Abstract:
Linear and star-shaped ArF photoresists were prepared, and lithographic comparisons were performed. An oligo-initiator, based on saccharose, forms the core of the star shaped photoresist, from which three standard ArF photoresist monomers, $\alpha$-gamma butyrolactone methacrylate (GBLMA), methyl adamantyl methacrylate (MAMA) and hydroxyl adamantyl methacrylate (HAMA) were polymerized. Conditions were adjusted to obtain a low polydispersity, 6 kg/mol star polymer with a degree of polymerization of approximately five mers per arm. For comparison, a linear photoresist control was prepared using the same scheme. The star resist architecture was found to improve roughness without reducing sensitivity or resolution.

Introduction:
Improving the roughness of resist sidewalls, quantitatively measured as line width roughness (LWR) and line edge roughness (LER), without sacrificing sensitivity or resolution is a key requirement for next generation photoresists [1]. Redesigning resist architecture offers intriguing possibilities to improve the performance of photoresists, which have traditionally been linear polymers [2]. The star polymer architecture is especially interesting, although it has not been studied as a chemically amplified resist. Star polymers, while chemically identical to their linear polymer counterparts, exhibit more compact size than linear polymers of the same molecular weight [3]. This suggests that less roughness will be introduced to the sidewall during the development step if a star resist is substituted for a linear resist.

Experimental:
Polymerization was carried out using a procedure that will be elaborated upon in a future publication. An aliquot was removed at the start of polymerization. 1H-NMR analysis of this sample and additional aliquots taken during polymerization were compared by integrating vinyl peaks corresponding to the monomers’ vinyl groups and calibrated to anisol.

The star polymer was polymerized for 30 minutes, leading to a conversion of 44% and a composition of 50% GBLMA, 30% MAMA and 20% HAMA. The linear polymer was polymerized for 150 min, resulting in a conversion of 40% and a composition of 47% GBLMA, 35% MAMA and 18% HAMA. After purification, gel permeation chromatography was used to determine polydispersity and molecular weight. The polydispersity of both the linear and star polymer was found to be 1.16. The number average molecular weight (M) was 7.3 kg/mol for the linear polymer. Due to radius of gyration differences between the linear calibration and the star polymer, M is underestimated for the star polymer with a value of 6.3 kg/mol.

Results and Discussion:
Comparing the lithographic properties of resists is difficult because lithographic performance varies greatly with processing conditions. Although the samples have the same composition, different processing conditions are required to optimize the lithographic performance of each photoresist. A thermal gradient was constructed by connecting a cold and hot reservoir with a thermally conductive stage. An infrared thermometer was used to characterize the linear thermal gradient once equilibrium was reached. The photoresist samples were spin-coated onto a silicon wafer and a post-apply bake (PAB) was carried out using this stage. The photoresist samples were exposed at CNF using a JBX-9300FS electron beam to place test patterns at 20 different doses in a two millimeter square, repeated every 5 mm across the length and width of the wafer. A post-exposure bake (PEB) was carried out at a 90° angle from the PAB to create a combinatorial wafer with three processing gradients. Using a scanning electron microscope, roughness and blur was measured for each processing condition; a subset is reported in Figure 1.

Processing conditions for the star resist that closely matched the sensitivity and blur of the linear resist were selected for a final roughness comparison. This was accomplished by
baking the star resist at a lower temperature than the linear resist. Under these conditions both resists exhibit similar blurring at the same doses. The resists therefore exhibit the same potential sensitivity and roughness. The mean roughness of both resists are compared at each dose (Figure 2). At every dose, the star resist demonstrates reduced roughness over the analogous linear resist. At many of these doses, the improvement is 10% or more. (Figures 3, 4) This corresponds to a one year roughness improvement on the International Technology Roadmap for Semiconductors [1].

**Conclusion:**

Sub-5 nm roughness is achieved with the star resist. This corresponds to an improvement of 12% over the equivalent linear resist without any loss to sensitivity or resolution. This suggests that star resists may perform fundamentally better than their linear counterparts. More generally, it is evidence that, although most photoresists have traditionally been linear polymers, linear polymers do not necessarily give the best performance. Additional research into alternative resist architectures, including star resists, has the potential to yield resists that can surpass linear resists.

**References:**

