## Thermal Atomic Layer Etching of Silicon Using an Oxidation and "Conversion-Etch" Mechanism

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Thermal atomic layer etching (ALE) is based on sequential, self-limiting surface reactions. Thermal ALE is the reverse of atomic layer deposition (ALD). Thermal ALE has been demonstrated for many materials including Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, ZrO<sub>2</sub>, TiN and W. This talk will focus on thermal Si ALE using oxidation and "conversion-etch". During this process, the Si surface is oxidized to a silicon oxide layer using O<sub>2</sub> or ozone. The silicon oxide layer is then converted to an Al<sub>2</sub>O<sub>3</sub> layer using trimethylaluminum (TMA) [1]. Subsequently, the Al<sub>2</sub>O<sub>3</sub> layer is fluorinated by HF to an AlF<sub>3</sub> layer prior to the removal of the AlF<sub>3</sub> layer by a ligand-exchange reaction using TMA [1]. This reaction sequence is shown in Figure 1.

Si ALE was studied using silicon-on-insulator (SOI) wafers in a warm wall reactor with a hot sample stage. *In situ* spectroscopic ellipsometry (SE) was employed to monitor the thickness of both the silicon and the silicon oxide layer during Si ALE. These studies observed that the silicon film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant. Using an O<sub>2</sub>-HF-TMA reaction sequence, the Si ALE etch rate was 0.4 Å/cycle at 290°C as shown in Figure 2. Comparable etching rates were observed using ozone instead of O<sub>2</sub> as the oxidant.

Thermal Si ALE should be useful in advanced semiconductor fabrication. Thermal Si ALE could also be utilized for atomic-scale polishing and cleaning of silicon surfaces. In addition, there may be applications in other areas such as silicon-based optoelectronics, photonics and MEMS fabrication.





Figure 2. Si and SiO<sub>2</sub> film thicknesses during thermal Si ALE using sequential exposures of O<sub>2</sub>, HF and TMA.

[1] J.W. DuMont et al., *ACS Appl. Mater. & Interfaces* **9**, 10296 (2017). <sup>+</sup> Author for correspondence: <u>Steven.George@Colorado.edu</u>