Effect of Crosslinker Structure on a Novel Post-Development Strategy to Prevent Pattern Collapse in Photoresist Nanostructures

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A potential roadblock for future lithographic processes is pattern collapse caused by unbalanced capillary forces experienced by the photoresist pattern during the final rinse and drying process. The capillary forces experienced by the resist are dependent upon a number of factors including the surface tension of the final rinse solvent, the contact angle of the final rinse liquid on the resist line side wall, and the dimensions of the pattern. Though methods have been proposed to reduce or prevent pattern collapse including the use of surfactants to lower the surface tension of the rinse liquid, many of these approaches have drawbacks or are inapplicable for use in modern high volume manufacturing. Rather than attempt to modify the rinse solvent by adding a surfactant or using a super critical fluid, our methodology involves the actual strengthening of the resist using a post-development crosslinking reaction while the resist structures are still in their wet state. We have previously investigated the pattern collapse of a hydroxystyrene-based positive tone copolymer (referred to here as ESCAP-1) using an e-beam lithography pattern with a predetermined series of line/space widths. This allowed the calculation of the critical stress at the point of collapse of the photoresist, i.e. the maximum stress a pair of parallel photoresist lines can withstand before pattern collapse occurs. The critical stress for a positive tone photoresist was studied as a function of feature width and it was found to decrease with decreasing feature width for a constant film thickness (Fig. 1). A post-development strategy to reduce pattern collapse was developed whereby the hydroxyl functional groups of the resist are cross-linked via a dicarboxylic acid, specifically adipic acid (Fig. 2 A), using carbodiimide chemistry. One advantage of this approach is that it is an aqueous process that should be easily compatible with high volume, track-based lithographic processes. Application of this reactive rinse on resist patterns of comparable thickness clearly resulted in an improvement in resistance to collapse as observed by SEM. A comparison of critical stress as a function of feature size for samples with and without the reactive rinse treatment also clearly shows the improvement (Fig. 1). The results of studies which compare the number of crosslinkable carboxylic acid functionalities in the crosslinker as well as the hydrophilicity of the crosslinker chain (Fig. 2 B) on the reactive rinse process will also be shown. Finally, thin-film buckling experiments were performed on ESCAP-1 photoresist thin films before and after application of the reactive rinse using several of the listed crosslinkers (Fig. 3), and this data was used to calculate the effective modulus of the resist films before and after treatment. The effect of these treatments on the resist modulus will be shown and correlated with the pattern collapse behavior. The ability to significantly reduce pattern collapse in small resist nanostructures will be demonstrated.

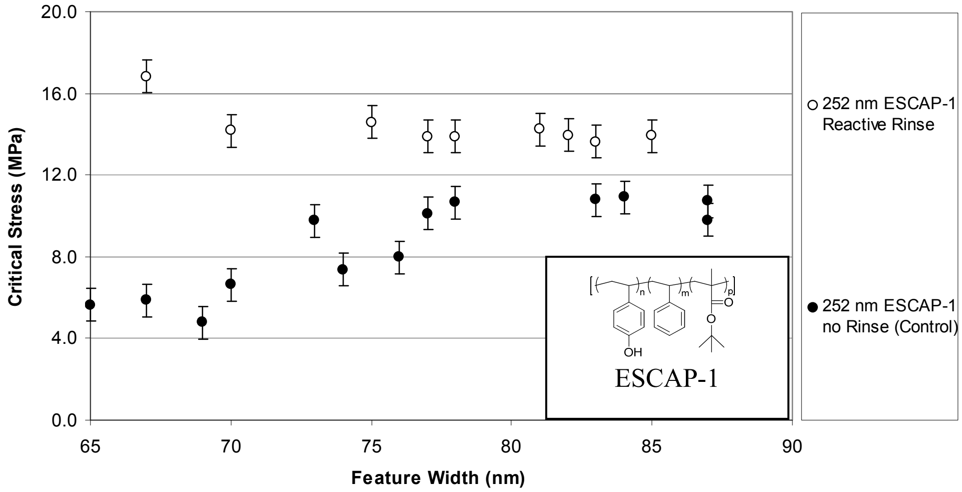

Figure 1. Critical stress as a function of feature width before and after application of the reactive rinse with adipic acid.

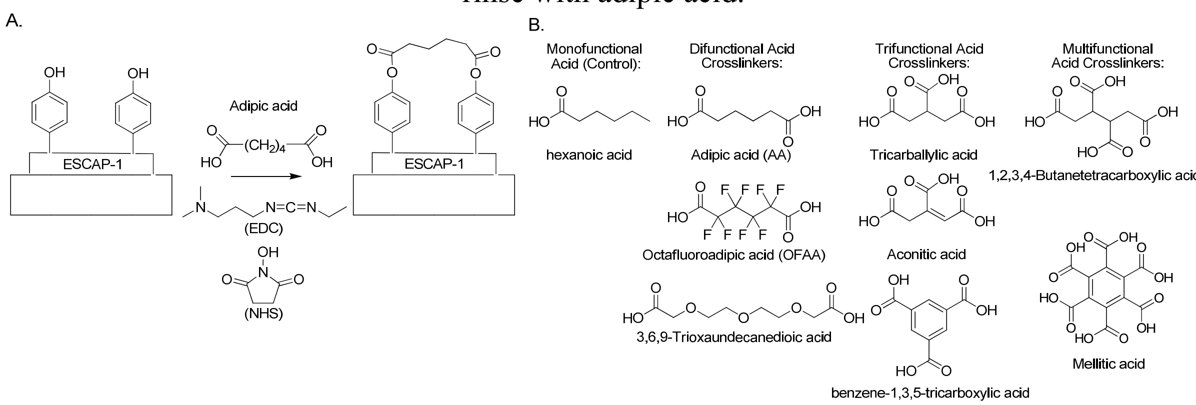

Figure 2. (A) Schematic of the reactive rinse process with adipic acid. (B) Carboxylic acid crosslinkers studied in this work.

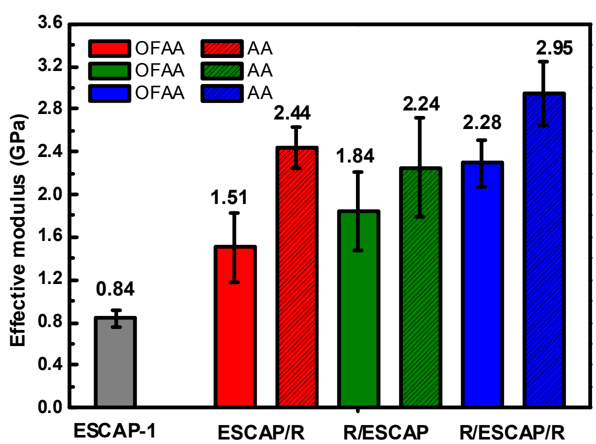

Figure 3. Thin-film buckling results showing the effective modulus before (ESCAP-1) and after application of the reactive rinse with the octafluoroadipic acid (OFAA) and adipic acid (AA) on one (ESCAP/R or R/ESCAP) or both (R/ESCAP/R) sides of the ESCAP-1 thin film.