

## **608f Segregation, Leaching, and Adsorption of Small Molecules in Polymer Thin Films: Implications for Immersion Lithography**

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The surface segregation, leaching, and adsorption behavior of anthracene, trioctylamine (base), and the photo-acid generator (PAG) triphenylsulfonium perfluoro-1-butanefluoroborate in thin films (<100 nm) of poly(methyl methacrylate) have been analyzed using near edge x-ray absorption fine structure (NEXAFS) spectroscopy. These phenomena were investigated with respect to the effect of immersion in water and aqueous formulations as well as casting, baking, and ultra-violet exposure conditions on the surface and bulk chemical composition. NEXAFS can probe the carbon, oxygen, nitrogen, and fluorine containing components in the system and differentiate between species in order to provide surface v. bulk chemical composition as well as surface depth profiling. Studies were carried out to understand how the surface concentration of small molecule additive relates to the overall composition of the formulation and the dependence on processing parameters and film thickness. Spin-coating is a dynamic process that results in a non-equilibrium surface rich in small molecule additives relative to the bulk of the film. Previously, it was found that water immersion immediately following post-apply bake (PAB) caused the greatest change in component (acid, base) concentration at the film surface while immersion after UV exposure had a less significant effect. There is evidence to support that a delay after PAB before the water immersion allows the surface of the photoresist film to relax and results in decreased removal of additives from the surface of the film. Films were prepared that contained PAG, base, or anthracene in varying compositions and the chemical composition of the surface measured with and without immersion. Taking into account possible film relaxation, studies were performed where the film was immersed immediately following PAB as well as with some delay. PAG containing films were UV exposed and immersed in water containing a low levels of base. Films of neat PMMA were immersed in aqueous formulations containing varying concentrations of PAG, base, or anthracene, to elucidate the effect of potential leaching and re-adsorption during the immersion lithography process.