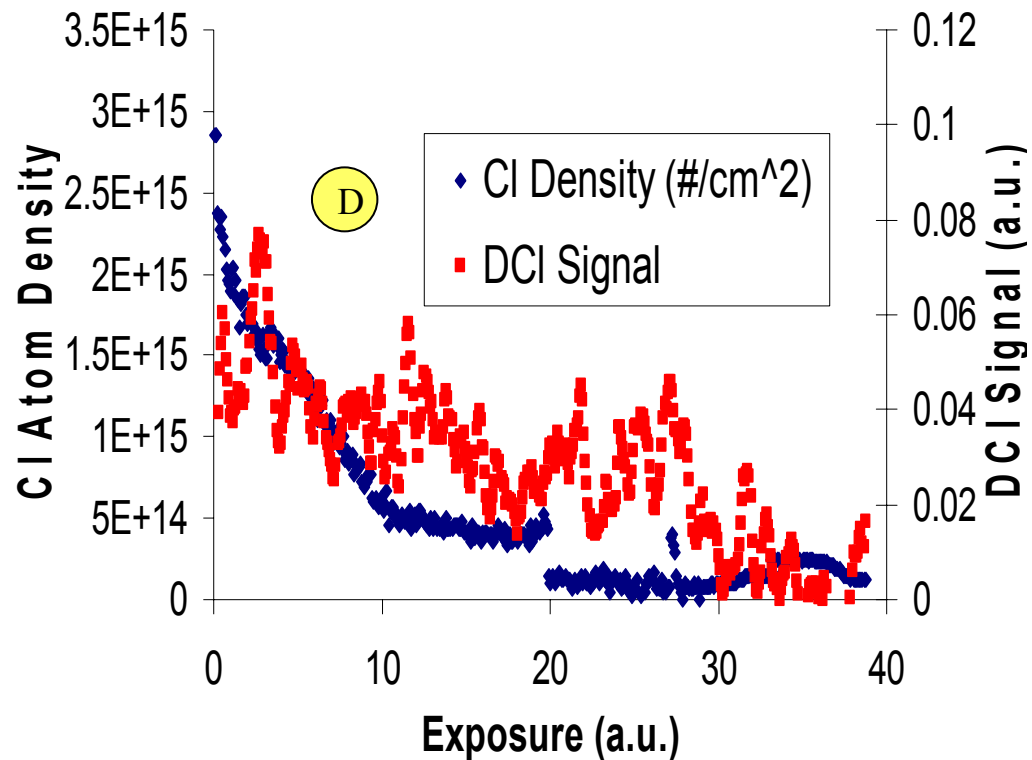
- $k_{D+Cl \rightarrow DCl} = 3 \pm 1 \times 10^{-4}$
 - Much lower than previously reported value for H abs. of Cl on Au (~ 0.1 at 25°C)¹
 - Fairly insensitive to T



Monitoring TiN Deposition with QMS

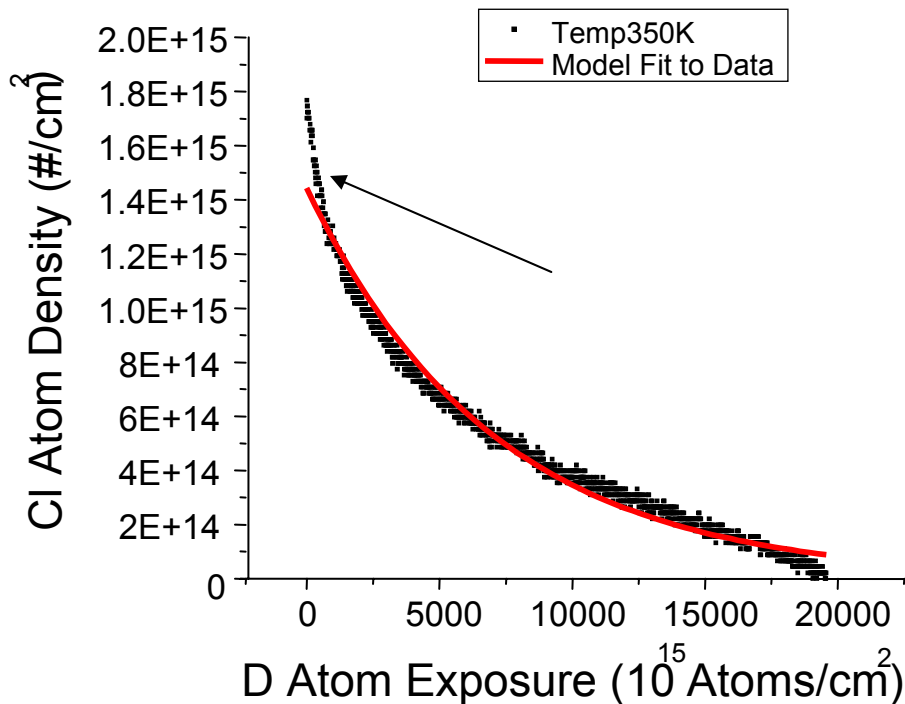
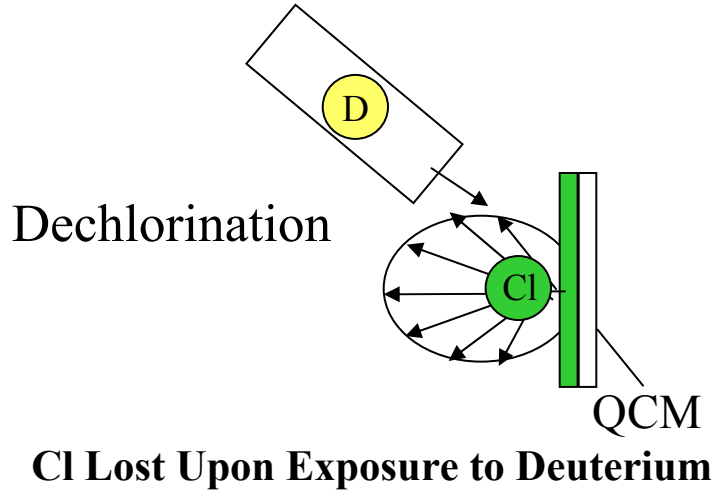


x = D from D_2
or H from NH_3



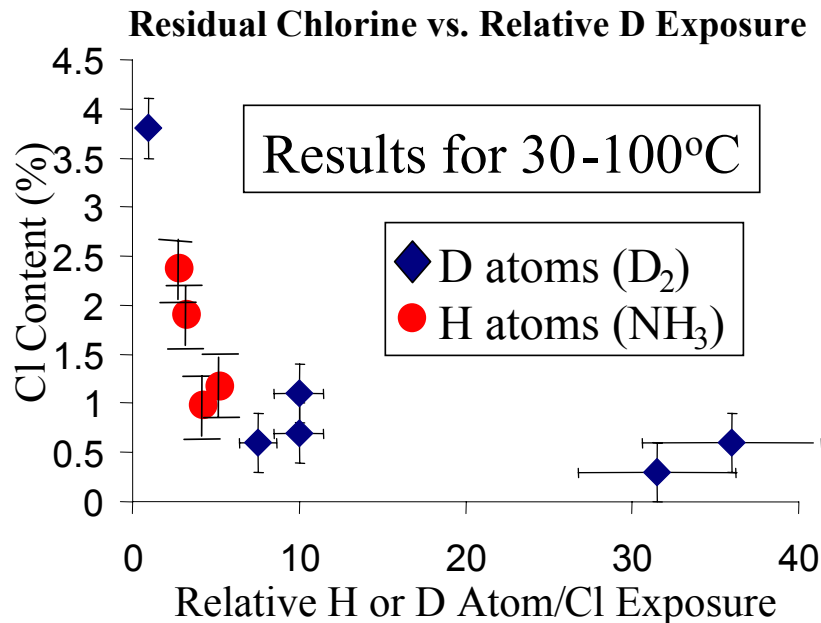
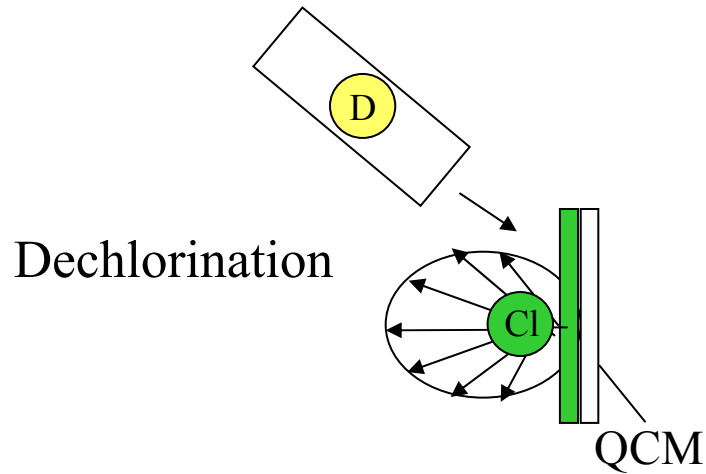
- QMS measures reaction products
 - DCI signal follows QCM data
 - HCl observed during H exposure

Dechlorination Results



- Calculated Cl density within a few% of ads. assumptions
 - Suggests TiCl_2 is appropriate surface species
- Disagreement between simple first order model and QCM for small exposures
 - Occurs when D step is preceded by long TiCl_4 exposure
 - Suggests two types of Cl bonds to surface
 - May be related to slowing in adsorption rate of TiCl_2 species

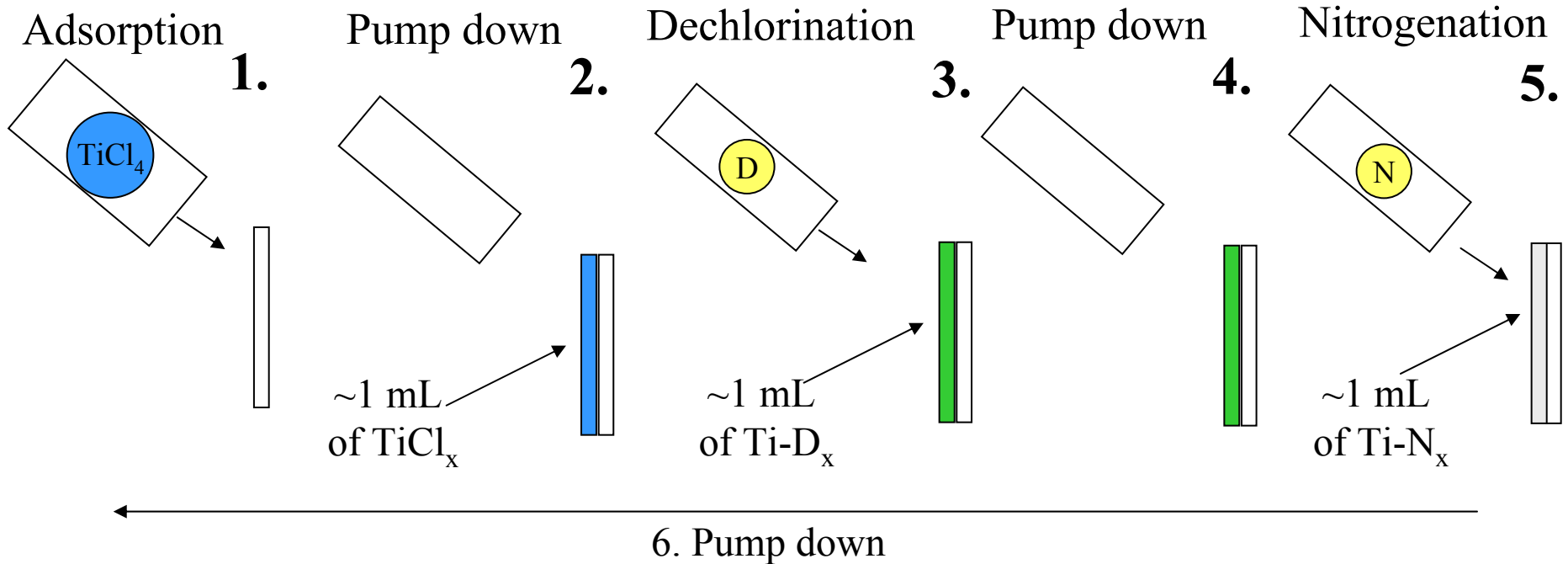
Dechlorination Results



- Residual Cl% can be controlled through $TiCl_4$ and D dosages
- Increasing relative D exposure time reduces Cl content to detection limit of XPS! (<0.3%)
- Comparable thermal ALD process yields 1.5% Cl at 400°C¹

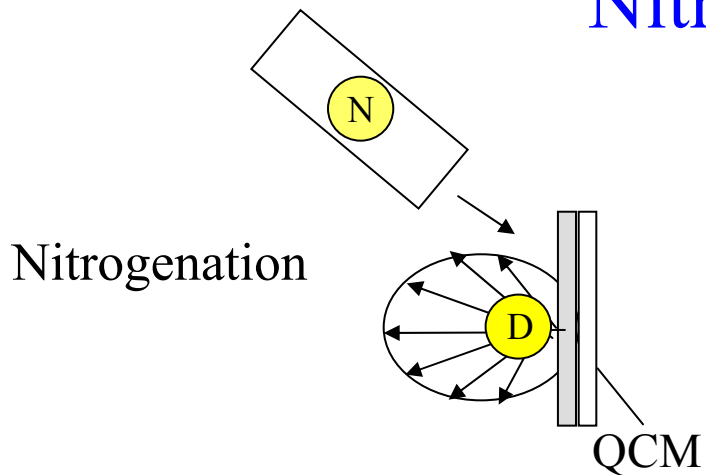
¹ Satta, A. *et al.* MRS 2000 Spring Meeting (Session D6.5)

Experimental Procedure



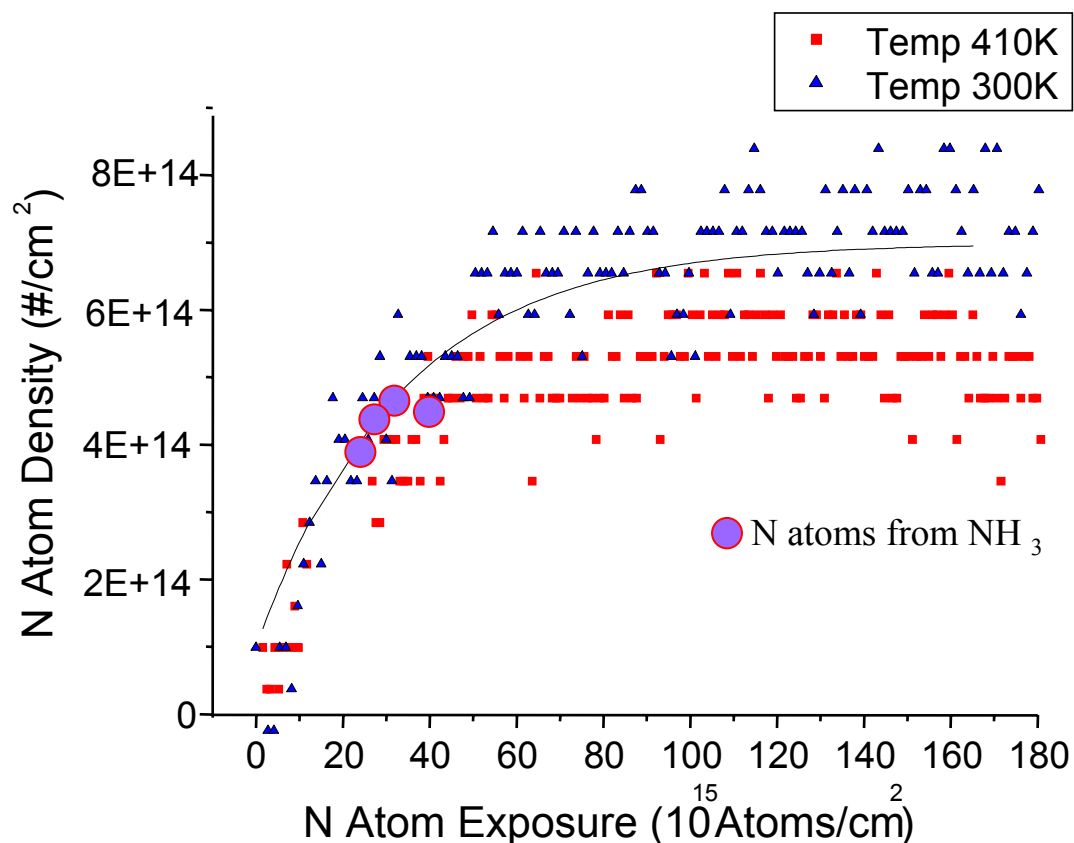
- Conventional ALD-like sequence
 - Each step in process monitored *in-situ* with QCM
 - Resulting films removed for *ex-situ* XPS analysis
- Surface temp varied (300K - 450K)

Nitrogenation of Film



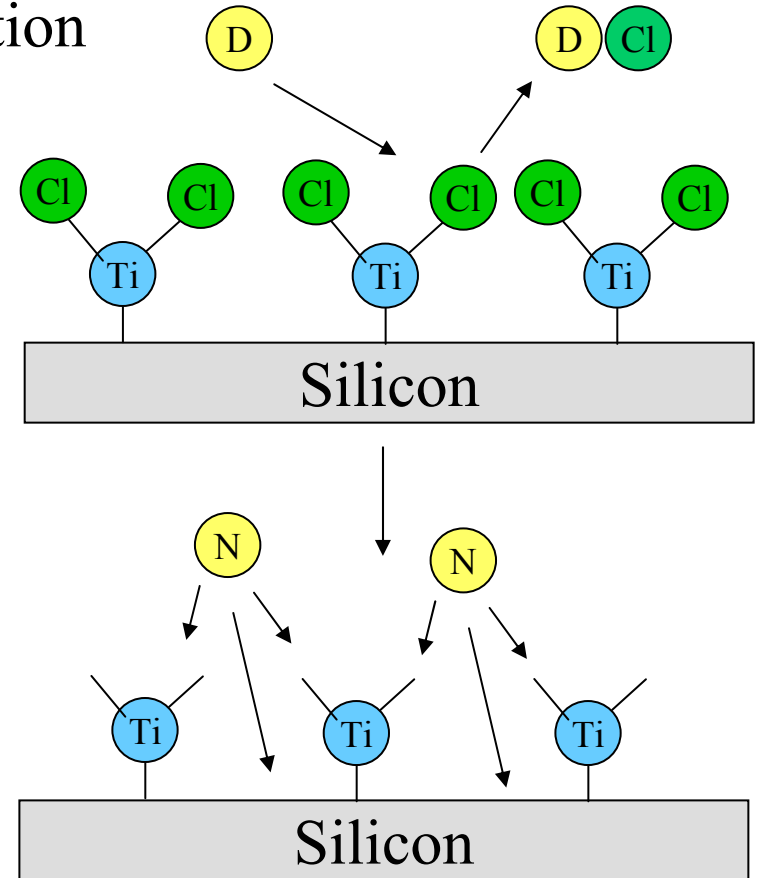
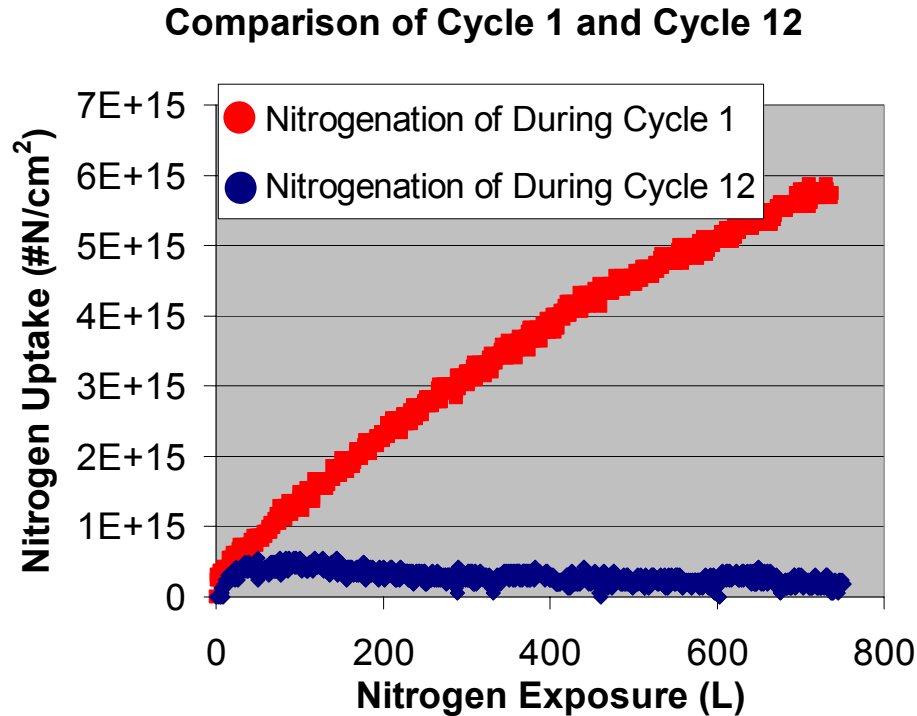
- Nitrogen atoms quickly saturate film
- Simple model predicts rxn. probability ~ 0.01
- Small mass change (N replaces D) difficult to detect
- No apparent temperature dependence

N Atom Density Versus N Atom Exposure



Nitrogenation Results

- Difference observed in N atom addition

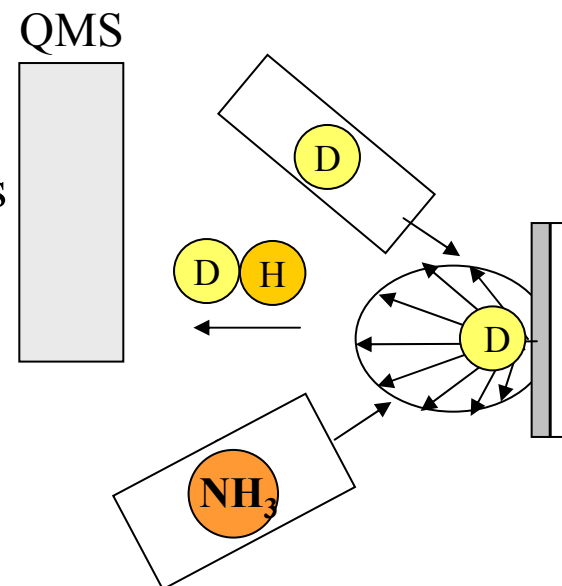
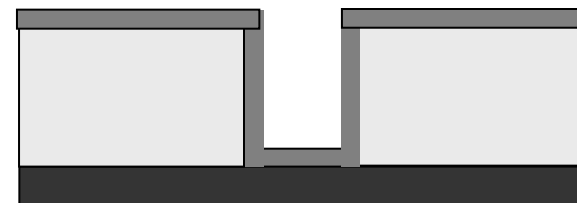


- Si left exposed during N atom step
- Excess nitrogen likely adsorbed by Si substrate¹
- *ex-situ* XPS measurement after 20 cycles shows N/Ti ~ 3
- Potential issue for sensitive substrates ($\text{Si}_3\text{N}_4 \rightarrow$ insulating)

¹H. Niimi, and G. Lucovsky, G., *JVST B* 17 (6) 1999.

Loss of Reactants in RE-ALD Systems

- Hydrogen radical recombination different on different surfaces
 - $\gamma_{\text{HH}} \sim O(10^{-4})$ on stainless steel chamber¹
 - $\gamma_{\text{HH}} \sim O(0.1)$ on silicon (etching also important)²
- REALCVD system used to test H radical recombination on TiN
 - Simulates reactions on feature sidewalls
 - $\gamma_{\text{DH}} \sim 0.04 \gg k_{\text{DCl}} (3 \times 10^{-4})$
 - Much of D from plasma lost in ineffective channels
- N recombination difficult to measure in this system
 - $\gamma_{\text{NN}} \sim O(0.1)$ for stainless steel chamber³
 - Likely important process on TiN



¹R. Grubbs, *et al.* AVS 2002 Fall Mtg. (TF+VT WeM4).

²J. Abrefah and D.R. Olander. *Surf. Sci.* 209, 201 (1989).

³H. Singh, D.B. Graves, *JAP* 38 (6) 2000.

Conclusions

- Low temperature processing questions
 - Precursor (TiCl_4)
 - Adsorption monolayer-like over the range of surface T investigated
 - Adsorption saturation approached more rapidly at lower temperatures
 - Radicals (D,N)
 - D radicals can reduce Cl content to $< 0.3\%$
 - N radicals likely nitride underlying substrate during first few cycles
 - H radical recombination coefficient much higher in feature than on chamber walls
- Promising approach for low surface T, highly conformal deposition
 - Organic thin film devices, MEMS, Nanotechnology

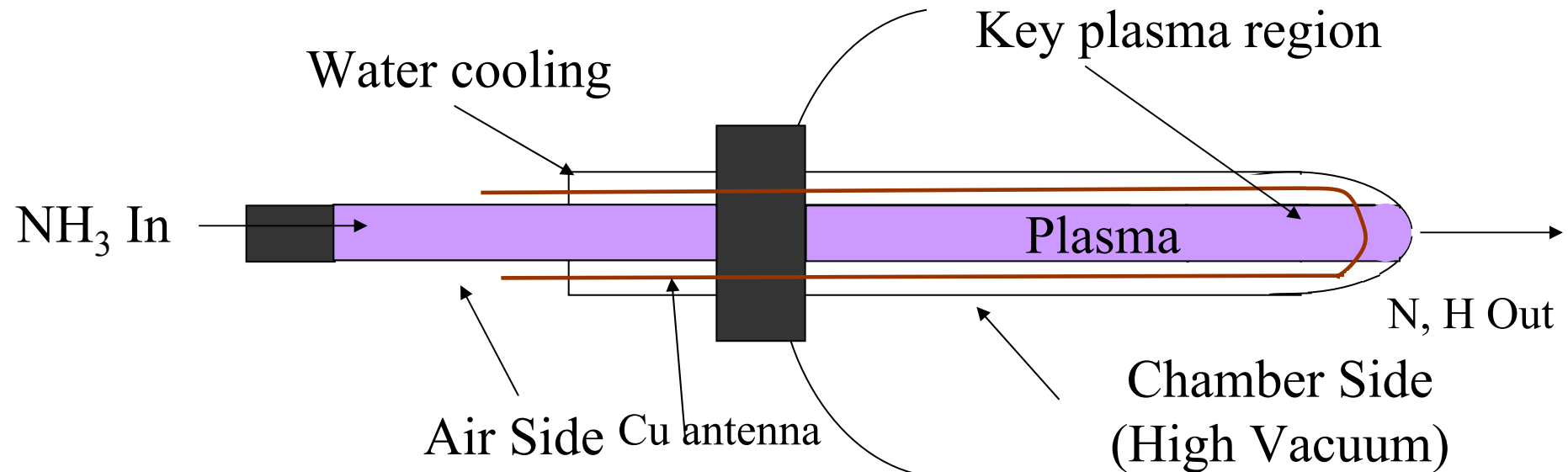


Acknowledgments

- Funding
 - UC SMART, NSF-SRC ERC, SEMATECH, NSF
- Equipment/Materials Donations
 - IBM, Lam Research Corporation, Novellus Systems
- Helpful Discussions
 - Dr. A. Sherman
 - Prof. T. Sands, Prof. E. Iglesia
- Analytical Help
 - UC Berkeley/Lawrence Berkeley National Lab (XPS)
 - Prof. J. Reimer
- Undergraduate Research Help
 - M. Chin, E. Chen, D. Bernards, C. Su, L. Tagawa, S. Boyce, P. Tabada, A. Tam, D. Tsang, C. Chi, R. Tsang, D. Tolentino

Inductively Coupled Plasma Radical Source

- Source design
 - Powered at 13.56 MHz
 - Projects into chamber to maximize radical flux to surface
 - Distance from sample ensures ion flux is negligible
- Important qualitative observations
 - Five turn coil in key plasma region needed to dissociate N_2
 - Repeated cycling of source leads to deposition of TiN in key plasma region
 - Requires etching with Cl plasma or HCl to remove



Process time/pressure predictions

Assumptions:

- 2 seconds allowed per step
- Reaction goes to 99.9% of completion

Example for H abs. of Cl:

$$\sigma \frac{d\theta}{dt} = -k\Gamma \theta$$

$$\theta = \exp\left(-\frac{k\Gamma}{\sigma} t\right)$$

where θ = Cl fractional coverage

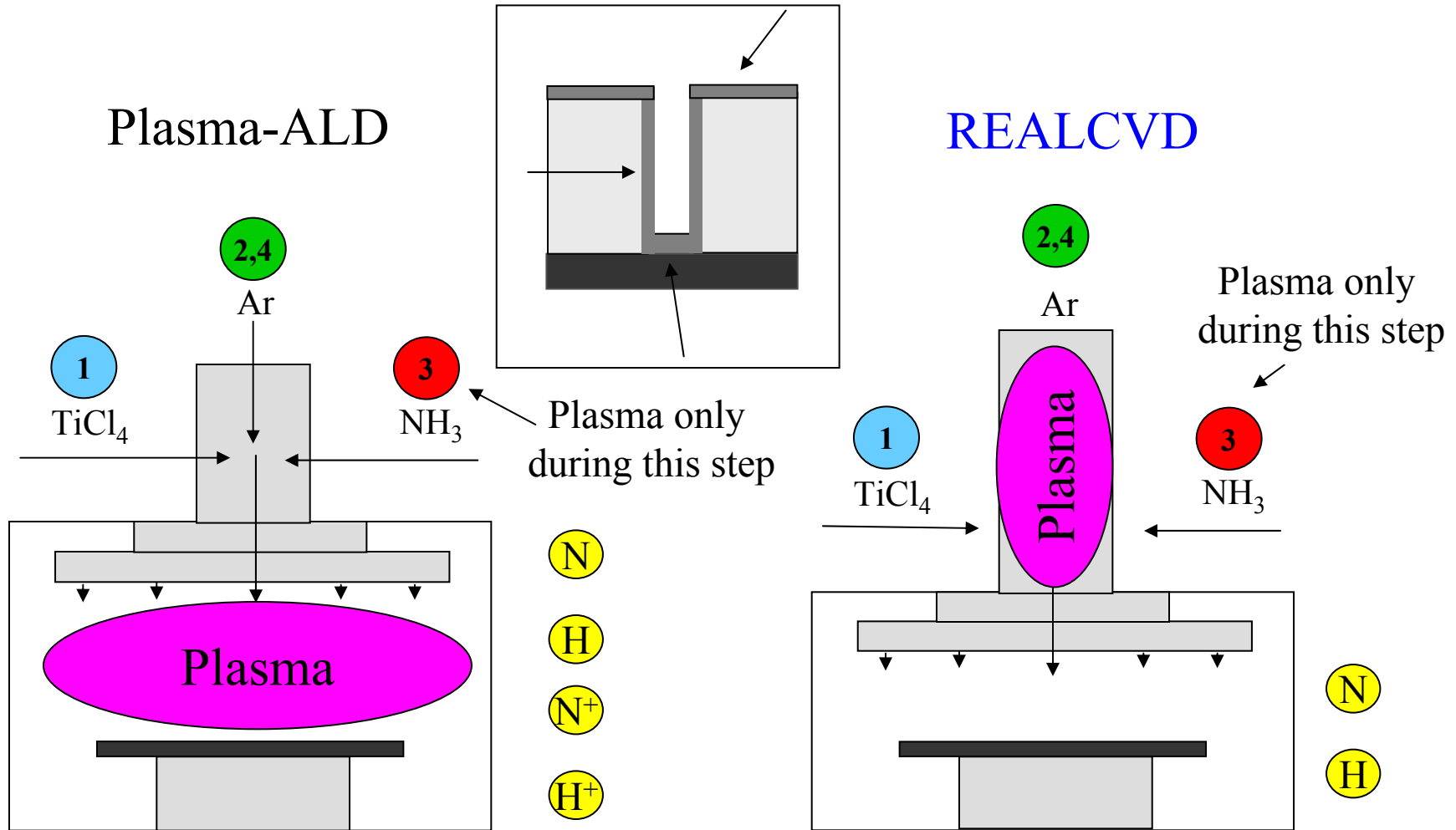
Γ = Flux of H to surface from plasma

σ = Number of Cl sites per cm^2

t = Exposure time

Reaction Step	Reactant Partial Pressure (mtorr)	Reactant Flux to Surface ($\#/\text{cm}^2/\text{s}$)
TiCl ₄	~1.5	2.2×10^{17}
H	~6	1.2×10^{19}
N	~0.4	2.2×10^{17}

Cal Differences Between REALCVD and Plasma-ALD



- Substrate immersed in plasma
- $E_{\text{ion}} \sim 10 \text{ eV}$
- ion flux = highly directional

- Substrate located downstream of plasma
- $E_{\text{rad}} \sim 0.052 \text{ eV}$
- radical flux \sim isotropic