Plasma-Enhanced ALD of TiO_2: From Ligands to Layers

S. E. Potts,* W. Keuning, E. Langereis, A. Sarkar,
M. C. M. van de Sanden and W. M. M. Kessels

Department of Applied Physics, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands. Tel. +31 40 247 4880. Fax +31 40 245 6442.
* s.e.potts@tue.nl

Homoleptic precursors (such as metal alkoxides or amides) are popular as ALD precursors, although they have some tendency for non-self-limiting growth due to low stability and/or decomposition mechanisms such as β-hydrogen elimination. Heteroleptic precursors are growing in popularity as asymmetric molecules tend to have a higher vapour pressures than their homoleptic equivalents and stability is given by chelating or strong π-electron-donating ligands. High stability can sometimes, however, lead to low or no reactivity in the ALD process, for example, Cp-based Ti precursors can show almost no reactivity towards water in the ALD process (N. Blasco *et al.*, *Sr and Ti Precursors Development for Next Generation Thin Film Application* at the 216th ECS Meeting, Vienna, 2009). This problem can be overcome with the use of a plasma as the co-reactant, which offers greater reactivity than is possible with thermal energy alone due to the radical species present in the plasma.

We present here a selection of precursors, which we have employed for plasma-enhanced ALD of TiO_2: [Ti(O^{i}Pr)$_4$] (**1**), [Ti(Cp^{Me})(O^{i}Pr)$_3$] (**2**), [TiCp*(OMe)$_3$] (**3**) and [Ti(Cp^{Me})(NMe$_2$)$_3$] (**4**) (Fig. 1). The thickness and optical properties of the films were monitored as a function of the number of cycles by *in situ* spectroscopic ellipsometry. Precursors **1-3** gave growths of 0.045-0.06 nm/cycle over the temperature range 25-300 °C (Fig. 2) and **4** gave ~0.075 nm/cycle at 200-300 °C. Rutherford backscattering spectroscopy showed the films had a O:Ti ratio of 2, with the exception of compound **1** at 25 °C, which was slightly higher at 2.3. For compounds **2** and **3**, the Ti atoms deposited per cycle did not vary significantly over the temperature range tested (1.6 and 1.4 × 10^{14} Ti atoms cm^{-2} cycle^{-1}, respectively), but this was not the case for compound **1**, where the variation was more significant (1.2-1.8 × 10^{14} Ti atoms cm^{-2} cycle^{-1}). For all precursors, the mass density of the films increased with increasing substrate temperature, indicating that the variation in density was the reason for the variation in growth per cycle. The more reactive, or Brønsted basic, ligands were found to be more reactive towards the surface groups, resulting in a higher overall growth per cycle. Based on these results, the reaction mechanism and choice of precursor ligands will be discussed and it will be shown that a plasma as a co-reactant may allow for the use of precursors previously considered unsuitable for ALD.

*The authors thank SAFC Hitech Ltd. for the donation of precursors **2** and **4**, and Air Liquide for the donation of precursor **3**. The research leading to these results has received funding from the MaxCaps Research Project.*

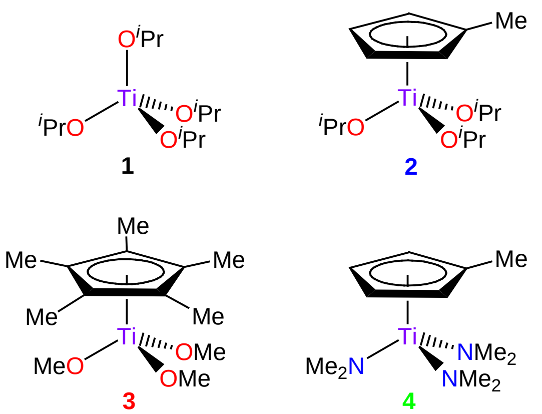

Fig. 1. The precursors used in this study, exhibiting alkoxide, amide and cyclopentadienyl ligands. Me = methyl, ^{i}Pr = isopropyl.

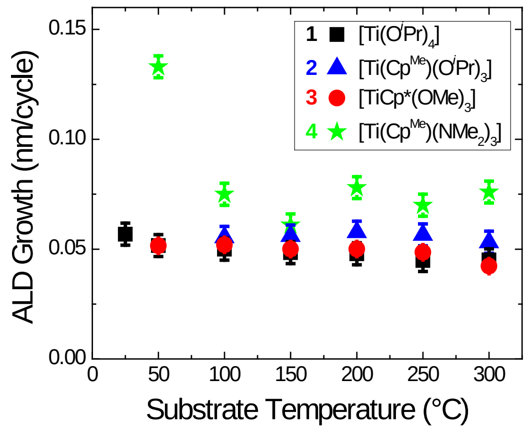

Fig. 2. Growth per cycle as a function of substrate temperature for compounds **1-4**.