Fundamental Beam Studies of Radical Enhanced Atomic Layer CVD (REALCVD)

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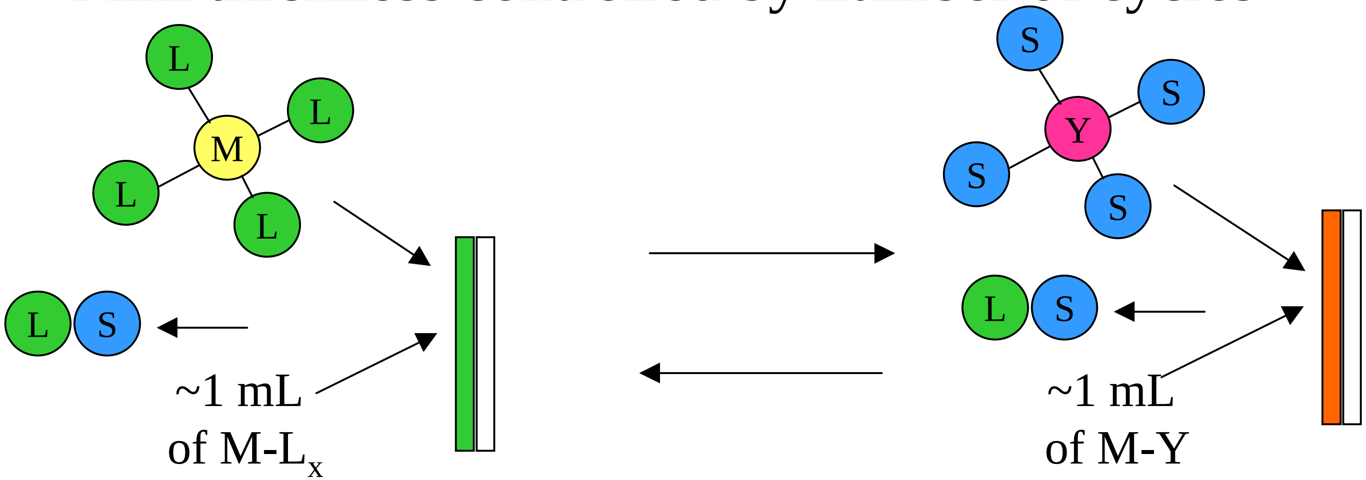
What is A.L.D.?

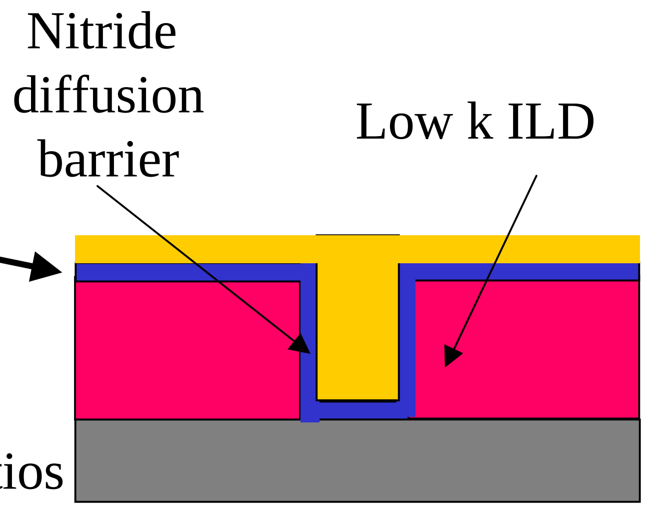
- Atomic Layer Deposition
  - A.K.A. – Sequential Deposition, MOALD, ALE, …
  - Usually a two step process
    - Chemisorption of a metallic precursor
    - Reactive ligand stripping by reactive stable molecule
  - Distinguishing feature → Each step is self-limiting
  - Film thickness controlled by number of cycles



Barrier Layer Deposition by A.L.D.

<u>Key Issues:</u>

Barrier Properties
Conductivity
Conformality
Thermal budget



Currently deposited via i-PVD

- Step coverage is a major challenge for high aspect ratios

<u>Barrier layer A.L.D. Results</u>

- $TiCl_4 + NH_3$ [1]
  - Resistivity is good (<500 μΩ cm)
  - Cl Content higher at lower T
    - 1.5% @ 400°C, 3.0% @ 350°C
    - 0.5% @ 500°C
- $TaCl_5 + NH_3$ [2]
  - Resistivity is bad (500,000 μΩ cm)
    - Due to formation of Ta_3N_5
  - Cl Content acceptable
    - <1% @ 400°C

3. $TDMAT + NH_3$ [3]
   - 180°C deposition T
   - Good barrier results, no conductivity information

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

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

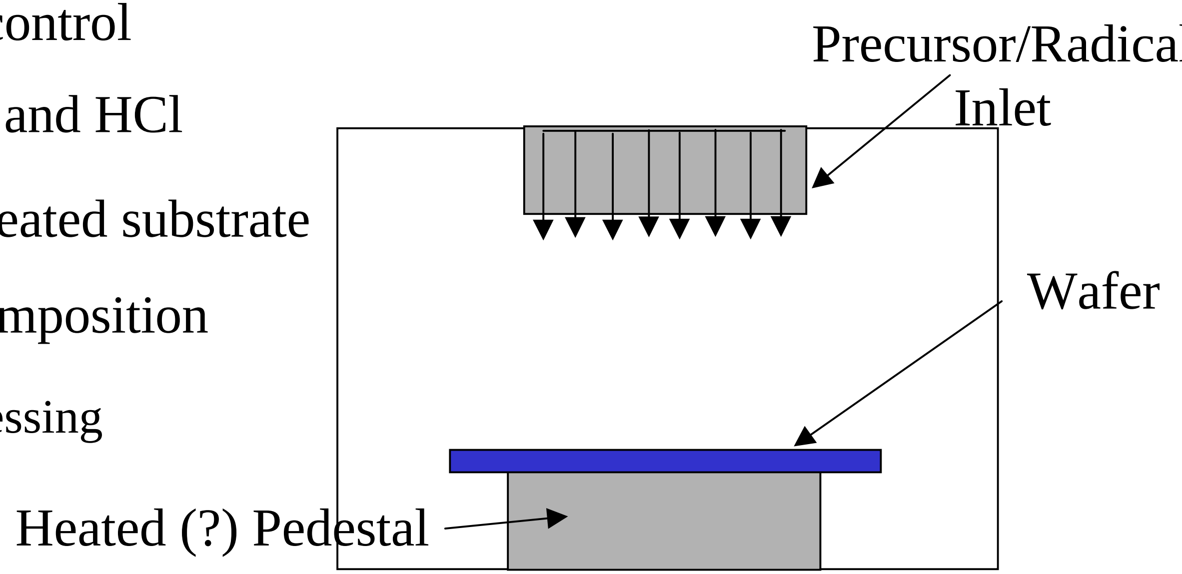
3. Min *et al.*, *JJAP* 1998

Radical Enhanced Atomic Layer CVD (REAL CVD)[1]

- Uses a volatile precursor and a radical source to deposit a film
- Reactants introduced in separate steps to achieve atomic layer control
- Products are nitride film and HCl
- Radical flux instead of heated substrate catalyzes precursor decomposition
  - Potentially lower processing temperatures

Step 1: $TiCl_{4\,(g)}$

Step 2: $TiCl_{x\,(ab)} + XH^{*}_{(g)} + N^{*}_{(g)} \rightarrow TiN_{(s)} + X\,HCl_{(g)}$



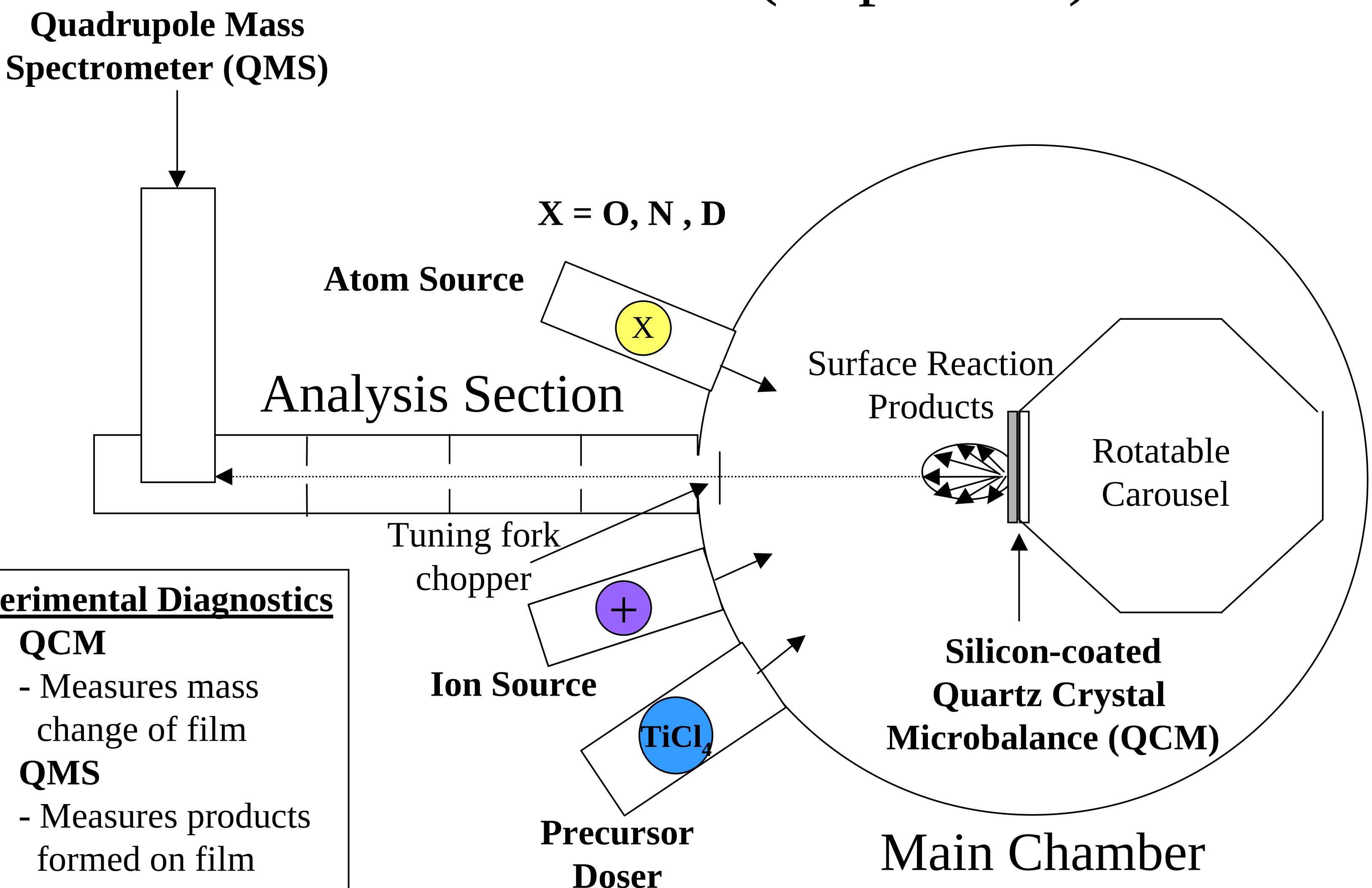
[1]A. Sherman U.S. Patent 1999.

REALCVD Questions

- Low temperature processing questions:
  - Precursor
    - How and when is monolayer-like adsorption achieved without precursor condensation?
  - Radicals
    - Are radicals sufficiently reactive to remove ligands from precursors?
    - Are radicals sufficiently unreactive to stop after one ML of reaction?

- Must determine the following:
  - $TiCl_4$ sticking probability
  - D abstraction probability for Cl removal
  - N insertion probability
  - Relative REALCVD ESH impact compared to other processes
  - Relative REALCVD ESH impact for different precursors/processes

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

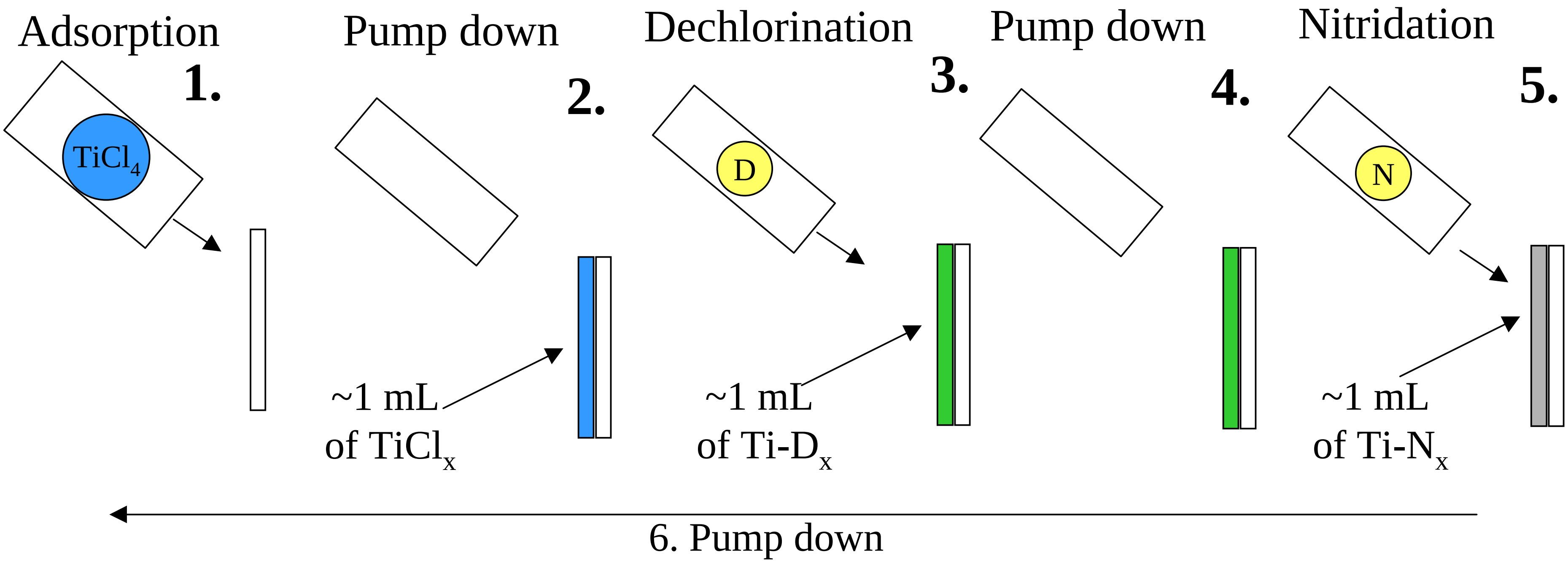


<u>Experimental Diagnostics</u>

- **QCM**
  - Measures mass change of film
- **QMS**
  - Measures products formed on film
  - Characterize beams

- Deuterium used to due to easier characterization in QMS

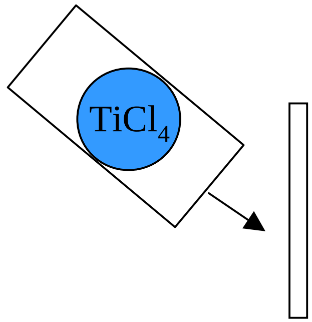
Experimental Procedure



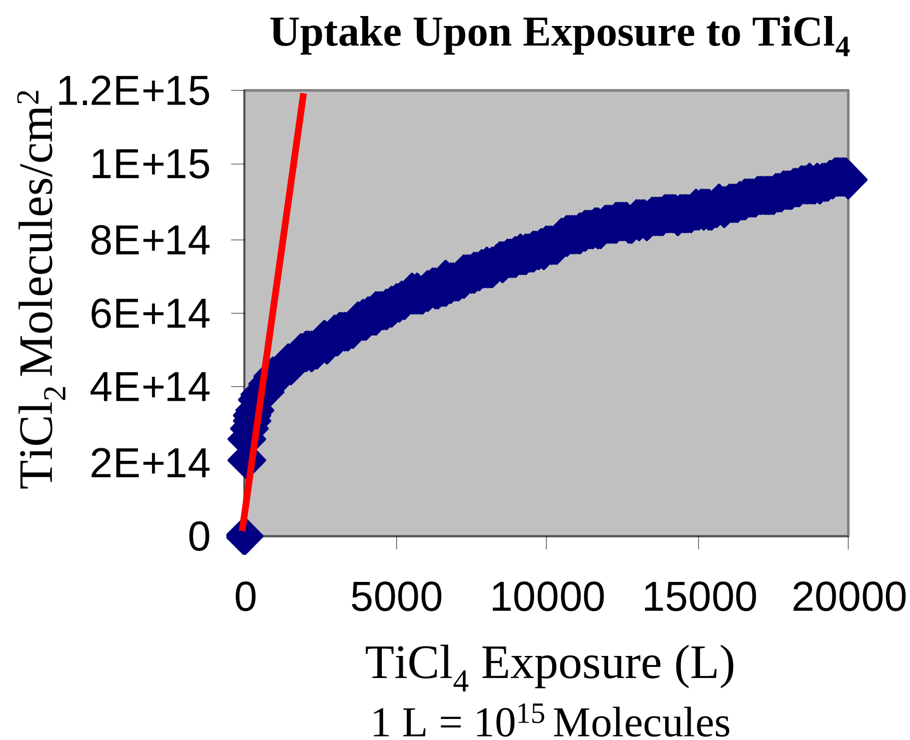
- Conventional ALD-like sequence
  - Each step in process monitored *in-situ* with QCM
- Surface temp varied (32-135 ^{o}C)

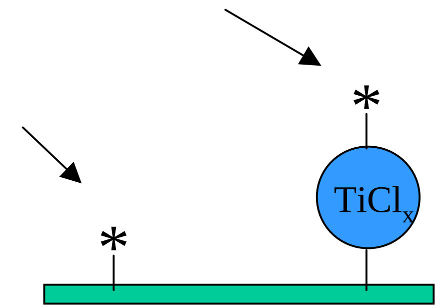
Precursor Adsorption QCM Results

Adsorption



- Two distinct uptake regimes
  - Initial rapid ads. followed by significantly slower ads.
- Adsorption may not be confined to a single monolayer
- Data fairly well represented by assuming precursor adsorbs two monolayers of $TiCl_2$ *
- Model fit allows estimation of:
  - Sticking probabilities
  - Active site (*) densities

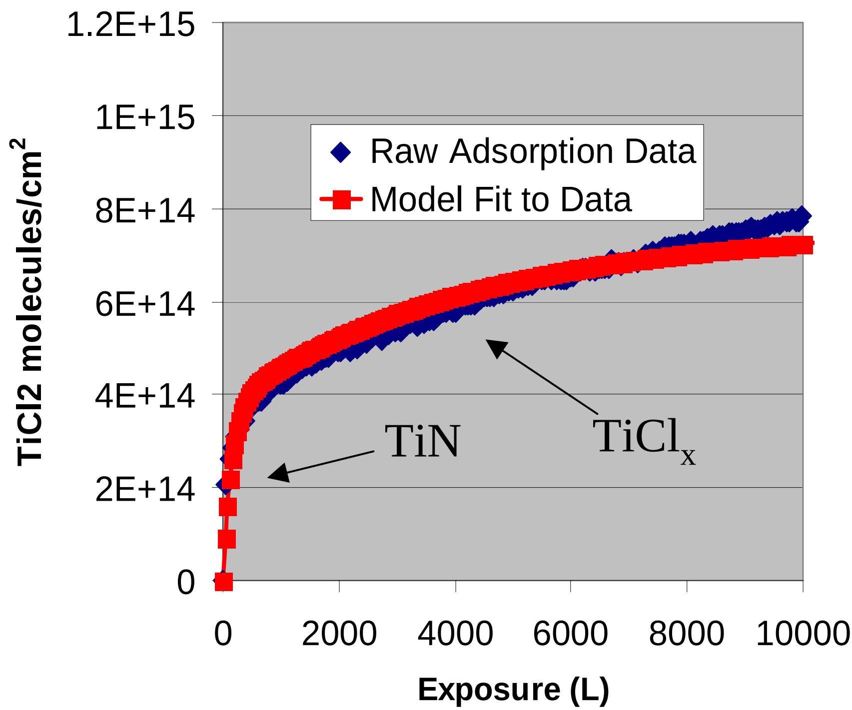




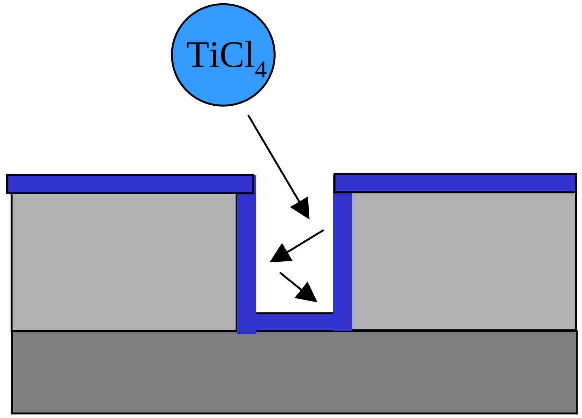
* Suntola, T. *et al.* 1996

Adsorption Model Results

Temperature (°C)	s(TiN) initial sticking	s($TiCl_x$) self sticking	Site Density (#/cm^2)
32	$8x10^{-3}$	$1x10^{-4}$	$5x10^{14}$
80	$8x10^{-3}$	$9x10^{-5}$	$5x10^{14}$
135	$8x10^{-3}$	$6x10^{-5}$	$5x10^{14}$

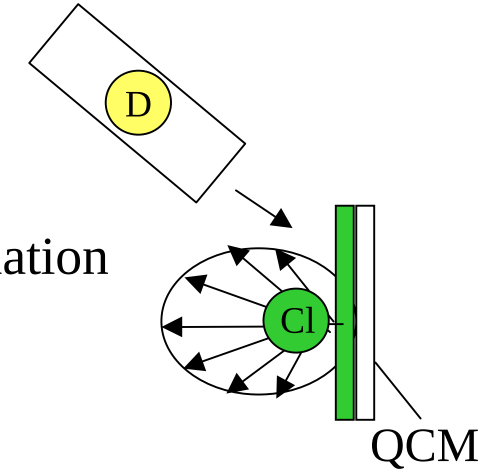


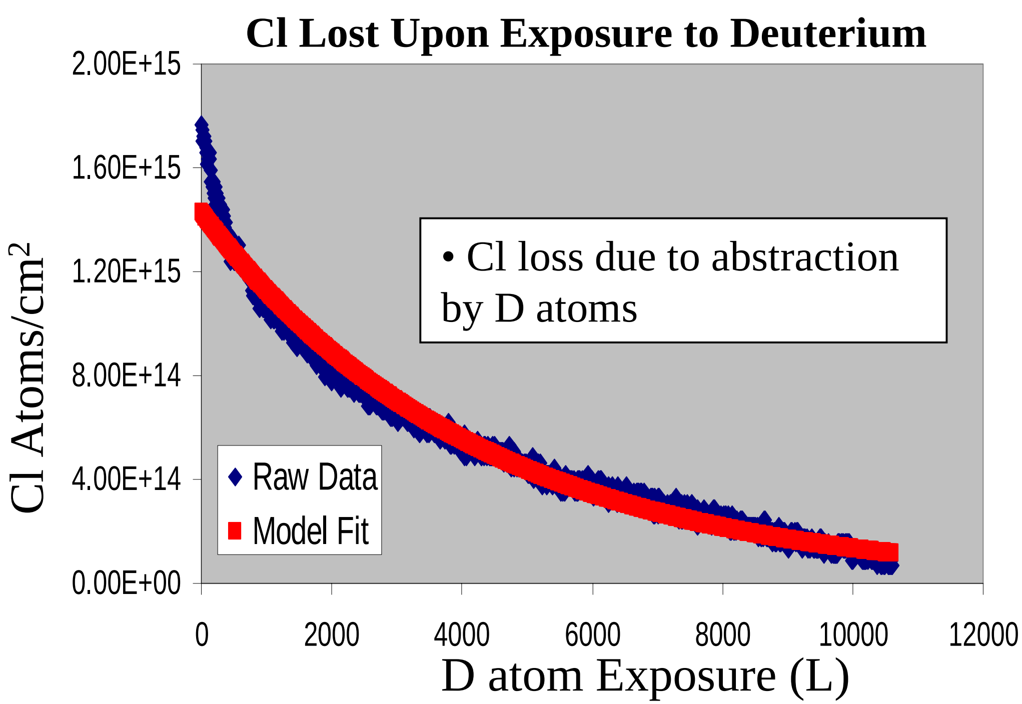
- initial sticking ~ 100x self sticking
  - contributes to uniformity
- self sticking decreases with inc. T
  - coverage is more monolayer-like at higher temperatures



Dechlorination Results

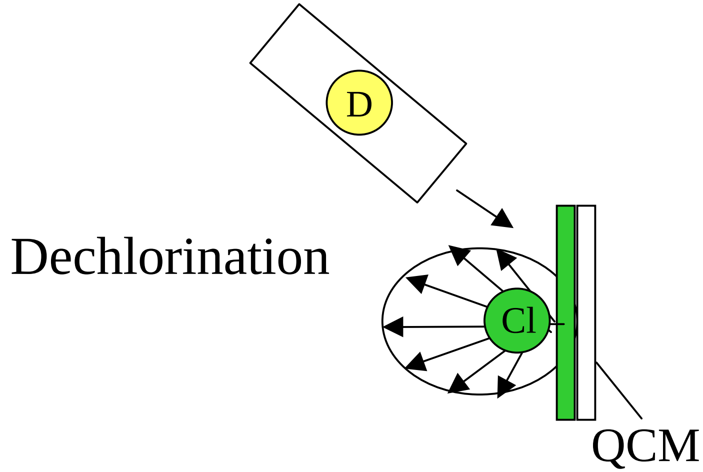
Dechlorination

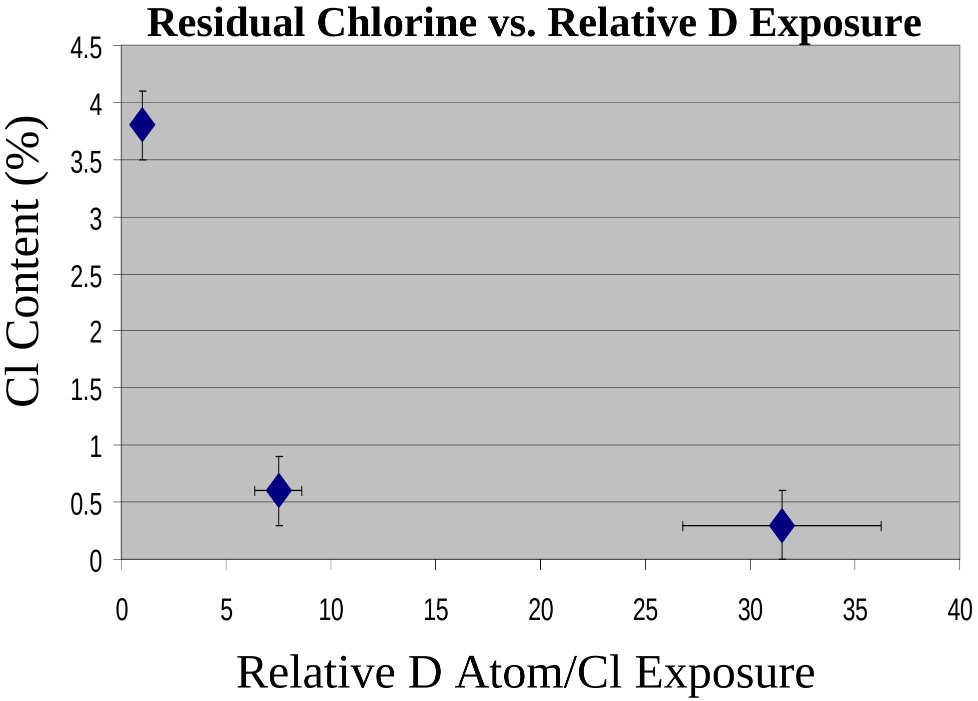




- Exponential decay in Cl surface conc. fit assuming replacement of Cl with D
  - $k_{D+Cl \rightarrow DCl} = 3x10^{-4}$
  - Fairly insensitive to T
- Calculated removed Cl density within a few% of ads. assumptions
  - Suggests $TiCl_2$ is appropriate surface species

Dechlorination Results



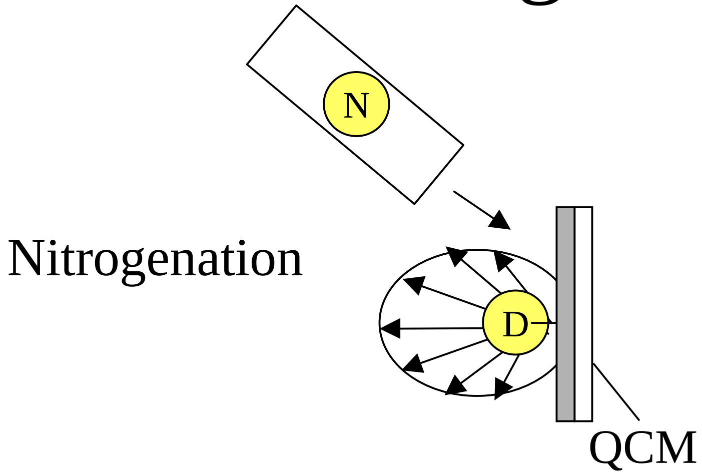


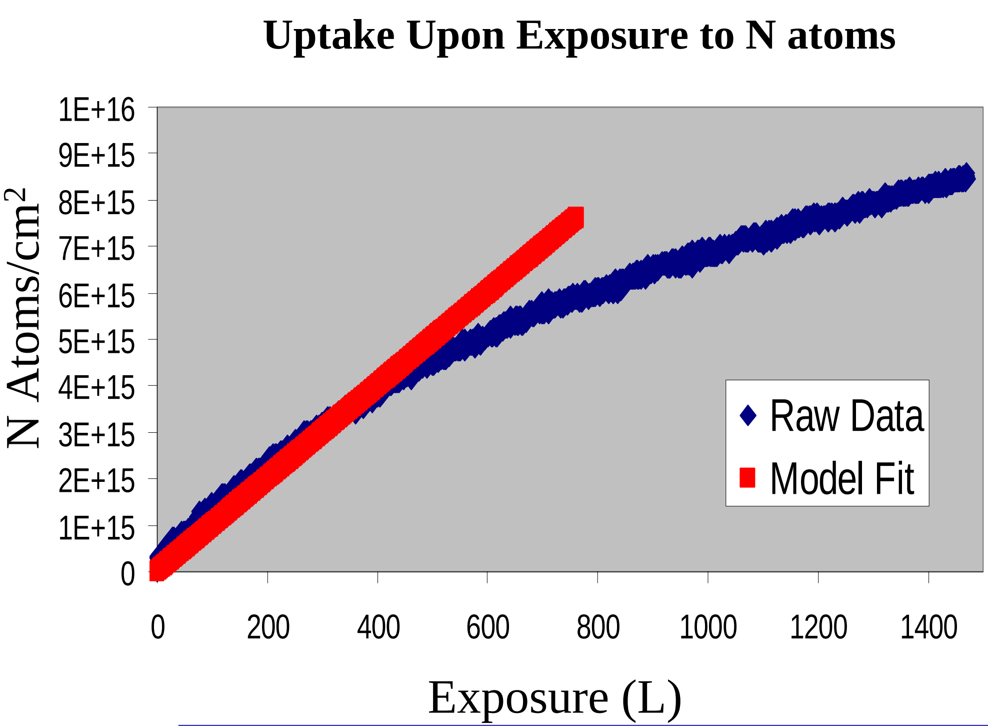
- Residual Cl% can be controlled through $TiCl_4$ and D dosages
- Increasing relative D exposure time reduces Cl content to detection limit of XPS! (<0.3%)
- Comparable thermal ALD process yields 1.5-3% Cl at 400^{o}C and 350^{o}C, respectively[1]
- Previously reported REALCVD of Ti shows Cl% "in the low percentage range"[2]

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

[2] Rossnagel, S.M. *et al.* *JVST B* **18**(4) 2000.

Nitrogenation Results





- Nitrogen uptake does not seem to saturate
  - *ex-situ* XPS shows N/Ti > 1
- Initial uptake of nitrogen fit to linear model
  - $s_N = 8x10^{-3}$
  - fairly insensitive to T
  - uptake slows over time suggesting diffusional limitations into the film
- Certain conditions can produce N deficient films as well (N/Ti ~0.5)

ESH Aspects of ALCVD

- Atomic Layer CVD shows great promise for applications ranging from high k gate dielectric material deposition to barrier film deposition, among others.
- Necessary to develop deeper understanding and control of technology to optimize for both technology and ESH.
- Precursors include *organometallics* and *halogenated compounds.*
- Variations on the presursors and processing technology are possible (eg. REALCVD), but few data currently available to allow optimization.

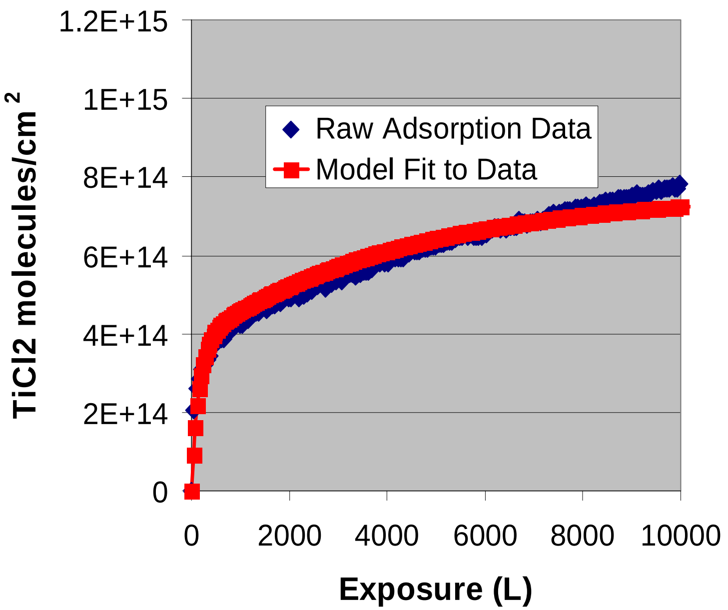
ESH Aspects of ALCVD, continued

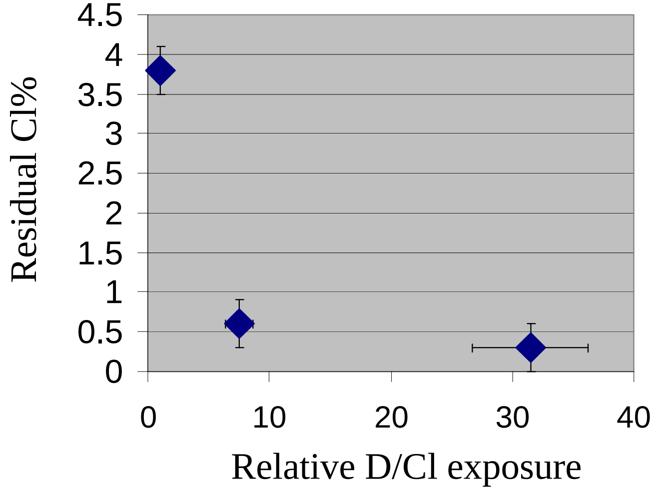
- Most ALCVD processing gases/precursors as well as decomposition products have not been tested for toxicity: *some materials may be expensive or impossible to use in the future.*
- <u>Suggests need for larger database and more processing options.</u>
- Start to develop predictive capability for compound reaction/decomposition/deposition so future choices can be made more systematically without testing all possible combinations
- Develop methodology for quantitative comparisons between alternative deposition technologies (thermal CVD, plasma, reactive sputtering, etc.)

Summary and Implications

Summary of Results

1. $TiCl_4$ has two adsorption regimes at these temperatures:
   - Initial rapid uptake ($s_1=8x10^{-3}$)
   - Slower continuing uptake ($s_2 \sim 8x10^{-5}$)
   - Change likely coincides with 1st monolayer coverage
- D atoms remove Cl from surface:
  $\gamma = 3 \text{ x}10^{-4}$
  - *ex-situ* XPS shows residual Cl% can be reduced below the detectable limit (<0.3%)





Summary and Implications

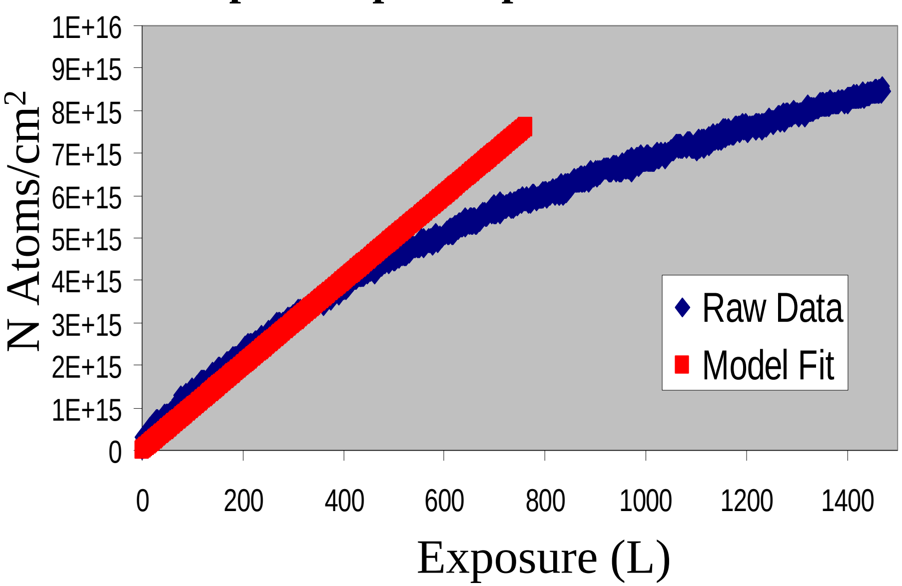
Summary of Results

3. N atoms react with surface

Initial Reaction Probability: s = 8x10^{-3}

- N content a strong function of exposure conditions

Uptake Upon Exposure to N atoms



- Low temperature processing questions
  - –Precursor ($TiCl_4$)
    - •Adsorption is monolayer-like over the range of temperatures investigated
  - –Radicals (D)
    - •D radicals can reduce Cl content to < 0.3%
  - –Radicals (N)
    - •N radicals may incorporate more than 1 monolayer of nitrogen per cycle
- REALCVD ESH impact to be explored through different precursors/processing conditions

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