Acid catalyst transport in chemically amplified resist films

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Processes occurring at nanoscale in lithographic films have attracted lot of attention in recent years as the smallest feature size on silicon chips continues to shrink. These processes play an important role in deciding the resolution and line edge roughness of the final features. Recent ITRS reports also emphasize the need of quantitative models to predict the behavior of the resists under different imaging and process conditions, and facilitate the screening of resist materials and process development.

We investigated controlling processes in chemically amplified resist films of poly(4-hydroxystyrene-co-tertbutyl acrylate) resin.[1] Resin was loaded with 1 to 4 wt% of photoacid generator and 300 nm thick films were spun coat on silicon wafer and photoacid was activated with UV light (254 nm). These films were then baked for different times ranging from 5 sec to 1 hr to get different extents of reaction. The reactions were always carried out at temperatures well below the glass transition temperatures of the resin. Extent of reaction was found out by tracking poly(t-butyl acrylate) peak present in the reactant using infrared spectroscopy. For simulations the reaction was assumed faster than diffusion of the acid catalyst in the polymer matrix. The mobility of the acid catalyst in the resin then becomes the rate limiting factor. We modeled acid hopping with two types of random walks that reproduce Fickian or anomalous (sub-diffusive) transport.

Experimental results for all temperatures show faster deprotection at shorter times and slower deprotection at longer times. There is stronger-than-linear dependence on acid concentration. The simulated deprotection rates using Fickian diffusion capture the correct time scale, but they underestimate the short-time conversion, overestimate the long-time conversion, and exhibit a linear dependence on acid concentration. However, the simulations based on anomalous acid transport show near quantitative agreement with experimental data at all temperatures and acid loadings, provided that a slow acid loss mechanism is included in the algorithm. Significantly, this model requires only two free parameters - an anomalous exponent ($\gamma < 1$) and characteristic time (τ). Anomalous diffusion implies that polymer dynamics are controlling the reaction kinetics in glassy CARs. The parameters extracted from these simulations and their scaling with temperature are remarkably consistent with other studies of probe diffusion in glass formers.

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[1] G.M. Perera, Y.N. Pandey, A.A. Patil, G.E. Stein, M. Doxastakis, J. Phys. Chem. C, **114**, 24706 (2012).

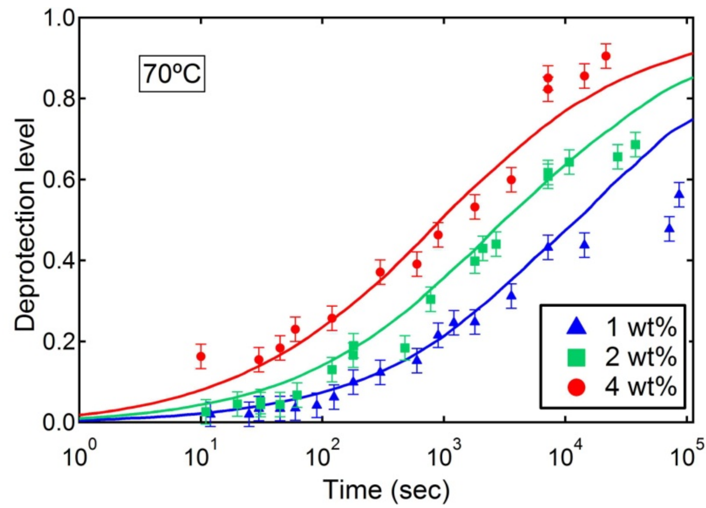

Figure (1). A simple model based on anomalous acid transport with slow acid loss matches experimental deprotection profiles. Post-exposure bake temperature of 70°C.