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

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Introduction

- Titanium dioxide (TiO_2) thin films are possible candidates for microelectronic and optic applications
- $Ti(OCH(CH_3)_2)_4$ is an important ALD precursor, not only for TiO_2 [1] but also for $SrTiO_3$[2]
- The oxygen source was deuterated 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 an orifice (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: Maxtec TM-400
Mass Resolution: 0.375 ng/cm^2@6MHz (0.01 Å TiO_2)

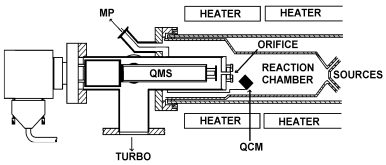

Figure 1. A schematic side view of the reactor.

Figure 2. A photo of the backside of the reactor.

Results

Simultaneous QMS and QCM data:

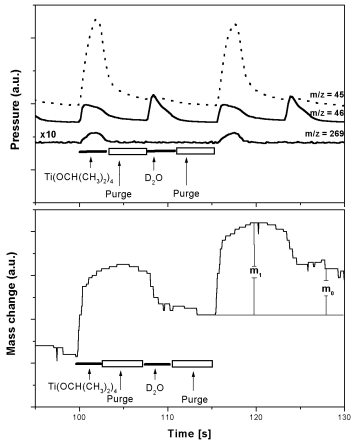

Figure 3. QMS data and QCM mass change in two complete ALD cycles at 250 °C
m/z=46: CH_3CHOD^+, m/z=45: CH_3CHOH^+, m/z=269: $Ti(OCH(CH_3)_2)_3OCHCH_3^+$

- m_0 increases as a function of temperature
- The amount of reaction product (m/z = 46) stays at constant level

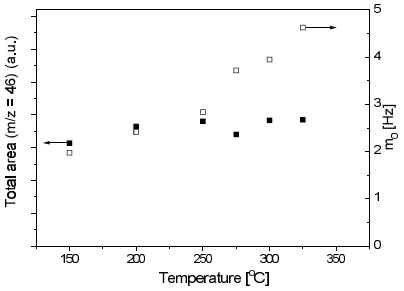

Figure 4. The growth rate measured with QCM (m_0) and the total amount of deuterated reaction products (m/z=46) measured with QMS.

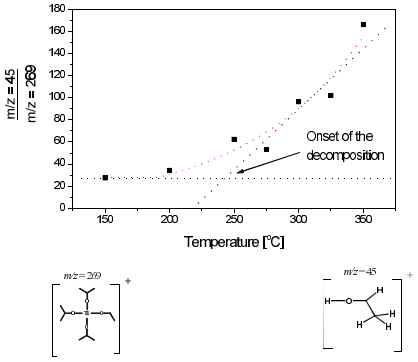

Figure 5. The ratio between the main decomposition product (m/z = 45) and the amount of precursor observed (m/z =269).

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

For QCM data the measured m_0 and m_1 values and the predicted reaction mechanism (Table 1.) have a relation:

$$\frac{m_0}{m_1} = \frac{M(TiO_2)}{M(TiL_4) - nM(DL)}$$

Table 1. Possible reaction mechanisms and the corresponding m_0/m_1 ratios.

n	Reactions	$\frac{m_0}{m_1}$
0	$Ti(OCH(CH_3)_2)_4(g) \rightarrow Ti(OCH(CH_3)_2)_4(s)$ $Ti(OCH(CH_3)_2)_4(s) + 2\,D_2O(g) \rightarrow TiO_2(s) + 4\,(CH_3)_2CHOD(g)$	0.28
1	$\equiv OD(s) + Ti(OCH(CH_3)_2)_4(g) \rightarrow \equiv O-Ti(OCH(CH_3)_2)_3(s) + (CH_3)_2CHOD(g)$ $\equiv O-Ti(OCH(CH_3)_2)_3(s) + 2\,D_2O(g) \rightarrow (\equiv O-)_2Ti(OD)(s) + 3\,(CH_3)_2CHOD(g)$	0.36
2	$2\equiv OD(s) + Ti(OCH(CH_3)_2)_4(g) \rightarrow (\equiv O-)_2Ti(OCH(CH_3)_2)_2(s) + 2(CH_3)_2CHOD(g)$ $(\equiv O-)_2Ti(OCH(CH_3)_2)_2(s) + 2\,D_2O(g) \rightarrow (\equiv O-)_2Ti(OD)_2(s) + 2\,(CH_3)_2CHOD(g)$	0.49
3	$3\equiv OD(s) + Ti(OCH(CH_3)_2)_4(g) \rightarrow (\equiv O-)_3Ti(OCH(CH_3)_2)(s) + 3(CH_3)_2CHOD(g)$ $(\equiv O-)_3Ti(OCH(CH_3)_2)(s) + 2\,D_2O(g) \rightarrow (\equiv O-)_3Ti(OD)(s) + (CH_3)_2CHOD(g)$	0.79
4	$4\equiv OD(s) + Ti(OCH(CH_3)_2)_4(g) \rightarrow (\equiv O-)_4Ti(s) + 4\,(CH_3)_2CHOD(g)$ $(\equiv O-)_4Ti(s) + 2\,D_2O(g) \rightarrow (\equiv O-)_2Ti(OD)_2(s)$	2.00

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

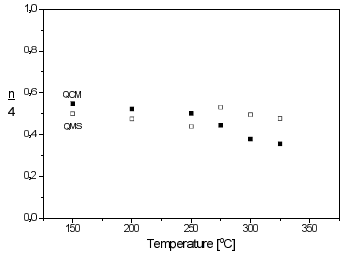

Figure 6. The fraction of ligands released during the titanium precursor pulse

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 1and Fig. 6)
- The thermal decomposition of the titanium precursor starts at 250 °C (Figs. 4 and 5)

Acknowledgment

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References

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[2] M. Vehkamäki, T. Hatanpää, T. Hänninen, M. Ritala and M. Leskelä, *Electrochem. Solid State Lett.*, 2 (1999) 504.
[3] A. Rahtu and M. Ritala, *Electrochem. Soc. Proc.*, in press.