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

\[ M \sim 1 \text{ mL of M-L}_x \]
\[ L \sim 1 \text{ mL of M-Y} \]
Barrier Layer Deposition by A.L.D.

**Key Issues:**
- Barrier Properties
- Conductivity
- Conformality
- Thermal budget

Currently deposited via i-PVD
- Step coverage is a major challenge for high aspect ratios

**Barrier layer A.L.D. Results**

- **TiCl₄ + NH₃¹**
  - Resistivity is good (<500 µΩ cm)
  - Cl Content higher at lower T
  - 1.5% @ 400°C, 3.0% @ 350°C
  - 0.5% @ 500°C

- **TaCl₅ + NH₃²**
  - Resistivity is bad (500,000 µΩ cm)
  - Due to formation of Ta₃N₅
  - Cl Content acceptable
  - <1% @ 400°C

- **TDMAT + NH₃³**
  - 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

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Radical Enhanced Atomic Layer CVD (REAL CVD)\textsuperscript{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

\begin{align*}
\text{Step 1: } & \text{TiCl}_4 (g) \\
\text{Step 2: } & \text{TiCl}_x (ab) + \text{XH}^* (g) + \text{N}^* (g) \rightarrow \\
& \text{TiN} (s) + \text{X HCl} (g)
\end{align*}

\textsuperscript{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)

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

- Deuterium used to due to easier characterization in QMS

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Experimental Procedure

1. Adsorption
   - TiCl$_4$
   - ~1 mL of TiCl$_x$

2. Pump down

3. Dechlorination
   - D
   - ~1 mL of Ti-D$_x$

4. Pump down

5. Nitridation
   - N
   - ~1 mL of Ti-N$_x$

6. Pump down

- Conventional ALD-like sequence
  - Each step in process monitored *in-situ* with QCM

- Surface temp varied (32-135 °C)

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Precursor Adsorption QCM Results

- 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

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>s(TiN) initial sticking</th>
<th>s(TiClₓ) self sticking</th>
<th>Site Density (#/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>8x10⁻³</td>
<td>1x10⁻⁴</td>
<td>5x10¹⁴</td>
</tr>
<tr>
<td>80</td>
<td>8x10⁻³</td>
<td>9x10⁻⁵</td>
<td>5x10¹⁴</td>
</tr>
<tr>
<td>135</td>
<td>8x10⁻³</td>
<td>6x10⁻⁵</td>
<td>5x10¹⁴</td>
</tr>
</tbody>
</table>

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

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Dechlorination Results

- Exponential decay in Cl surface conc. fit assuming replacement of Cl with D
  - $k_{D+Cl \rightarrow DC1} = 3 \times 10^{-4}$
  - Fairly insensitive to T
- Calculated removed Cl density within a few% of ads. assumptions
  - Suggests TiCl$_2$ is appropriate surface species

Dechlorination

Cl Lost Upon Exposure to Deuterium

- Cl loss due to abstraction by D atoms

Cl Atoms/cm$^2$

D atom Exposure (L)
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 400ºC and 350ºC, respectively\textsuperscript{1}
- Previously reported REALCVD of Ti shows Cl% “in the low percentage range”\textsuperscript{2}

\textsuperscript{1} Satta, A. \textit{et al.} MRS 2000 Spring Meeting (Session D6.5)
\textsuperscript{2} Rossnagel, S.M. \textit{et al.} JVST B 18(4) 2000.

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Nitrogenation Results

- Nitrogen uptake does not seem to saturate
  - \textit{ex-situ} XPS shows N/Ti > 1
- Initial uptake of nitrogen fit to linear model
  - $s_N = 8 \times 10^{-3}$
  - 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 \approx 0.5)
• 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 precursors 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.

• Suggests need for larger database and more processing options.

• 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. TiCl₄ has two adsorption regimes at these temperatures:
   - Initial rapid uptake \( s_1=8\times10^{-3} \)
   - Slower continuing uptake \( s_2\sim8\times10^{-5} \)
   - Change likely coincides with 1st monolayer coverage
   - D atoms remove Cl from surface:
     * \( \gamma = 3 \times 10^{-4} \)
     * *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:
   \[ s = 8 \times 10^{-3} \]
   - N content a strong function of exposure conditions

Uptake Upon Exposure to N atoms

- Low temperature processing questions
  - Precursor (TiCl₄)
    - 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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