Plasma-Enhanced ALD for Opening the ALD Temperature Window

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

Eindhoven University of Technology, Eindhoven, The Netherlands
*s.e.potts@tue.nl

Ever since the idea of the ALD temperature window was first reported by Suntola,[1] it has become a well-used concept in ALD circles. It spans typically 150-300 °C for most ALD processes and work has been carried out towards extending the temperature window to both higher and lower temperatures. Better quality films with respect to electronic and optical properties are often obtained at the high temperature end of the temperature window while temperatures <150 °C are required for applications requiring temperature-sensitive substrates. Many current processes cannot easily reach these targets and our work aims to address methods by which this can be achieved. In this presentation, we report on plasma-enhanced ALD of thin films of TiO_2 and Al_2O_3 for electronic materials and for barrier layers (moisture and corrosion), respectively.

TiO_2 is currently of interest for a variety of microelectronics applications and particularly the deposition of ternary oxides such as $SrTiO_3$. In order to obtain the best properties for the films, $[Ti(O^iPr)_4]$ (**1**), $[Ti(Cp^{Me})(O^iPr)_3]$ (**2**), $[Ti(Cp^*)(OMe)_3]$ (**3**) and $[Ti(Cp^{Me})(NMe_2)_3]$ (**4**) were used as precursors to see which could give high quality films at high deposition temperatures. Precursors **1-3** gave growths of 0.045-0.06 nm/cycle over the temperature range 25-300 °C and **4** gave ~0.075 nm/cycle at 200-300 °C. At 100-300 °C, all films had a O:Ti ratio of 2 and refractive indices of ~2.47 (at 630 nm). For all precursors, the mass density of the films increased with increasing substrate temperature, with the mass densities of 3.7-4.1 g cm^{-3} at 300 °C. Precursors **1**, **2** and **4** started to show evidence of possible decomposition at ~300 °C in our ALD reactors.

ALD processes to Al_2O_3 are versatile and we have previously reported its deposition down to room temperature using plasma-enhanced ALD.[2,3] Amorphous films of fair to good quality Al_2O_3 were deposited from $Al(CH_3)_3$ at 25-400 °C with growths per cycle between 0.13 and 0.18 nm/cycle for the O_2 plasma and H_2O processes depending on the temperature. The films grown at lower substrate temperatures were over-stoichiometric due to a relatively high hydroxyl density. The ratio decreased with increasing substrate temperatures. The refractive indices increased from 1.55 at 50 °C to 1.58 at 150 °C, as did the mass density of the films, rising from 2.6 to ~3.0 g cm^{-3}, respectively. 10-50 nm thick Al_2O_3 films were applied to 100Cr6 steel at 50-150 °C to test their effectiveness as corrosion-resistant coatings. Neutral salt spray tests showed that the thicker films offered the best corrosion-resistance and the porosity of the films was lower than 5% on 100Cr6. The 50 nm films were found to be the least porous (<0.5%). For 10 nm thick films deposited at 150 °C, plasma-enhanced ALD afforded a lower porosity than thermal ALD. Additionally, when optimising the process for deposition on organic LED substrates, that 40 nm thick films deposited at 25 °C had approximately half the defects than those detected in a standard 300 nm Si_3N_4 film. Calcium tests showed that water vapour transmission rates increased with increasing deposition temperature, the lowest value being 2×10^{-6} g m^{-2} day^{-1} at 25 °C.

Using these results, the use of plasma-enhanced ALD and the precursor choice will be addressed, taking into consideration suitable ALD processes for modern applications at high and low temperatures. The concept of the ALD temperature window, and where its boundaries lie, will also be discussed.

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