Atomic Layer Deposition of HfO_2 Thin Films Exploiting Novel Cyclopentadienyl Precursors at High Temperatures

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Abstract:

Atomic layer deposition (ALD) of HfO_2 thin films was studied using four novel cyclopentadienyl precursors, namely, $(CpMe)_2HfMe_2$, $Cp_2Hf(OMe)_2$, $(CpMe)_2Hf(OMe)Me$, and $(CpMe)_2Hf(OMe)_2$. Ozone was used as the oxygen source. Among the cyclopentadienyl precursors, $(CpMe)_2HfMe_2$ and $(CpMe)_2$-Hf(OMe)Me were the most promising, showing ALD-type growth characteristics at high temperatures as the self-limiting growth mode was confirmed at 400 °C. ALD-type growth was verified also on 50:1 aspect ratio trench structures even at 450 °C, where perfect conformality was obtained. The growth rate stayed nearly constant at around 0.5 Å/cycle at substrate temperatures between 350 and 500 °C. When $Cp_2Hf(OMe)_2$ and $(CpMe)_2Hf(OMe)_2$ were applied, slight decomposition of the precursor was detected at 350-400 °C, and thus a self-limiting growth mode was not achieved. Time-of-flight elastic recoil detection analyses demonstrated stoichiometric HfO_2 films, where impurity concentrations were below 0.1 at % for C, H, and N in films deposited from each of the four Hf precursors. In addition, thin HfO_2 films showed good dielectric properties such as low hysteresis, nearly ideal flatband voltage, and effective permittivity values similar to previously reported HfO_2 films obtained by the alkylamide-based processes.