Architectural Studies in High Resolution, Versatile Resists

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Abstract
Multifunctional atom transfer radical polymerization (ATRP) initiators based on sugars were utilized to grow short tert-butyl methacrylate (tBMA) arms. The kinetics of this system was studied using nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC), and shown to be living. The polymerization was further engineered to obtain samples of controlled degrees of polymerization such that the polymer component only accounted for 55-85% of the total molecular weight of the hybrid molecule. A sucrose-based system was examined using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), demonstrating a clear architectural effect on glass transition temperature ($T_g$). Finally a sample engineered for high $T_g$ but low molecular weight was evaluated using e-beam lithography and scanning electron microscopy (SEM).

Summary of Research
Understanding the role of architecture on photolithographic performance will be crucial in designing new photoresists capable of meeting the requirements of the semiconductor industry for next generation lithography. Block copolymers have been successfully used as additives to enhance resolution [1] and as photoresists themselves to create patterns with sublithographic features [2]. Molecular glass photoresists [3] have also been examined as a viable alternative to conventional polymers [4]. This study lays the groundwork for creating hybrid photoresists containing molecular glass cores and polymeric arms. Hybrid photoresists can be used to study architectural effects on lithographic performance by varying the number of polymer arms ($f$) and the degree of polymerization of those arms ($n$). In the limit of $n = \infty$ the hybrid is a polymer, while in the limit of $n = 0$ the hybrid is a molecular glass. Polymer and molecular glass photoresists can be viewed, not as separate entities, but rather two ends of an architectural spectrum, as seen in Figure 1. Therefore a systematic study of architecture, its effect on properties and ultimately lithographic performance is possible.

Star poly(tBMA) has been grown from fully converted glucose and sucrose multifunctional ATRP initiators (with $f_{\text{max}} = \{5,8\}$ respectively) to study polyelectrolytes [5]. In this study, molecules with arms with a degree of polymerization an order of magnitude lower than previously reported were required to observe the hybrid photoresist in the limit as $n$ approaches zero. Kinetics studies were performed in order to obtain samples of the required degrees of polymerization. These were characterized using NMR to determine conversion and GPC to determine molecular weight and polydispersity. Molecular weight versus conversion plots (not shown) were linear—revealing that the systems were living. However the polydispersity was high and polymer arms with $n < 10$ were unobtainable due to rapid initial conversion. The sucrose system was engineered by modifying the reaction temperature, solvent volume and Cu(I):Cu(II) ratio. This prevented the rapid initial conversion of a monomer resulting in controlled conversion immediately upon initiation as demonstrated in Figure 2. GPC data indicated that the system was still living and samples had a polydispersity index between 1.05 and 1.10.

A series of hybrid resists were synthesized for $1 < n < 10$ utilizing the sucrose based initiating system. TGA and DSC were used to characterize the samples effectively mapping the effect of architecture on $T_g$ as the hybrid resist approaches the molecular glass regime as seen in

Figure 1: Schematic of architectural spectrum. From left to right: segmented block copolymer resist, glass-coil block copolymer resist, glass-brush resist, molecular glass resist.
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Figure 3. This result is significant as it demonstrates that high molecular weights can be achieved with very short polymer arms.

One of the higher $T_g$ samples was selected for lithographic testing. The photoresist with five weight percent photoacid generator was spin coated onto a primed wafer, exposed to e-beam, developed and viewed with a SEM in Figure 4. Resolutions as low as 70 nm were achieved with 1:3 line spacing before the poor adhesion and insensitivity due to the resist being fully protected with tert-butyl groups became limiting. Further work is required to examine a partially protected resist in order to determine its ultimate resolution.

Figure 3: $T_g$ results were obtained using DSC and are reported in % tBMA by weight.

Figure 2: Percent conversion obtained from NMR for a sample with $f = 8$ and $[M]/[I] = 50$.

Figure 4: SEM image demonstrating that the hybrid molecule functions as a photoresist.

References


