ABSTRACT

The incorporation of fluorine into photoresist materials imparts a variety of highly desirable properties for deep ultraviolet lithography at 193 nm and 157 nm. Chief amongst these benefits are the high optical transparency of partially fluorinated materials and the high acidity of fluorocarbinols. Yet, significant challenges remain to incorporate sufficient fluorine necessary for high transparency into functionalized norbornene monomers without adversely affecting transition metal polymerization processes.

Chapter 2 details the synthesis and characterization of a series of partially fluorinated tricyclo[4.2.1.$0^{2,5}$]non-7-ene (TCN) monomers. The fused cyclobutane ring serves as an additional scaffold onto which additional fluorinated groups can be incorporated in order to increase transparency at 157 nm without adversely affecting the polymerization behavior of the monomer. The synthesis and imaging of TCN-based photoresist polymers is explored in Chapter 3.

Chapter 4 introduces a series of 3-oxa-tricyclonon-7-ene and 4-oxa-tricyclonon-8-ene monomers synthesized from quadricyclane and fluorinated ketones. In chapter 5, addition and ring-opening metathesis polymers of fluorinated oxatricyclononenes are shown to offer transparencies similar to a hexafluorocarbinol-functionalized norbornene addition polymer, revealing the effect of the alicyclic backbone structure on transparency at 157 nm. 4-Oxatricyclononenes are valuable comonomers for the elevation of glass transition temperatures in ROMP polymers, while low molecular weight ROMP copolymers of 3-oxatricyclonene are being evaluated as crosslinking agents in negative tone resist formulations.

Chapter 6 details the use of cross-metathesis and ring-opening cross-metathesis in the synthesis of multifunctional monomers and oligomers for 193 nm immersion and 157 nm lithography. Cross-metathesis with unsaturated hexafluorocarbinols is a facile method to generate functionalized olefins without using hexafluoroacetone. These developments culminate in the synthesis of difunctional norbornenes containing both ester and hexafluorocarbinol

functionalities which display dramatically increased transparency at 157 nm and will potentially afford unique dissolution behavior.

Finally, chapter 7 explores the synthesis of trisubstituted olefins via ruthenium-catalyzed cross-metathesis. 2-Methyl-2-butene is a convenient isobutylene surrogate in the formation of prenyl groups via cross-metathesis. Understanding of the reactivity of second-generation metathesis catalysts with 1,1-disubstituted and trisubstituted olefins has prompted the exploration of ring-opening cross-metathesis of low strain cyclic olefins and three component cross-metathesis reactions with high product selectivity.