Room-Temperature ALD of Al_2O_3, TiO_2, SiO_2 and SiN_x Enabled by Energy-Enhanced ALD Techniques

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Atomic layer deposition (ALD) is known to give high quality films at relatively low temperatures (≤200 °C) [1]; however, as ALD is driven by surface reactions, there is the potential to obtain saturating ALD at the lowest extreme of room temperature. For room-temperature ALD (RT-ALD), thermal ALD processes are generally not suitable due to a lack of thermal energy, especially with respect to the ligand removal step when using H_2O or NH_3, making the deposition times and purge times impractically long. Energy-enhanced ALD techniques [2], such as plasma-enhanced [3] or ozone-based ALD, can help to overcome these problems. However, despite employing energy-enhanced co-reactants, RT-ALD is not always possible. Using Al_2O_3, TiO_2, SiO_2 and SiN_x as examples, we discuss here the mechanisms and fundamentals of RT-ALD processes.

To test the viability of RT-ALD processes, $Al(CH_3)_3$ (TMA), $Ti(O^iPr)_4$ (TTIP), $SiH_2(NEt_2)_2$ (BDEAS) and $SiH_2(NH^tBu)_2$ (BTBAS) were employed as high-vapour-pressure metalorganic precursors to Al_2O_3, TiO_2, SiO_2 and SiN_x, respectively (Fig. 1). For oxides, an O_2 plasma or O_3 gas was used as the co-reactant [4]. All plasma-enhanced RT-ALD processes gave growth at room temperature (Fig. 1a-c), which was a result of the high reactivity of the O_2 plasma. For the O_3-based processes, growth was only observed for Al_2O_3 (1.1 Å/cycle). In the case of TiO_2, the lack of growth with O_3 was a result of insufficient thermal energy, which could also be the case for SiO_2. However, the heteroleptic nature of the BDEAS precursor was also an important factor, as O_3 exhibits a low reactivity towards Si–H surface groups [5] under ALD conditions. For SiN_x, growth was obtained using a remote plasma (Fig. 1d), but the films contained significant quantities of C and O.

It is evident that the viability of an RT-ALD process is not straightforward. It is essential that both the metalorganic precursor and the co-reactant be sufficiently reactive with the surface groups left after the preceding respective RT-ALD half-cycle. High-vapour-pressure precursors and short purge times are desirable. Using these results, the practicalities and possibilities for RT-ALD will be demonstrated and discussed.

This work is supported by NanoNextNL, a micro and nanotechnology programme of the Dutch ministry of economic affairs, agriculture and innovation (EL&I) and 130 partners. Air Liquide and Air Products are thanked for the donations of BDEAS and BTBAS, respectively.

[1] S. E. Potts *et al.*, *J. Electrochem. Soc.*, **157**, P66 (2010); [2] S. E. Potts and W. M. M. Kessels, *Coord. Chem. Rev.*, submitted (2013); [3] H. B. Profijt *et. al.*, *J. Vac. Sci. Technol. A*, **29**, 050801 (2011); [4] S. E. Potts *et al.*, *Chem. Vap. Deposition*, in press (2013); [5] C. K. Fink *et al.*, *J. Phys.: Condens. Matter*, **21**, 183001 (2009).

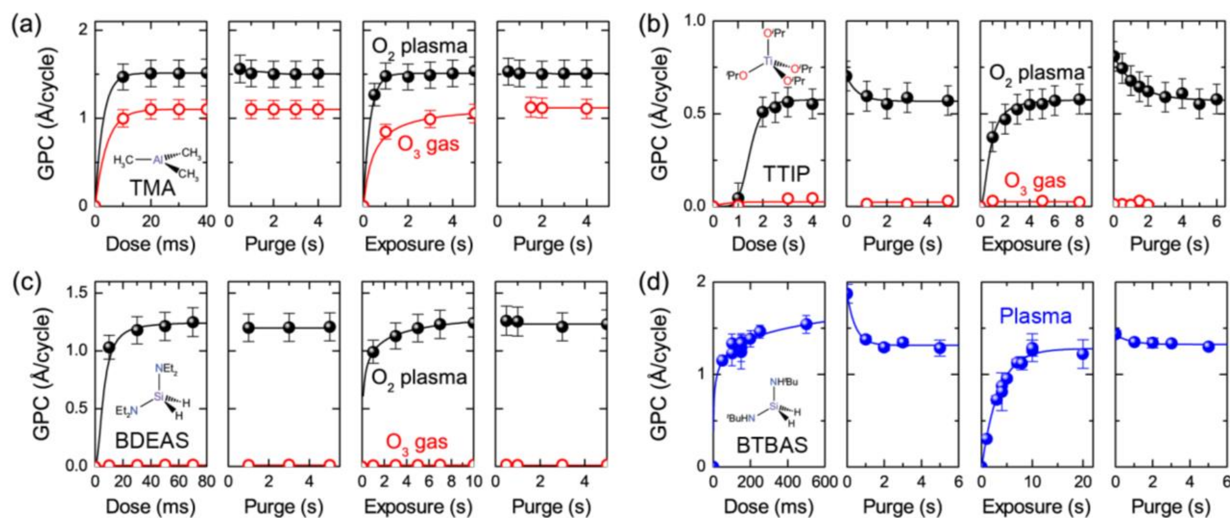

Fig. 1. RT-ALD saturation curves for (a) Al_2O_3, (b) TiO_2, (c) SiO_2 and (d) SiN_x as measured by *in situ* spectroscopic ellipsometry. All plasma-enhanced RT-ALD processes gave saturating growth-per-cycle (GPC) values of (a) 1.5, (b) 0.6 and (c) 1.2 Å/cycle for Al_2O_3, TiO_2 and SiO_2, respectively. Growth was only obtained with O_3 where TMA was the precursor (1.1 Å/cycle). RT-ALD of SiN_x afforded a GPC of 1.3 Å/cycle.