Photochemistry of photoresist model compounds: from deep UV to extreme UV

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The next step along the roadmap of lithography for high volume manufacturing of microelectronic devices involves the use of extreme ultraviolet light (13.5 nm).^[1] Current EUV photoresist materials are derived from those optimized for deep UV lithography (DUV, 193 nm). Alternative materials have been proposed in the past years that have a more favorable absorption cross section at 13.5 nm and potentially a higher etch resistance.^[2-5]

In the recently established Advanced Research Center for Nanolithography we address the fundamental issues related to Extreme Ultraviolet Lithography. We have selected a small set of model systems that have been proposed as hybrid organic/inorganic EUV photoresists^[2-5] for our experimental and computational photochemistry studies. In this presentation we focus on tin oxo cages (Figure 1).



Figure 1. Structure of the tin cage compounds under study

This class of molecular compounds has been demonstrated to work as negative EUV photoresists by Brainard and co-workers,^[5] and it is related to promising commercial materials developed by Inpria.^[6]

Variation of the R-groups and of the counterions allows to probe structure/photoreactivity relationships. We have explored the response of these materials to deep ultraviolet laser

irradiation, and to extreme ultraviolet exposure. Deep UV irradiation applied to the compounds dissolved in organic solvents allowed to identify the molecular reaction products. Analysis of thin films by means of X-ray photoelectron spectroscopy revealed loss of carbon upon DUV irradiation in inert gas atmosphere, with uptake of oxygen when air is present during or after irradiation. The most likely primary reaction in these systems is homolytic cleavage of the tin-carbon bonds. Precise determination of the structure of the reaction products is challenging because the tin cages have multiple sites with similar reactivity, and after conversion of one reactive site, the reactivity of the others does not change much. Thus, complex product mixtures result already at low conversion. Preliminary picosecond pump-probe experiments show the formation of transient species with a lifetime beyond the nature of the counterion X^- . Ongoing work is focused on quantifying the dynamics and the efficiencies of these processes, with the ultimate aim of controlling photoresist performance with respect to sensitivity, resolution and line edge roughness.

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