High Resolution Negative Tone Resists via Controlled Polymerization

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Classical positive tone resists have limitations for sub-20 nm patterning due to a number of different problems. Among the biggest problems is pattern collapse due to the high capillary forces experienced by the resist features during wet development and drying of such small features.[1] The problematic increase in the capillary forces that results as the space between adjacent features decreases is further compounded by the fact that the modulus of polymeric positive tone materials appear to consistently decrease as the feature dimensions are decreased below 50 nm.[2] The authors have shown in recent years that negative tone resists based on cross-linking are promising alternatives that provide a platform with which to increase the overall modulus of the resist material and to potentially improve the small feature modulus of resists. Negative tone resists based on polymerization and cross-linking have shown the capability for high resolution patterning with good LER and sensitivity.[3,4] However, their ultimate resolution can be limited due to propagation of polymerization outside of the nominally exposed region. In conventional acid catalyzed positive tone resists, base quenchers can be added to neutralize the photoacid and prevent its diffusion outside of the exposed area and control its diffusion within the exposed area. This will in general not work in negative tone resists based on cationic polymerization since the photoacid is not the primary "active species" in the resist and is in fact a very temporally and spatially short lived species. It exists as an acid only long enough to protonate an epoxide which initiates polymerization via a living cationic site. Likewise, resolution in radical polymerization type systems cannot be significantly improved through the use of conventional base quenchers. Thus to improve resolution in these systems, the polymerization itself must be controlled via different mechanisms.

In this work, multiple approaches have been used to control the polymerization in such negative tone resist systems. In some cases, methods adapted from controlled solution polymerization techniques have been investigated for use in solid state thin resist films. In addition, entirely novel methods have also been developed. One of the most successful approaches used so far is based on the use of a photo-sensitive chain termination agent that changes to a chain transfer agent upon exposure. This greatly reduces the propagation outside of the nominally exposed area, thus improving resolution and line edge roughness (LER), while still allowing for good rates of polymerization in the exposured regions which allows the resist to maintain good sensitivity. Figure 1 shows the immediate improvement in EUV performance for a 4-functional epoxide functionalized molecular resist when using such a photo-sensitive chain

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[3] R. A. Lawson, L. M. Tolbert, T. R. Younkin, and C. L. Henderson, *Proc. SPIE* **7273**, 72733E (2009).
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termination agent. The resolution obtained when no polymerization control agent was used was 32 nm with an LER (3σ) of 4.9 nm. When 2.5 wt% of the photo-sensitive chain transfer agent was used with no other changes in formulation or processing, the resolution was improved to 25 nm with an LER (3σ) improvement to 4.0 nm. This specific polymerization control agent for cationic polymerization resists will be further discussed along with additional approaches for controlling radical polymerization resists. Results of extensive lithographic testing of these materials and resist formulation schemes will be presented and discussed.

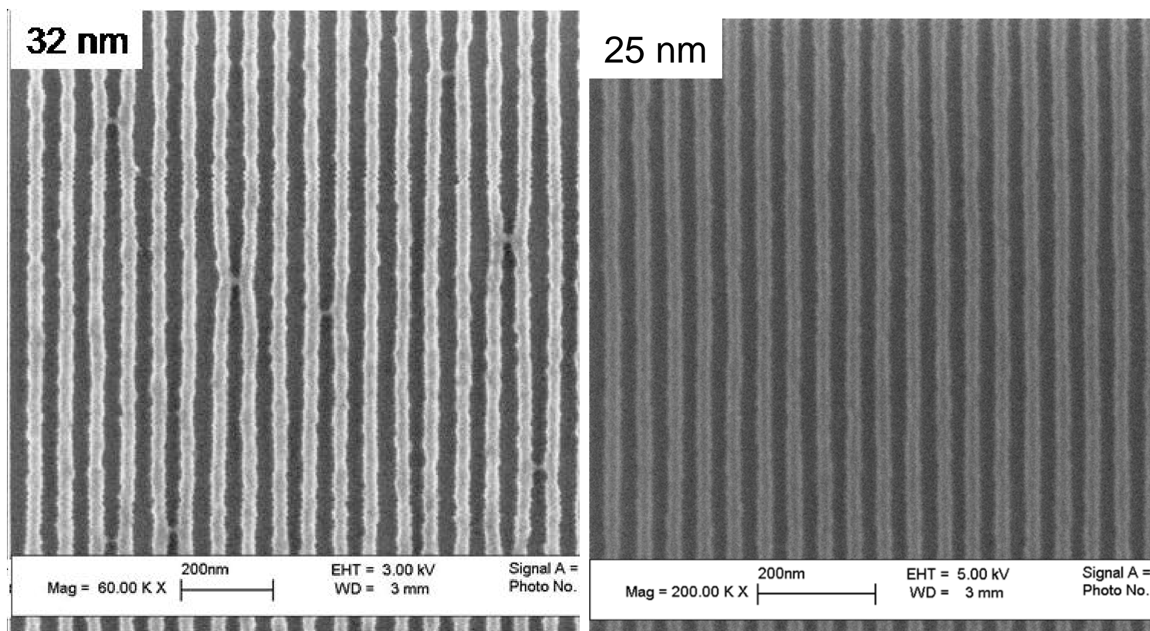

Figure 1. Resolution improvements for EUV exposures of the same cationic polymerization resist without (left) and with (right) 2.5 wt% of a polymerization control additive. With no other modifications to the material, the resolution improves from 32 nm to 25 nm and the LER (3σ) decreases from 4.9 to 4.0 nm.