Plasma-Surface Interactions of Polyurea Deposited on SiO_2 and SiN_x with HF Plasmas

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Fluorocarbon plasmas have been traditionally used to etch SiO_2 and SiN_x during semiconductor processing. Because fluorocarbon radicals inherently lower the etch rate by depositing a polymer on the SiO_2 or SiN_x surface, the industry is transitioning to C-free reactive plasmas, such as HF. As a result, new techniques are needed to enhance surface passivation and etch selectivity during HF plasma etching. During etching of high aspect-ratio (HAR) features, sidewall passivation is needed to preserve the profile. Molecular layer deposition (MLD) is a technique for depositing organic and hybrid organic-inorganic films. We studied the HF plasma interactions after a polyurea film deposited by MLD on top of SiO_2 or SiN_x. We have shown in previous work that MLD polyurea film deposited on top of SiO_2 or SiN_x can protect the underlying material from etching. During HF plasma etching of blanket films on a planar substrate, the polyurea film acted as a sacrificial layer and prevented SiO_2 or SiN_x etch while the polyurea was present. When the polyurea was completely consumed by reaction, the SiO_2 or SiN_x film was etched at its baseline etch rate (see Figure 1). The presence of polyurea also delayed the formation of ammonium fluorosilicate on the SiN_x surface, which is known to form on the surface in the presence of HF, and SiF_4 and NH_3 generated as etch products.

In this work, we also deposited polyurea onto 65:1 aspect ratio holes in SiO_2-SiN_x stacks, which were then exposed to an etching plasma to evaluate sidewall passivation. Scanning electron microscopy images show that the polyurea film reduced the diameter throughout the entire depth, showing both the conformality of the MLD film as well as successful passivation of the sidewalls. Subsequent etching of these features preserved the critical dimension compared to etching without the polyurea film (see Figure 2). Further, *in situ* infrared spectroscopy was used to monitor polyurea interactions with plasma species to better understand the etch mechanism. We exposed the films to a remote HF plasma and HF gas to mimic the conditions in HAR structures. While the radical species in the remote HF plasma gradually removed the polyurea film, it remained largely intact during exposure to HF gas. Fluorination of the polymer film was observed prior to its removal, suggesting that polyurea is removed as volatile hydrofluorocarbon fragments during HF plasma etching. Additionally, we show that during etching at a higher substrate temperature of 150 °C, the presence of polyurea enhanced the SiO_2 etch rate: we attribute this to activation of HF through hydrogen-bonding interactions with the amines in the polyurea film.

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Figure 1: The decrease in SiN_x thickness during HF etch extracted from infrared data. The initial polyurea thicknesses were 0 nm (gray), 10 nm (red), and 15 nm (blue). The corresponding polyurea thickness during etch, when applicable, is shown in the inset.

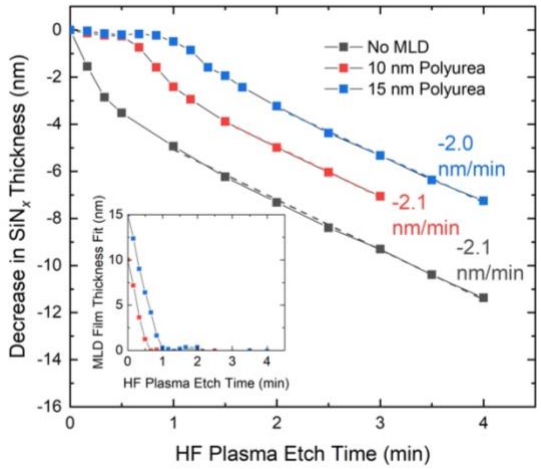

Figure 2: Cross-section SEM images of AR~65:1 holes in SiO_2-SiN_x stacks with an overlaying carbon hardmask. While the chip shown in a) had no MLD, the chip shown in b) had ~10 nm of polyurea deposition targeted. The same chips shown in a) and b) were exposed to an HF-containing plasma and then reimaged as shown in c) and d), respectively. The post-etch average critical dimension (CD) with (blue) and without (red) MLD is plotted as a function of etch depth in e).