

Plasma-Enhanced ALD of TiO₂ using Cp-Based Precursors and Various Plasma Compositions: Experiments and DFT Calculations

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Ultra-thin films of TiO₂ or Ti-containing ternary oxides, such as SrTiO₃, are currently of interest for high-*k* dielectrics, particularly in RRAM applications. For related ALD processes, the current trend is going towards using higher deposition temperatures to reduce the need for post-deposition annealing, as this can induce cracking in the film. Heteroleptic cyclopentadienyl-based precursors, such as [Ti(Cp^{*})(OMe)₃] (**1**) and [Ti(Cp^{Me})(NMe₂)₃] (**2**), are becoming more popular as they offer a higher thermal stability than their homoleptic counterparts. However, this can lead to low or no reactivity in the ALD process. The use of a plasma as the co-reactant can improve the reactivity of such precursors, maintain a high growth per cycle (GPC) without affecting the film density, and allow for easy tuning of the film composition.

We address here the ALD of TiO₂ using compounds **1** and **2** as precursors on Si(100) substrates, using plasmas of O₂, N₂O and an N₂/O₂ mixture as co-reactants. These were chosen to investigate the influence of the plasma composition and surface species on the GPCs, which were measured using *in situ* spectroscopic ellipsometry. GPCs of ~0.38 and ~0.47 Å/cycle were obtained using compounds **1** and **2**, respectively, which did not vary significantly with plasma composition (Fig. 1), suggesting that the GPC is primarily dependent on the metal precursor.

To gain further insight into the surface reactions ruling the TiO₂ growth for compounds **1** and **2**, *in situ* quadrupole mass spectrometry measurements were performed using an O₂ plasma as the co-reactant. The data showed that HOME was easily visible during the precursor dose of **1**, whereas no HNMe₂ was observed during the dose of compound **2**. Comparing these data with the DFT calculations on the adsorption of compounds **1** and **2** on a hydroxylated TiO₂ surface, it seems that different phenomena are involved in the adsorption mechanisms of **1** and **2**. The energy change on physisorption (H-bonding) with the surface was calculated to be -0.35 eV and -0.70 eV for compounds **1** and **2**, respectively. The OMe ligands on **1** were calculated to be less Brønsted basic than the NMe₂ ligands on **2**, exemplified by the instantaneous H-transfer to an NMe₂ ligand (Fig. 2). This suggests that compound **2** is more reactive with a hydroxylated surface than **1**, which may account for the higher GPC. The reactivity of compound **2** may also be enhanced by intramolecular decomposition *via* α-H abstraction, resulting in the loss of HNMe₂ and reducing the steric crowding around the Ti centre. Using these and other results, the mechanisms for the plasma-enhanced ALD of TiO₂ using cyclopentadienyl-based precursors will be discussed.

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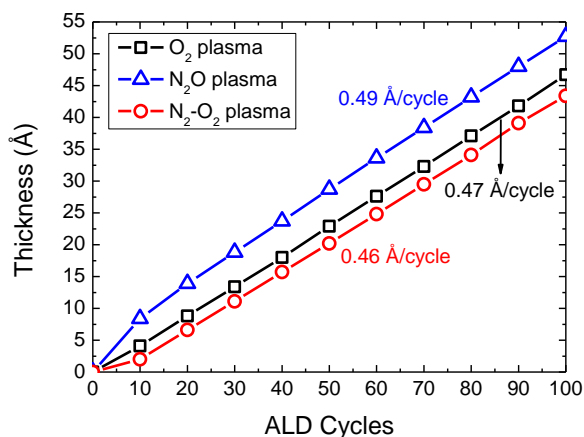


Fig. 1. GPC of precursor **2** at 200 °C using different plasma compositions.

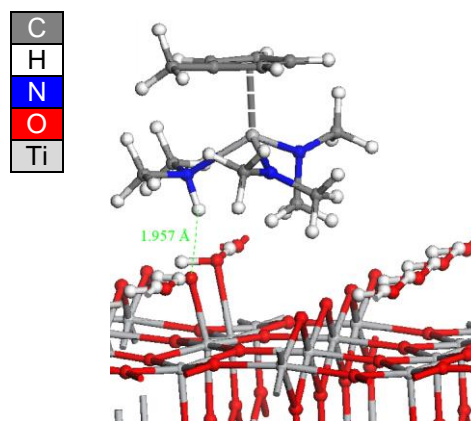


Fig. 2. Ball and stick representation, from DFT calculations, of the H-bonding of **2** to a hydroxylated TiO₂ surface.