Novel Designs for Non-Chemically Amplified Molecular Resists

Richard A. Lawson[1], Jing Cheng[2], Laren M. Tolbert[2], and Clifford L. Henderson[1]*
[1] *School of Chemical & Biomolecular Engineering,* [2] *School of Chemistry and Biochemistry*
Georgia Institute of Technology, Atlanta, GA 30332
** Corresponding Author: cliff.henderson@chbe.gatech.edu*

It is well established that chemically amplified resists (CARs) have an intrinsic limitation, namely that any two parameters chosen from resolution, line edge roughness, and resolution can be improved at the expense of the third, which is known as the RLS tradeoff. While improvements in resist formulation have led to improved RLS performance, current CARs still lag far behind the desired International Technology Roadmap for Semiconductors (ITRS) performance targets due to this RLS tradeoff. In particular, current champion CAR LER performance is still poor relative to ITRS roadmap targets. Non-chemically amplified (non-CA) resists such as PMMA and HSQ have shown superior resolution and LER compared to CARs, but at the cost of significantly inferior sensitivity. One important question is whether non-CA resists are limited to such poor sensitivity and this same RLS tradeoff. Furthermore, recent work has shown that molecular resist designs may in fact offer substantial improvements over traditional polymeric resists in some cases. While HSQ and a few other examples of non-CA molecular resists have been studied, relatively little work has been done in designing and characterizing non-CA molecular resists and their RLS performance as compared to polymer systems. Therefore, the goal of this work has been to explore novel non-CA molecular resist designs and to characterize the basic lithographic performance of such systems.

As a result, a series of high sensitivity non-CA resists has been designed, synthesized, and characterized for 193 nm, EUV, and e-beam lithography. While most reported non-CA molecular resists have been negative tone materials which have demonstrated high resolution, such designs also have led to poor sensitivity because an electron or photon is required to cause nearly each individual molecular cross-linking event. In contrast, the work presented here has focused on large solubility changes in the resist matrix and the basic concept of dissolution inhibitors which allows for a single reaction event to affect the solubility of several surrounding molecules rather than a single molecule. DNQ dissolution inhibitor based systems cannot be effectively used for positive tone resists under e-beam and EUV because the high vacuum in these systems removes the water required for the Wolff rearrangement, and the DNQ instead cross-links the matrix. The approach to be discussed here uses photo-sensitive protecting groups which are cleanly removed even under vacuum. Figure 1 shows some typical dissolution inhibitor molecules used in this study. Some of the photo-sensitive protecting groups used release phenols, carboxylic acids, or sulfonic acids. Recent work by our group on non-ionic PAGs and the dissolution behavior of soluble/insoluble molecular resist blends has directed the design of resist blends that exhibit good sensitivity and contrast using such concepts. Figure 2 shows contrast curves from early formulations of one of these non-CA molecular resist materials. In this case, the sensitivity and contrast can be tuned by changing the formulation to obtain sensitivities as low as 1 mJ/cm^2 and a contrast ratio as high as 8.3. The synthesis and characterization of these dissolution inhibitors, molecular resist formulations, and the high resolution patterning and performance of these and related non-chemically amplified molecular resists under e-beam, EUV, and 193 nm will be presented.

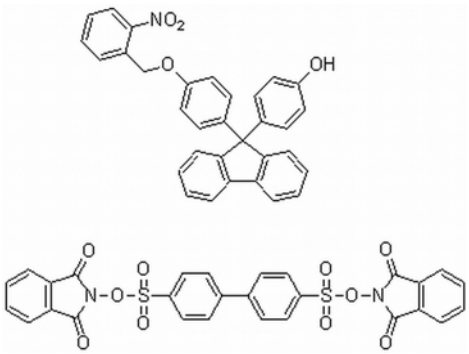

Figure 1. Examples of some of the non-chemically amplified molecular glass dissolution inhibitors used in this study.

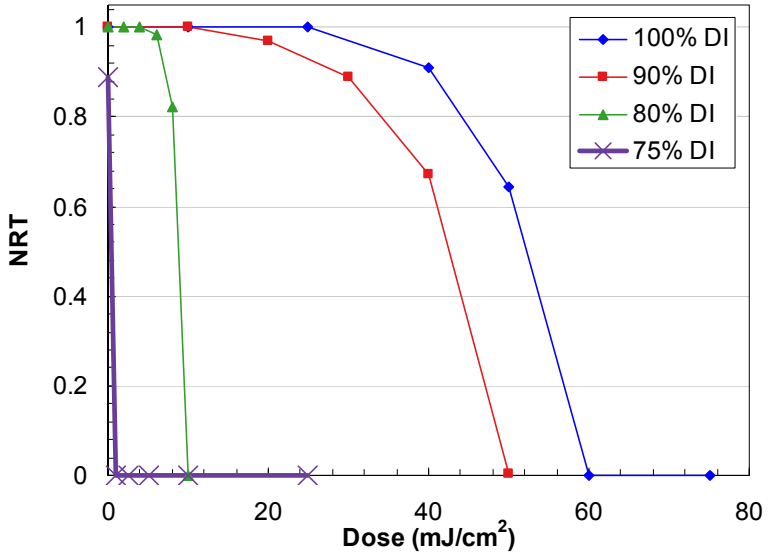

Figure 2. DUV (248 nm) contrast curves demonstrating sensitivity as low as 1 mJ/cm^2 and a contrast ratio as high as 8.3 at 10 mJ/cm^2 by changing the amount of dissolution inhibitor in the formulation.