Effect of microstructure on deprotection kinetics in photoresist

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This work describes an experimental and modeling study of the effect of polymer chain microstructure on deprotection kinetics in photoresist. We report results from an analysis of kinetic FTIR data for acrylate based photoresist materials with known monomer reactivity ratios and polymer microstructure. The best fit to the measured deprotection kinetics requires two postulates: (a) the statistical polymer chain in photoresist can contain blocks of up to 3 neighboring monomer pendants, and (b) the rate constant for the de-protection reaction involving isolated pendants is as much as 25% higher than the rate constant for pendants with neighbors. A modeling method to represent the statistics of de-protection with neighboring pendants on a polymer chain is derived using a continuum approximation. The modeling results indicate that for high levels of neighboring repeat units in a photoresist, the latent image contrast can improve by as much as 10% over the case with only isolated pendants. Patterning conditions in which the new kinetics model predicts measured resist CD with greater accuracy than a conventional kinetics model are detailed. Finally, we suggest simple pendant group de-protection chemistry which can explain the dependence of reaction rate on neighboring pendants in resist and predict with simulation an ideal microstructure for high contrast photoresists.