566d Tert-Butylimido-Tris(Diethylamido)Tantalum and Nh_3 Precursor Combination for Ald of Tan for Barrier Applications

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TaN was successfully deposited by Atomic Layer Deposition (ALD) using TBTDET (tert-butylimido tris(diethylamido) tantalum) and NH3 as precursors. The flow sequence of TBTDET:N2:NH3:N2 was used to deposit TaN in a low pressure reactor (1 Torr). The N2 purge time was held constant at 10 sec and total flow rate of 200 sccm. X-ray reflectivity (XRR) thickness measurements confirmed that the adsorption of TBTDET was self-limiting as the deposition rate (2.6 Å/cycle) was independent of the TBTDET exposure time in the relatively narrow time range 9 to 11 sec. The growth rate increased to 3.4 Å/cycle for an exposure time of 12 sec, presumably due to additional reactions involving TBTDET beyond those involved in adsorption. The process temperature window for ALD with this precursor combination was also identified. The film thickness increased with increasing temperature in the low temperature region (< 200 oC), likely as a result of incomplete precursor (dissociative) adsorption or reaction between the precursor or a derivative and surface species. The thickness was constant (200 +/- 10 Å) in the range 200 to 300 oC for this set of conditions. This temperature window for ALD mode is sufficiently wide to allow good controllability and reasonably low to contribute minimally to the thermal budget. Above 300 oC the thickness for constant cycle number, and hence growth rate, increased with increasing temperature, likely due to additional TBTDET decomposition reactions.

A series of films was grown with variable cycle number in the range 5 to 100 on Si (100) in ALD growth mode. The thickness of each film (XRR) showed non-linear behavior when the number of cycles was less than 10 cycles. This is not surprising since the adsorption characteristics of TBTDET on bare Si or SiOx/Si are expected to be different than those on Ta or N terminated TaN. Furthermore, the crystal structure of Si and TaN differ as well as the lattice constants. Thus self-limiting adsorption likely did not occur during the first few cycles, but once the surface was fully covered and presumably a few layers thick, relaxed TaN replaced Si as the growth surface to allow repeatable, self-limiting adsorption. After about 10 cycles the thickness varied linearly with cycle number, consistent with a growth rate of 2.4 +/- 0.1 Å/cycle.

To test the barrier quality of ALD TaN films, a thin Cu layer (100 nm) was sputter-deposited onto samples with a TaN barrier layer 4 to 100 Å thick. The test samples were then annealed at 500 oC for 30 min in inert gas atmosphere (N2). The XRD spectra of the annealed samples revealed that when the ALD-TaN thickness was 7 Å or less, peaks attributable to Cu15Si4 were present, suggesting barrier failure of the Cu/TaN/Si structure. On the other hand films 12 Å or thicker showed strong reflections from TaN and Cu phases but none related to copper silicide. The annealed structures were next treated with a Secco etchant after removal of the Cu/TaN, which gives a more sensitive detection of Cu in Si. Etching annealed samples that incorporated ALD-TaN barrier film of 7 Å or less in thickness produced a high etch pit density, indicative of barrier failure. In contrast when samples that included TaN barrier films 12 Å or thicker were annealed and etched, no etch pits were observed. These results indicate that ultra-thin ALD-TaN is a good candidate for a diffusion barrier to potentially the 25 nm feature size node, which requires 2.5 nm thick diffusion barriers around the year 2016.