Conformality of Molecular Layer Deposited Polyurea for Sidewall Passivation

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As the semiconductor industry transitions from fluorocarbon plasma chemistries to carbon-free reactive plasmas, new techniques are needed to passivate the sidewalls of high aspect-ratio (HAR) features during etch. Molecular layer deposition (MLD) is a vapor-phase thin film growth technique comprised of alternating surface reactions for deposition of organic and hybrid organic-inorganic chemistries. While MLD is an analogous technique to atomic layer deposition (ALD), the growth mechanism of MLD has added complexity due to the possibility of double reaction of both functional groups in the precursor molecule with the growth surface and physisorption of molecules into the film. Previous work on ALD has found that conformal deposition on HAR features requires very high precursor doses to supply necessary diffusive flow. However, we have found that MLD polyurea films are surprisingly conformal using the saturation doses for a flat surface.

Polyurea was deposited via MLD using toluene diisocyanate and ethylene diamine as precursors. Figure 1 a) and b) shows scanning electron microscopy (SEM) images of AR~65:1 holes in SiO_2-SiN_x stacks, both with and without ~10 nm of polyurea deposited via MLD. The chips were then exposed to an etching plasma and imaged again [see Figure 1 c) and d)], and the presence of polyurea was found to result in a smaller CD throughout the entire feature. This result shows that during MLD, polyurea was deposited throughout the entire hole and then was able to protect the sidewalls during etch. We have attributed the unexpectedly high conformality of MLD to the physisorption contribution to film growth which we have shown in detail in previous work. This physisorbed material is free to diffuse throughout the film, which may assist in deposition at the bottom of the hole. However, the process must be carefully designed with this effect in mind, as physisorbed molecules can also diffuse out of the film, resulting in chemical vapor deposition when precursor molecules react in the gas phase. Further, we have studied the plasma-surface interactions of polyurea with HF plasma and shown that polyurea can act as a sacrificial layer during HF etch. When polyurea was deposited on top of SiO_2 or SiN_x and then exposed to an HF plasma, only the polyurea film was etched during initial plasma exposure, while the underlying material was protected. Only once the polyurea was completely consumed by reaction was SiO_2/SiN_x etch observed (see Figure 2). This work presents a new technique for sidewall passivation during HF etch.

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Figure 1: SEM images of AR~65:1 holes in SiO_2-SiN_x stacks with an overlaying C mask. While the chip shown in a) had no MLD, the chip shown in b) had ~10 nm of polyurea deposition targeted. The same chips shown in a) and b) were exposed to an etching plasma and then reimaged as shown in c) and d), respectively. The post-etch average CD with (blue) and without (red) MLD is plotted as a function of etch depth in e).

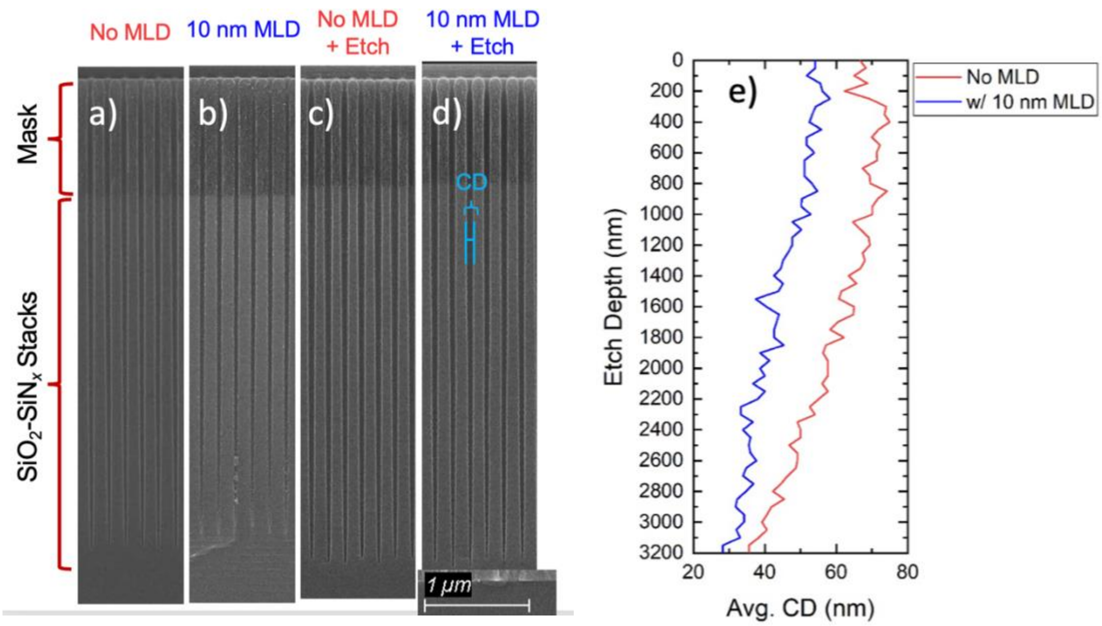

Figure 2: The decrease in thickness during HF etch of SiO_2 (red) and SiN_x (green), extracted from infrared data. The overlaying polyurea was 15 nm thick prior to etch. The corresponding polyurea thickness during etch is shown in the inset.