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The shrinking device dimensions in integrated circuits combined with the introduction of 3-D device architectures has created a need for atomic layer etching (ALE) processes for a variety of materials including Si-based dielectrics such as SiN<sub>x</sub> and SiO<sub>2</sub>. Development of new ALE processes that can meet the demands for semiconductor manufacturing requires an atomistic-level understanding of the surface reaction processes. In our group, in collaboration with Lam Research Corporation, we have pioneered the use of in situ optical diagnostic techniques including highly surface sensitive attenuated total reflection Fourier transform infrared spectroscopy and multi-wavelength ellipsometry to study the surface processes that occur during ALE.

In this presentation, I will discuss the atomistic level details of an SiO<sub>2</sub> and SiN<sub>x</sub> ALE process consisting of CF<sub>x</sub> deposition from a C<sub>4</sub>F<sub>8</sub>/Ar plasma, and an Ar plasma activation step in which the CF<sub>x</sub> film is activated, and the underlying substrates are etched. Sequential cycles of ALE of SiO<sub>2</sub> show a drift in the etch per cycle (EPC) with increasing cycle number. We attribute the drift in EPC to excess CF<sub>x</sub> that is liberated from the reactor walls in the Ar plasma step. This increase in the EPC occurs even though the infrared spectra confirm that the CF<sub>x</sub> deposition onto the SiO<sub>2</sub> film is reproducible from cycle to cycle. To minimize the drift in EPC, Ar plasma half cycles of twice the length are employed, which allows for the removal of CF<sub>x</sub> from the reactor walls during each cycle, thus creating more reproducible chamber wall conditions. To further control the EPC, and obtain selective etching of SiN<sub>x</sub> over SiO<sub>2</sub>, we have explored selective attachment of surface functional groups such as hydrocarbons of different chain lengths. We have demonstrated that attachment of hydrocarbons to the surface prior to the start of ALE retards the EPC.