142bg Photoacid Diffusion in Photoresist Polymer Thin Films: Approaches for Measurement and Control of Thin Film Acid Diffusion

Cheng-Tsung Lee and Clifford L. Henderson

Fabrication of modern micro- and nanoelectronic devices relies on the use of high resolution lithographic processes for forming the intricate nanometer scale features which comprise such devices. Current lithographic processes are capable of resolving features on the order of 100 nm using "chemically amplified photoresists" as imaging layers. Conventional chemically amplified photoresists in their simplest form consist of a two component mixture polymer matrix, which has been rendered insoluble in aqueous developer solutions through a reactive protection of hydroxyl sites on the polymer (i.e. the hydroxyl sites are converted to a non-ionizable, more hydrophobic group), and a photoacid generator (PAG). Exposure of the photoresist mixture to ultraviolet light results in the product of a strong photoacid from the PAG, and this photoacid catalyzes the "deprotection" reaction which regenerates the hydroxyl sites on the polymer. Regeneration of the hydroxyl sites on the polymer renders the exposed regions of the polymer soluble in aqueous developer solutions. This differential solubility change created by exposure to ultraviolet light allows for formation of relief images in the photoresist which allows for microstructure fabrication. Unfortunately, the creation of small molecule acids in the photoresist film is also believed to permit substantial diffusion of the photoacid as compared to the length scale of the features being formed in such materials. It is believed that such diffusion of photoacid from exposed to nominally unexposed regions in the photoresist film results in resolution limitations for conventional chemically amplified materials on the order of 50 nm. Furthermore, such diffusion results in "biasing" of the printed feature size as compared to the intended feature size for small features. We have been developing both (1) methods for characterizing photoacid diffusion in polymer thin films and (2) materials design strategies for overcoming this diffusion limitation in conventional chemically amplified resists. This paper will first present an overview of our work on characterizing photoacid diffusion in polymer thin films using both (1) impedance spectroscopy on interdigitated electrode sensors and (2) a combination of fourier transform infrared spectroscopy and high resolution electron beam lithography. A materials design strategy in which photoacid generator moieties are covalently linked to the photoresist polymer backbone will then be discussed. Using the thin film acid diffusion characterization methods previously discussed, the impact of different approaches for attaching the photoacid generator moieties to the polymer backbone on the resulting photoacid diffusion coefficient and polymer lithographic properties will be discussed.