**In situ** Characterization of Atomic Layer Deposition of Titanium Dioxide from Titanium Isopropoxide and Water

Antti Rahtu and Mikko Ritala
Laboratory of Inorganic Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland
E-Mail: antti.ranta@helsinki.fi
Website: helsinki.fi/.../www

**Introduction**

- Titanium dioxide (TiO₂) thin films are possible candidates for microelectronic and optical applications.
- TiO(CH₂)₄ is an important ALD precursor, notably for TiO₂ [1] but also for SrTiO₃ [2].
- The oxygen source was deionized water. It was used instead of normal water to distinguish the reaction products and the background coming from the unreacted precursor.

**Experimental**

The key features of the QMS-ALD system are the following [3]:

- QMS in a steel chamber
- Sampling through a nozzle (20 - 200 µm)
- Pressure in reaction chamber is about 1 mbar and at QMS about 10⁻⁶ mbar

QMS: Hiden HAL-3F 501 RC, 1 = 510 amu, variable 0 - 150 eV ionization energy, dual Faraday/electron multiplier detector

The key features of the QCM-ALD system are the following [3]:

- The highest operation temperature is about 400 °C
- Fast reading frequency of 20 Hz

QCM: Mavor MTA-400, Mass Resolution: 0.375 ng/cm² at 6 MHz (0.01 Å TiO₂)

**Results**

Simultaneous QMS and QCM data:

![Graph showing simultaneous QMS and QCM data.](image)

**Figure 1.** A schematic side view of the reactor.

**Figure 2.** A photo of the back side of the reactor.

![Graph showing reaction mechanism.](image)

The reaction mechanisms can be evaluated from both QCM and QMS data.

For QCM data, the measured m₁ and m₂ values and the predicted reaction mechanism (Table 1) have relation:

\[
\frac{m_1}{m_2} = \frac{M(TiO_2)}{M(DL)}
\]

Table 1. Possible reaction mechanisms and the corresponding m₁/m₂ ratios.

<table>
<thead>
<tr>
<th>Reaction Mechanism</th>
<th>m₁/m₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.01</td>
</tr>
<tr>
<td>2</td>
<td>0.97</td>
</tr>
<tr>
<td>3</td>
<td>0.93</td>
</tr>
<tr>
<td>4</td>
<td>0.89</td>
</tr>
</tbody>
</table>

From QMS data, the reaction mechanism can be evaluated by comparing the amounts of ligands released during the metal and water pulses.

**Conclusions**

- The exchange reactions increase up to 250 °C (Fig. 4).
- At 150 - 250 °C about half of the ligands are released during the titanium precursor pulse which refers to the reaction mechanism n = 2 (Table 1 and Fig. 6).
- The thermal decomposition of the titanium precursor starts at 250 °C (Figs. 4 and 5).

**Acknowledgment**

Financial support from the Academy of Finland and the National Technology agency (TEKES), Helsinki, Finland is gratefully acknowledged.

**References**