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Interface- and Chemical-Specific Soft X-ray Measurements of the Distribution of Small Molecule Components in Advanced Polymer Thin Film Photoresists

E.K. Lin, J.L. Lenhart, D.A. Fischer, C.L. Soles, R.L. Jones, and W.-I. Wu (NIST), D.L. Goldfarb and M. Angelopoulos (IBM)

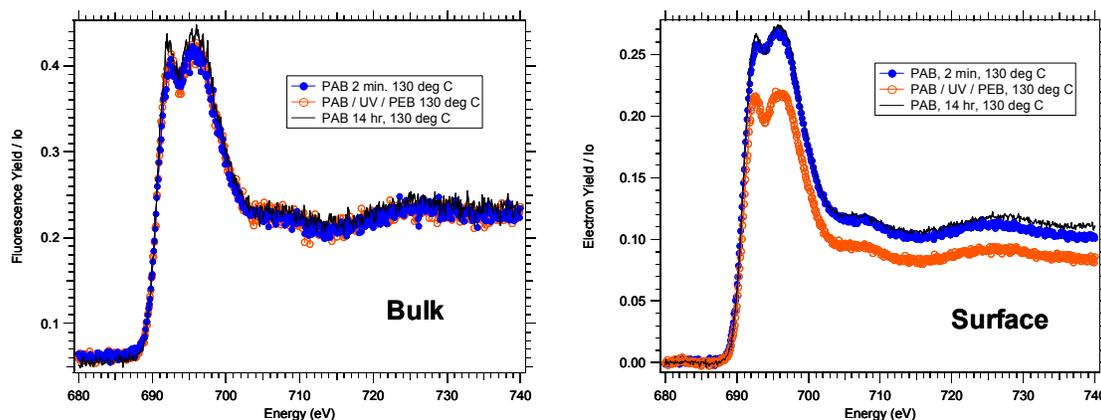
Beamline(s): U7A

Introduction: Next generation lithographic materials and processes that are able to fabricate sub-100 nm features are critical for continued improvements in the performance of integrated circuit devices. The development of sub-100 nm features places severe restrictions on the acceptable resolution of the lithographic process. Advanced photoresist formulations make use of photosensitive molecules, photoacid generators (PAGs), which decompose to form acids after exposure to photons. The photo-generated acids (PGAs) then catalytically alter the solubility of the resist polymer through a deprotection reaction during a post-exposure bake so that exposed areas of an image are removed by a developer solution. As imaging wavelengths decrease, the photoresist film thickness must decrease to less than 100 nm due to the high optical absorbance of the organic components at these wavelengths. With thin material layers, the patterning of nanoscale features with lithography (profile control) becomes increasingly dominated by interfacial chemistry and materials issues rather than on the bulk photoresist properties.

Methods and Materials: Near-edge X-ray absorption fine structure (NEXAFS) measurements were performed on thin films of poly(hydroxystyrene) (PHS) and its protected analog poly(t-butoxycarboxystyrene) (PBOCSt) loaded with bis(p-tert-butylphenyl) iodonium perfluorooctanesulfonate (PFOS) photoacid generator (PAG) to determine the surface behavior of the PAG in the resist matrix as a function of lithographic processing steps (post-apply bake, PAB; exposure; and post-exposure bake, PEB). Since both the film surface and bulk are measured at the same time, the surface segregation and chemical bonding structure of the film components are analyzed with reference to the overall composition of the film.

Results: Data from the fluorine-edge for a PHS film with PFOS show that the fluorinated PAG component is present at the film surface in the as prepared film and for thermal bakes at 130 °C for up to 14 h. However, after a UV dose and a 5 min post-exposure bake (PEB) at 130 °C, the fluorinated component is depleted from the surface. However, the overall mass fraction of fluorine through the entire film remains essentially unchanged. It is surprising that a low surface energy species such as PFOS is depleted from the surface because fluorinated hydrocarbons generally segregate preferentially to the surface. These results demonstrate the surface sensitivity of NEXAFS to distinguish the surface behavior of important photoresist components. NEXAFS measurements were also performed on the protected polymer, PBOCSt, and PFOS. By measuring films near the carbon-edge, fluorine-edge, and oxygen-edge, we observe, in detail, both the deprotection chemistry (PBOCSt to PHS) and the PAG concentration after processing steps such as PAB and UV/PEB. Near the fluorine-edge, the bulk film measurements of the fluorine spectra are nearly identical showing that the overall PFOS concentration in the film remains essentially unchanged. However, at the PBOCSt film surface, the fluorine concentration is significantly enhanced after PAB/UV/PEB. In these first measurements, the behavior of fluorinated PAG segregation for PHS and PBOCSt are qualitatively different. We have successfully demonstrated the use of NEXAFS to distinguish the surface and the bulk concentrations of PAGs and deprotection chemistry. These are unique data currently unavailable in the semiconductor industry and are expected to help provide the fundamental science needed to understand interfacial effects that limit the development of future photoresist materials.

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NEXAFS data for the bulk film and at the surface near the fluorine-edge for a PHS film with PFOS after PAB for 2 min at 130 °C, PAB for 14 h at 130 °C, and after PAB (2 min), UV exposure, and PEB (5 min at 130 °C). The PFOS is apparently depleted from the surface after the full processing treatment.