Room-Temperature ALD of Metal Oxide Thin Films by Energy-Enhanced ALD

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Atomic layer deposition (ALD) is known for its ability to deposit high quality films at relatively low temperatures (≤200 °C). Despite this, depositions at room temperature (25 °C) are not very common. Requirements for successful room-temperature ALD (RT-ALD) are different from those for conventional ALD. Precursors with lower decomposition temperatures can be employed that would otherwise be overlooked for conventional ALD, but they must have a high vapor pressure and not require (significant) heating in the bubbler, thereby reducing the possibility of precursor condensation on the substrate. Additionally, surface groups should be sufficiently reactive toward the metal precursor or co-reactant (e.g., water, ozone or a plasma) at room temperature. Moreover, the precursors, co-reactants and reaction products must be very volatile and easy to remove from the reactor to reduce purge times, and therefore cycle times.

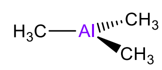
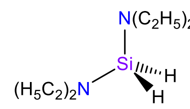
Some examples of successful thermal RT-ALD have been reported in the literature, although generally with a low growth-per-cycle (GPC) and impractically long purge times [1]. These problems can be overcome using energy-enhanced ALD; so termed because energy is supplied to the co-reactant gas to give a reactive species. In this contribution, plasma-assisted ALD [2] and ozone-based ALD as viable RT-ALD processes will be discussed. The high reactivity of the reactant species leads to an increased GPC and allows for fast reactant dosing and reduced purging times and, therefore, short cycle times, which are attractive to industry when films have to be deposited on temperature-sensitive substrates.

Feasible RT-ALD processes will be demonstrated for Al_2O_3 and SiO_2, where trimethylaluminum (TMA) and bis(diethylamino)silane (SAM.24) are the respective precursors (Table 1). For Al_2O_3, plasma-assisted and ozone-based RT-ALD processes with TMA gave GPCs of 1.5 and 1.1 Å/cycle, respectively (Fig.1). Plasma-assisted RT-ALD of SiO_2 using SAM.24 also afforded a high GPC of 1.2 Å/cycle (Fig. 2). However, virtually no growth was observed when using ozone with SAM.24. The fundamentals behind the latter will be discussed in terms of oxidation efficiency of the reactants with the surface groups. The film composition, obtained using Rutherford backscattering spectrometry (RBS), will be compared and discussed for films deposited using all feasible RT-ALD processes. For Al_2O_3, for example, the ozone-based process yielded films with a lower mass density, higher carbon and hydrogen contents and less Al deposited per cycle, compared with the plasma-assisted RT-ALD process (Table 2).

Applications of RT-ALD include moisture barriers for (flexible) LED displays or the deposition of spacer materials onto photoresists for direct spacer-defined double patterning. The RT-ALD of Al_2O_3 and SiO_2 thin films directly onto polymer substrates will be illustrated and the resulting films' suitability for these applications will be assessed.

We will show that the enhanced reactivity of the reactant species allows for the efficient deposition of metal oxide thin films at room temperature. The practicalities and possibilities of RT-ALD will be demonstrated and discussed, and the implications for reactor design (including, e.g., spatial or roll-to-roll ALD) will be addressed.

Table 1. Properties of the TMA and SAM.24 precursors.

Property	TMA	SAM.24
Structural Formula		
Melting Point	15 °C	< -10 °C
Boiling Point	125 °C	188 °C
Vapor Pressure at 25 °C	~13 Torr	~2 Torr

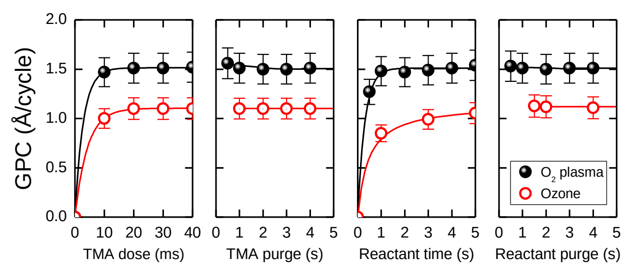


Fig. 1. RT-ALD saturation curves for Al_2O_3 from TMA and an O_2 plasma or ozone.

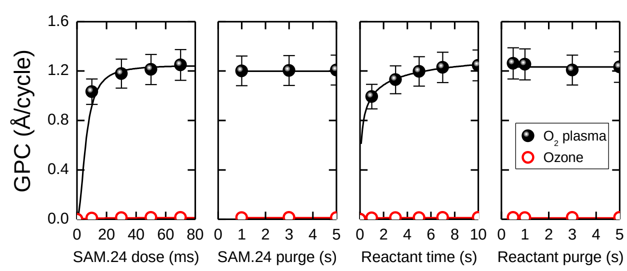


Fig. 2. RT-ALD saturation curves for SiO_2 from SAM.24 and an O_2 plasma or ozone.

Table 2. Film properties of Al_2O_3 deposited using RT-ALD processes obtained using RBS.

Property	O_2 plasma	Ozone
GPC (Å/cycle)	1.5 ± 0.1	1.1 ± 0.1
Al deposited (atoms nm^{-2} $cycle^{-1}$)	4.8 ± 0.1	1.9 ± 0.1
Density (g cm^{-3})	2.6 ± 0.2	2.4 ± 0.2
[O]/[Al]	2.1 ± 0.1	2.1 ± 0.1
[C] (at.%)	Not detected	9.0 ± 0.1
[H] (at.%)	15.0 ± 1.0	20.8 ± 1.0

References:

[1] S. E. Potts *et al.*, *J. Electrochem. Soc.*, **157**, P66 (2010).

[2] H. B. Profijt *et. al.*, *J. Vac. Sci. Technol. A*, **29**, 050801-1 (2011).