Advancements in Cross-linked Resist Materials for High Resolution Patterning

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Negative tone resists based on polymer cross-linking were an early staple used for fabrication of integrated circuit devices. Over the years, they were abandoned in favor of positive resist tone systems due to a variety of factors, a critical one of which was their perceived limitations due to swelling and low contrast. Fast forwarding many decades, the IC industry is now patterning features at sub-40 nm length scales, and at these small dimensions the instability of conventional positive tone resists against pattern collapse has become a serious problem. Our work in characterizing the mechanical behavior of polymer ultra-thin films and nanostructures led us back to negative tone cross-linked resists due to their superior mechanical behavior. By utilizing cross-linking mechanisms in conjunction with small molecular resist type resins, we have been able to dramatically improve the capabilities of negative tone cross-linking resists. This paper will review our efforts in this area and present future directions for the work that are aimed at producing organic resist materials with sub-10nm resolution at high photospeeds.

We initially showed that negative tone molecular resists based on cationic polymerization/cross-linking of epoxide functional groups have the capability for high resolution patterning with good LER and sensitivity. However, producing resists capable of sub-20 nm patterning is a challenge with any resist platform. In negative tone cationic cross-linking systems, a major challenge was that their resolution can be limited by propagation of polymerization outside the nominally exposed region. Conventional methods of controlling diffusion of active photoacids such as addition of base quenchers are ineffective in cationic polymerization resists because the photoacid is not the primary "active species". The photo-generated acid exists as a small molecule acid only long enough to protonate an epoxide which initiates polymerization via a living cationic or oxonium site. Neutralization of the photoacid with a base is also statistically unfavorable since the epoxide or other cationic polymerizable groups are generally at an order of magnitude higher concentration than a catalytic amount of base or acid. Therefore, the polymerization itself must be controlled in order to improve resolution in these systems. We have developed multiple novel approaches to control the polymerization in these negative tone systems ranging from simple additives to structural modifications of the cross-linking molecules. We will review some of these polymerization and discuss their mechanisms and show their efficacy through EUV patterning studies. We will also discuss novel alternative schemes in which cross-linking and/or depolymerization can be used to design both positive tone and negative tone resists for high resolution patterning that yield cross-linked final resist structures.

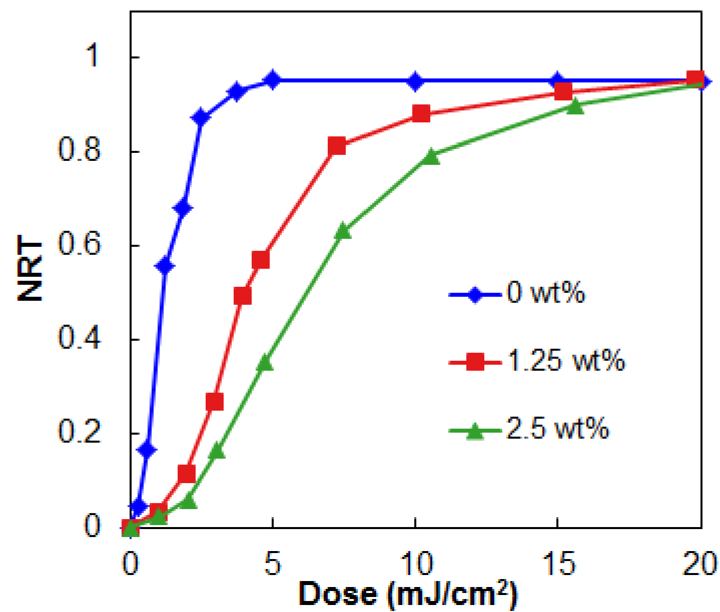

Figure 1. DUV (248 nm) contrast curves illustrating the effect of added wt% of a photo-sensitive polymerization control additive (i.e. triphenylsulfonium triflate or TPS-Tf) on patterning of a 4-functional epoxide functionalized molecular resist formulated with triphenylsulfonium hexaflouroantimonate (TPS-SbF_6).

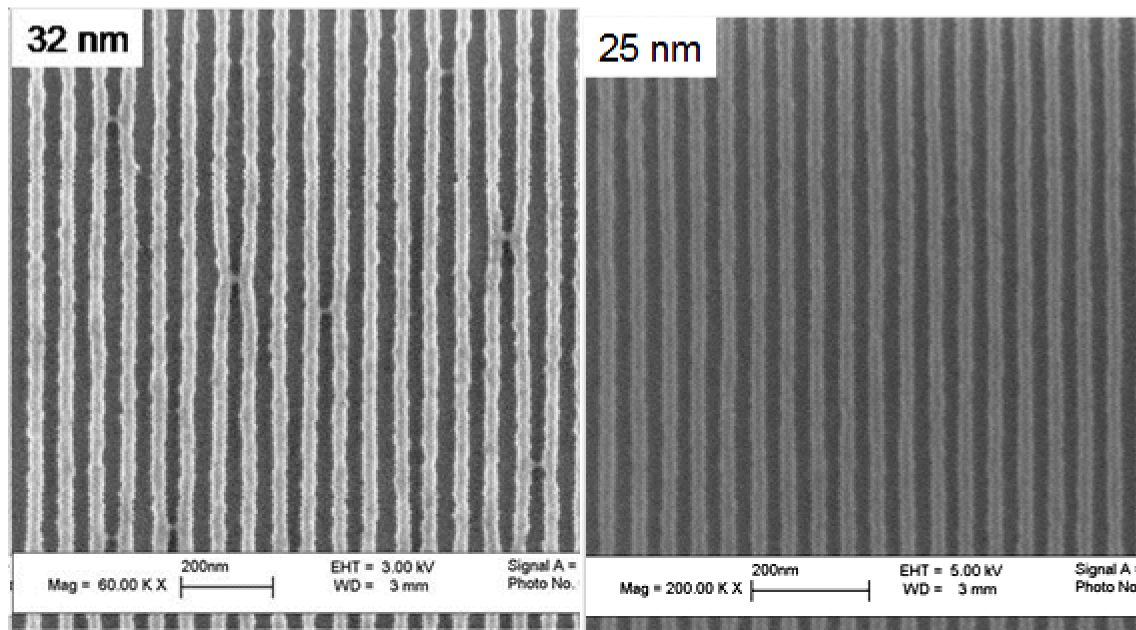

Figure 2. Resolution improvements for EUV exposures of the same cationic polymerization resist without (left) and with (right) 2.5 wt% of a photo-sensitive polymerization control additive. With no other modifications to the material, the resolution improves from 32 nm to 25 nm and the LER (3σ) decreases from 4.9 to 4.0 nm.