Polyallylamine as an Adhesion Promoter for SU-8 Photoresist

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Abstract/Introduction
Resist lithography is an important microfabrication technique in the electronics industry in which patterns are transferred using a selective irradiation source on a photosensitive polymer that alters the physical and chemical properties of exposed regions. SU-8 (Fig. 1) has emerged as a favorite photoresist for High Aspect Ratio (HAR) lithography, showing high chemical and mechanical stability and biocompatibility.[1] Unfortunately, its poor adhesion to substrates is a major drawback,[2] with possible solutions being the use of low-viscosity SU-8,[5] surface modification with a low molecular weight adsorbate like HMDS, or a commercial adhesion promotion reagent. However, HMDS and the commercial reagent require extensive surface dehydration and/or curing. Here we demonstrate the use of a water-soluble, amine-containing polymer, polyallylamine (PAAm, Fig. 1), as a simple, easy-to-apply adhesion promoter for SU-8. An overview of this process is shown in Fig. 2. Conditions for the use of PAAm are explored, and the resulting materials are characterized by X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and wetting.

Experimental
PAAm (20 wt. % in water, Mw ~ 17,000) was obtained from Sigma-Aldrich, and SU-8 2025 and SU-8 developer from Microchem Corp. These materials were used as received. XPS was performed with an SSX-100 instrument (serviced by Service Physics, Bend, OR) with a monochromatic Al Kα source and a hemispherical analyzer. Survey scans were recorded with a spot size of 800 µm x 800 µm and a resolution of 4 (nominal pass energy of 150 eV). Water contact angles (WCA) were measured with a Ramé-Hart (Netcong, NJ) Contact Angle Goniometer (Model 100-00) fitted with a manual syringe that was filled with high purity (18 MΩ) water. The drop sizes for measuring static water contact angles were ca. 10 µL. Film thicknesses on planar substrates were measured at an incident angle of 75° with an M-2000 spectroscopic ellipsometer (J.A. Woollam, Co. Lincoln, NE), and the data were analyzed using the instrument software over a wavelength range of 190 – 1700 nm. PAAm depositions were performed with 0.1 wt. % aqueous solutions with immersion times of 35 min.[6] After immersion, surfaces were removed and washed thoroughly with water, and then dried with nitrogen. The SU-8 was spin coated to a thickness of ca. 25 µm and the immersion time in the SU-8 developer solution was 1.5 min. After removal from the developer solution, substrates were rinsed with isopropyl alcohol and blown dry with nitrogen. Air plasma treatment/cleaning of the surfaces was with a PDC-32G Harrick Plasma Cleaner.

Results and Discussion
Fig 3a shows the average thickness of the native oxide and contamination on our substrate, ‘Before Piranha’, the small decrease in thickness corresponding to removal of adventitious hydrocarbon, ‘After Piranha’, and the thickness of the native oxide and PAAm after PAAm deposition, ‘After PAAm’. Immediately after coating with PAAm, samples were spin coated with SU-8. Fig. 3a further shows the effect of PAAm on SU-8 adhesion/removal. After development, much more SU-8 remains on the PAAm-coated surface, which points to a favorable interaction between these materials. Fig. 3b shows air plasma cleaned, PAAm-coated surfaces in contact with SU-8 in either a heated (65 °C) or unheated state for 10, 20, 30, or 40 minutes, after which the SU-8 was removed. Here we see that i) the heated surfaces
generally have more residual SU-8 on them after development, and (ii) more residual SU-8 is found on these surfaces after shorter periods of time. It may be that, with time, the PAAm reorganizes such that its amines turn inward and interact with surface SiOH groups, leaving the hydrophobic PAAm backbone in contact with the polymer. Surface reorganization of amine-containing adsorbates has been reported. The increased amount of SU-8 that remains after heating is consistent with a reaction between the primary amines of the PAAm and the glycidyl (epoxy) groups of the SU-8. Fig 3c shows the water contact angles corresponding to the materials in Fig. 3b. As expected, the water contact angles of the plasma-cleaned surfaces are very low, that of PAAm is a little higher, but still low, and the water contact angles of the SU-8 containing surfaces are still higher. As expected, XPS N 1s narrow scans (Fig. 4) show no nitrogen in the plasma-cleaned surface (S1), substantial nitrogen on the PAAm surface (S2, the narrow scan here suggests the nitrogen is in two oxidized states that presumably correspond to protonated and deprotonated –NH₂ groups), no nitrogen on the surfaces with the thicker residual SU-8 coatings (S3 and S4), and some or no nitrogen on the thinner samples (S5 and S6, the SU-8 removal from these surfaces was irregular). Overall, an important result from these studies is that SU-8 deposits on PAAm-coated Si/SiO₂ in a much more uniform fashion than on uncoated Si/SiO₂, e.g., comets are not present on the PAAm-coated Si/SiO₂ surfaces, but are on the others.

See text for description of figures.

References