Low Temperature Plasma-Enhanced Atomic Layer Deposition of Metal Oxide Thin Films

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Atomic layer deposition (ALD) is a method of depositing thin films by alternate dosing of gaseous precursors, affording pure and highly conformal films with excellent step coverage. Each ALD process has a temperature window governed by the reactivity and stability of the precursors and the surface groups. The typical temperature range for the majority of ALD studies on metal oxides is 100-600 °C. Few ALD processes have been reported at considerably low temperatures, examples being: Al_2O_3 below 100 °C using $[Al(CH_3)_3]$ and water (1) or ozone (2), TiO_2 at 100 °C from $TiCl_4$ and water (3) or H_2O_2 (4), and Ta_2O_5 at 80 °C from $TaCl_5$ and water (5). In all cases, the films grown at these low temperatures contained higher concentrations of impurities, such as carbon or chlorine. However, it is these low temperatures that are a necessity for temperature-sensitive substrates, such as organic polymers (6,7) or metals (8,9), the mechanical properties of which may be altered by higher temperatures. Plasma-enhanced ALD may provide a route to higher quality films at lower temperatures (10). As such, this project aims to develop and optimise the plasma-enhanced ALD of Al_2O_3, TiO_2 and Ta_2O_5 at 25-250 °C as an alternative to thermal processes, and to assess how the films compare with those deposited by thermal ALD at similar temperatures.

Investigations on the low temperature plasma-enhanced ALD of Al_2O_3 from $[Al(CH_3)_3]$ gave linear growth (Fig. 1) of amorphous films and the growth per cycle varied from 0.13-0.18 nm depending on the substrate temperature (Fig. 2). In all cases, these values were higher than that found for the thermal process (11), which was 0.09 nm/cycle at 100 °C. Rutherford backscattering (RBS) measurements showed that the films grown at lower substrate temperatures had a higher [O]/[Al] ratio than that required for stoichiometric Al_2O_3, where [O]/[Al] = 1.5. The ratio decreased with increasing substrate temperatures, suggesting that impurities where more prevalent at lower temperatures. The FTIR spectra confirmed this, showing that the intensity of the O–H stretch was greatest at 25 °C and decreased with increasing temperature. Conversely, the intensity of the Al–O vibration showed a positive correlation with temperature, which implied that the films were becoming more dense as the temperature increased. The refractive indices showed a similar correlation, rising from 1.55 at 50 °C to 1.58 at 150 °C, as did the mass density of the films, rising from 2.6 g cm^{-3} at 50 °C to ~3.0 g cm^{-3} at 150 °C.

Studies of the plasma-enhanced ALD of TiO_2 involved optimisation of the process using $[Ti(O^iPr)_4]$ and $[Ti(Cp^{Me})(O^iPr)_3]$ (kindly donated by SAFC Hitech Ltd.) as precursors. The films were generally amorphous, although peaks in the XRD patterns were present, accounting for microcrystalline anatase TiO_2 where $[Ti(Cp^{Me})(O^iPr)_3]$ was the precursor. The peaks were sharper at higher deposition temperatures and were almost absent for films grown at < 200 °C. In all cases, the [O]/[Ti] ratio was 2 for $[Ti(Cp^{Me})(O^iPr)_3]$ although it was higher at 2.05-2.30 for $[Ti(O^iPr)_4]$ at 25 °C only. The hydrogen content was < 2 at.% and the carbon content was below the detection limit for RBS. The growth per cycle was ~0.05 nm for both precursors over the temperature range 100-250 °C (Fig. 2), which was comparable with the thermal ALD route (12).

Our ALD experiments using $[Ta(NMe_2)_5]$ gave stoichiometric Ta_2O_5 with no nitrogen incorporation and < 5 at.% H at temperatures below 200 °C. The growth per cycle was consistently ~0.08 nm (Fig. 2).

We have shown metal oxide thin films can be deposited by ALD, using an O_2 plasma as the oxidant, at temperatures as low as room temperature. Higher hydrogen concentrations were obtained at lower substrate temperatures, although at higher substrate temperatures, the film quality was comparable to that in films deposited *via* their corresponding thermal processes.

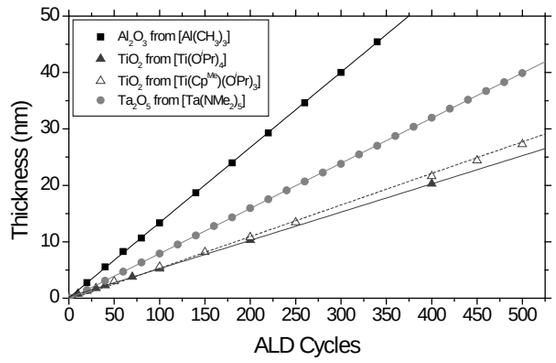

Figure 1. Linear growth of the metal oxides (T_s = 100 °C).

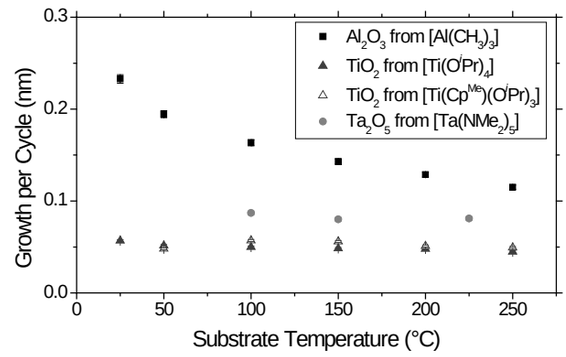

Figure 2. Growth per cycle as a function of substrate temperature for each precursor.

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