A radiation-resistant stencil mask coating for neutral particle nanolithography with reduced stabilization implant

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Neutral particle lithography is a proximity printing technique where a beam of helium atoms floods a stencil mask and transmitted beamlets transfer the mask pattern to a substrate.¹ Stencil masks are typically based on Si membranes in an integral frame. They are extremely sensitive to radiation damage, wrinkling after only a few hundred exposures. Radiation resistant coatings have been developed to solve this problem by preventing lithography atoms from reaching the membrane. The general approach is to deposit a carbon-containing precursor on the membrane and subjecting it to a He⁺ *stabilization implant*. This drives off the volatile species (e.g. H, O, N) and vitrifies² the remaining carbon. The stress of the vitrified coating is independent of ion dose up to at least 1 C/cm².³ Since a portion of the precursor film must remain between the implanted layer and the membrane, the stress of the precursor itself must be stable in a laboratory environment. Ref.4 describes a stable precursor but the stabilization dose ~60 mC/cm² is very costly for large membranes. Ref. 2 shows that the route to a low stabilization dose requires a highly carbonized precursor.

Briefly, precursors were deposited in a parallel plate reactor using methylmethacrylate (MMA) with He dilution. Our goal was to emulate the "low energy" deposition conditions of ref. 5 which produce films with a cross-linked matrix filled with a polymer similar to PMMA. Thermal oxidation at 250° C in air removes the filler, leaving a low stress, tensile film with ~80 wt. % C. Fig. 1 shows that the films shrink, becoming more tensile during the oxidation process. Fig. 2 shows that the films shrink again during vitrification and that stress stabilizes after a dose of ~ 4 mC/cm². Fig. 3 shows a coated stencil mask after the sidewall coating been cleaned up by O₂-RIE. Note the absence of undercut and that fine striations in the silicon side-wall are faithfully transferred to the film.

Thus, we have found a process for forming an atmospherically stable precursor films under very low power conditions (0.1 W/cm^2) that reach a low stress vitreous state after an implant dose of ~4mC/cm², about 6% of the value in ref. 4. The membrane experiences very low tensile stress throughout the coating, oxidation, and stabilization processes; thus, minimizing the risk of breakage.

¹ 1. B. Craver et al., J. Vac. Sci. Technol. B 26, pp. 1866-1870 (2008).

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³ J.R. Wasson et al., Journ. Vac. Sci. Technol. B 15, pp. 2214-2217 (1997).

⁴ P. Hudek et al., Journ. Vac. Sci. Technol. 17, 3127 (1999).

⁵ M. Ohno et al. Journ. Poly. Sci. Part A: Poly. Chem. 25, 1273-1284 (1987).



Figure 1: Stress and thickness of precursor films on membrane and solid substrates, respectively, as functions of time on a hot plate at 250°C. Since film thickness is changing, the stress measurements are normalized to the membrane thickness. Shrinkage is due to the volatilization of PMMA-like compounds within a cross-linked matrix.



Figure 2: Dependence of stress and normalized layer thickness on radiation dose. The graph below 0.45 mC/cm^2 is shown in the inset. Shrinkage is believed to be due the release of H and O atoms leaving a highly carbonized film. Mask stress converges to a stable end state about 10 MPa more tensile than the silicon membrane (solid line).



Figure 3: Stencil mask coated by a radiation resistant coating and etched by O_2 reactive ion etching. Inset shows 100 nm wide lines on a solid substrate.