

## Methods for Controlled Polymerization in Negative Tone Resists

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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 walls when developing such small features.<sup>1</sup> The increase in the forces as the gap between walls is increased is compounded by the fact that the modulus of the materials appear to consistently decrease as their dimensions are decreased below 50 nm.<sup>2</sup> Negative tone resists based on cross-linking are therefore promising as a means to increase the overall modulus of the material and to potentially improve the small feature modulus. Negative tone resists based on polymerization/cross-linking have shown the capability for high resolution patterning with good LER and sensitivity.<sup>3,4</sup> 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 not work as well or at all in cationic polymerization types of negative tone resists because the photoacid is not the primary “active 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.

Multiple approaches have been used to control the polymerization in these negative tone systems. Some methods from controlled polymerization for solution polymerization have been investigated and other novel methods have been developed as well. 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 improving resolution and line edge roughness (LER), while still allowing for good rates of polymerization in the exposed regions to maintain good sensitivity. Figure 1 shows the immediate improvement in EUV performance for a 4-functional epoxide functionalized molecular resist. The resolution obtained when no control agent was used was 32 nm with LER ( $3\sigma$ ) of 4.9 nm. When 2.5 wt% of the additive is used with no other changes, the resolution is immediately improved to 25 nm with an LER ( $3\sigma$ ) improvement to 4.0 nm. This specific agent for cationic polymerization resists will be further discussed along with additional approaches for controlling radical polymerization resists.

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<sup>1</sup> D.E. Noga, R. A. Lawson, C-T. Lee, L. M. Tolbert, and C. L. Henderson, *Proc. SPIE* **7273**, 727334 (2009).

<sup>2</sup> W-M. Yeh, R. A. Lawson, and C. L. Henderson, *Proc. SPIE* **7972**, 79721X (2011).

<sup>3</sup> R. A. Lawson, L. M. Tolbert, T. R. Younkin, and C. L. Henderson, *Proc. SPIE* **7273**, 72733E (2009).

<sup>4</sup> R. A. Lawson, C-T. Lee, L. M. Tolbert, T. R. Younkin, and C. L. Henderson, *Microelectronic Engineering* **86** 734 (2009).

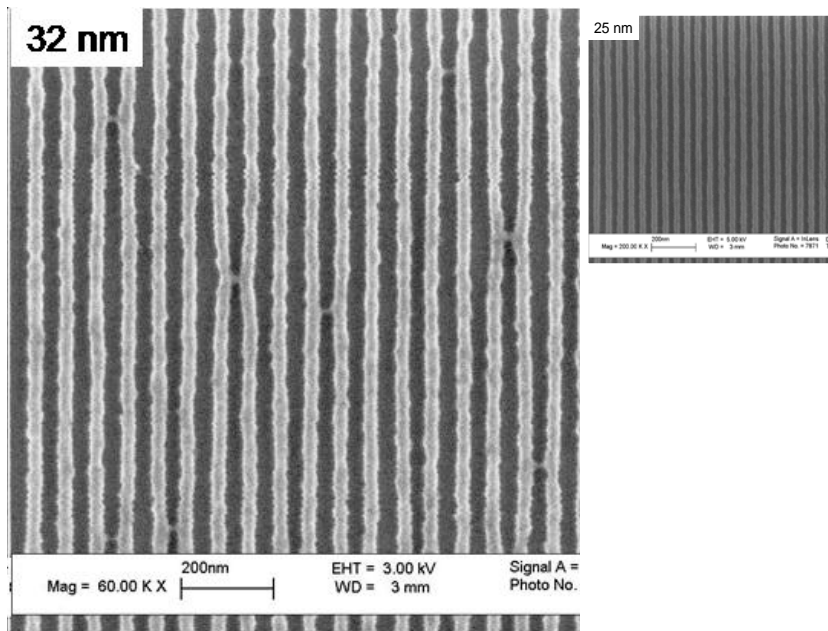


Figure 1. Resolution improvements for EUV exposures of the same cationic polymerization resist without (left) and with (right) 2.5 wt% of a polymerization control additive. With no other modifications to the material, the resolution improves from 32 nm to 25 nm and the LER ( $3\sigma$ ) decreases from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