High Performance Negative Tone Molecular Resists Using Cationic Polymerization

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We have recently been designing, synthesizing, and characterizing a number of negative molecular resists based on cationic polymerization such as epoxide cross-linking, some of which are shown in Figure 1. Despite the fact that it is often thought that high resolution cannot be achieved in negative tone systems due to swelling, these materials based on molecular resists have all achieved sub 50 nm half-pitch resolution. This has been achieved while maintaining the good sensitivity that these types of systems are known for. Even though these materials show high resolution and good sensitivity, they show excellent LER as well. Under 100 keV e-beam lithography, they have shown resolution down to sub-25 nm half-pitch, sensitivity as low as 20 $\mu C/cm^2$, and LER (3σ) of 2.3 nm (Fig. 2). Despite the excellent performance of these materials, we were able to improve the performance even further by exploiting knowledge of the fundamental reaction chemistry. The first of these improved resists was patterned under EUV at the Paul Scherrer Institute to test its performance. It obtained 25 nm half-pitch, dose-to-size of 15 mJ/cm^2, and LER (3σ) of 4.0 nm (Fig. 3); comparable to the best of current positive tone EUV resists. This study further examines these resists and new similar molecular resists in an attempt to both improve the current performance even further and to explain the excellent properties. The newly designed additives which are applicable to any cationic polymerization negative tone system will be also be discussed. Additionally, new resist designs that can be patterned in both aqueous base and organic solvents will be discussed and their performance in both compared.

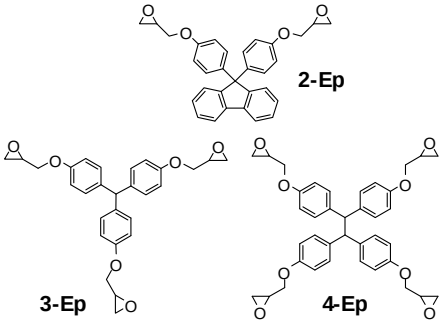

Figure 1. Examples of molecular resists based on epoxide cross-linking.

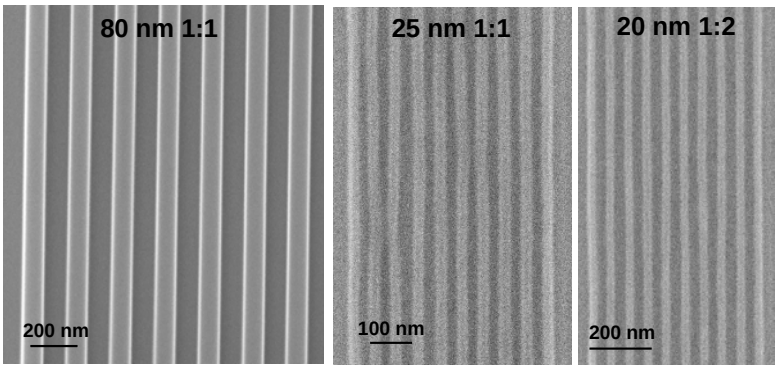

Figure 2. SEM of e-beam patterning of epoxide molecular resist **3-Ep** and **2-Ep**, imaged at 50 μC/cm^2 (100keV) demonstrating the low LER and high resolution of these materials.

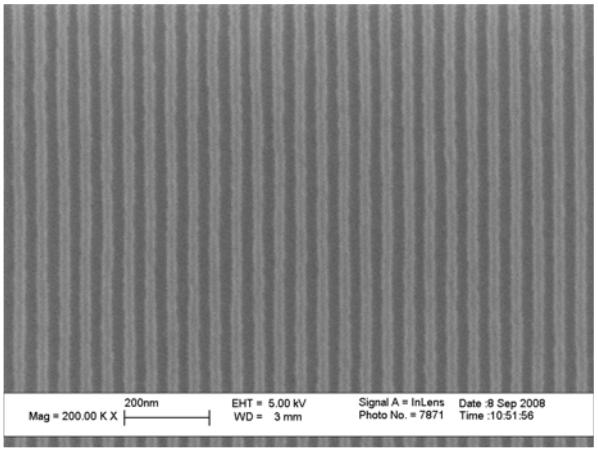

Figure 3. SEM of EUV patterning of epoxide molecular resist **4-Ep** with additives; 25 nm half-pitch, E_{size} of 15 mJ/cm^2, and LER (3σ) of 4.0 nm.