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FOR MORE INFORMATION

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Quantitative Depth Profiling of Photoacid Generator Molecules in Photoresist Materials by Near-Edge X-ray Absorption Fine Structure Spectroscopy

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Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to quantify the surface composition and depth profiling of photoacid generators in thin film photoresist materials. By considering model compositional profiles, NEXAFS distinguishes the surface molar excess within the top 6 nm from the bulk. A surface enriched system, triphenylsulfonium perfluorooctanesulfonate (TPS-PFOS), is contrasted with a perfluorobutanesulfonate (TPS-PFBS) photoacid generator, which displays an appreciable surface profile within a 6 nm segregation length scale. These results, while applied to 193-nm photoresist materials, highlight a general approach to quantifying NEXAFS partial electron yield data and find application to immersion lithography fundamentals.

Chemically amplified photoresist materials are the enabling technology for photolithography –the process by which all modern microelectronics are manufactured by the semiconductor industry. These multi-component materials are comprised primarily of polymeric photoresist, photoacid generators, and base-quencher additives. The exposure of the photoresist to radiation through a mask leads to the generation of photoacids that catalyze a chemical reaction rendering exposed areas soluble in a developer. Perturbations in the component distributions therefore are critical to print sub-65 nm features by 193 nm photolithography. The industry is ready to extend this technology to 32 nm half-pitch dimensions by immersion lithography, which increases the resolution by applying a high refractive index fluid between the lens and resist thin film to reduce the effective wavelength of light. This process change leads to additional demands and constraints on the photoresist material.

Any change in surface structure or chemistry from the top few



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nanometers due to leaching of photoacid generator and base additives during immersion can

compromise the performance of the resist as well as contaminate the lens system. Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy provides a sensitive bond-selective and depth-selective method to quantify the thin film surface structure. In a NEXAFS experiment, tunable soft x-rays are preferentially absorbed by the sample when the incident radiation is at the appropriate energy to allow the excitation of a core shell electron of a specific element (C, N, O, or F) to a chemical bond specific unoccupied molecular orbital. Due to the well-defined energy gap associated with a core shell to unoccupied orbital transition, NEXAFS is sensitive to the bond-

ing characteristics of the element giving a discrete peak(s) for each chemical bond. Electrons originating from near the top (1 nm to 6 nm for carbon *K*-edge electron yield spectra) of the film surface will have different final kinetic energies upon detection, depending on their inelastic energy loss (depth of creation). By applying a negative voltage entrance grid bias at the partial electron yield detector, electrons of low kinetic energy can be rejected. As the negative entrance grid bias voltage is gradually increased, lower kinetic energy electrons are discriminated and the effective electron yield sampling depth gets closer to the film surface.

Figure 1 shows the NEXAFS carbon *K*-edge spectra for the pure methacrylate photoresist (dotted line) and photoresist containing TPS-PFOS (solid lines) shown in **Figure 2**. The incident photon energy is scanned from 280 eV to 330 eV and the electron yield is measured at the detector as a function of the entrance grid bias from -250 V (immediate surface) to -50 V (top several nm). The sharp peak at 285 eV is the C 1s $\rightarrow \pi^*_{C=C}$ transition arising from the triphenyl groups on the photoacid generator as highlighted in the inset. This region is of specific interest for depth profiling as seen from the strong bias dependence for the resist/photoacid genera-

tor mixture. The integrated peak intensity is directly proportional to the C=C molar bond (number) density allowing a quantification of the PAG composition as a function of depth without interference of the photoresist chemistry.

The measurement method is described in the *Applied Surface Science* article as well as approaches to quantify the photoacid generator depth profile over the top 2 nm to 6 nm. This method can be extended to a diverse set of materials systems without the need for special labeling or preparatory procedures.

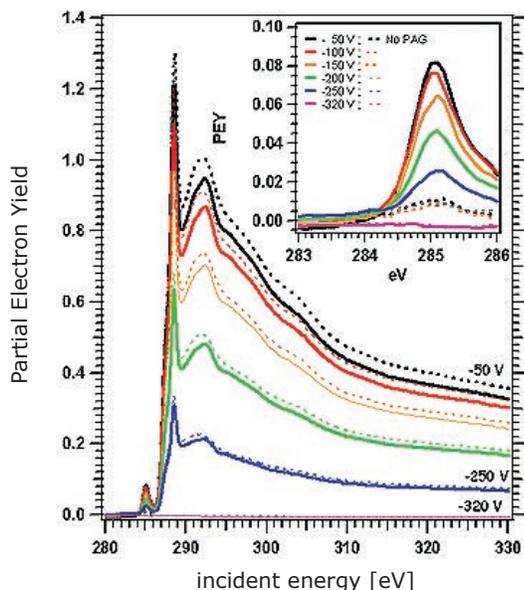


Figure 1. NEXAFS spectra of the pure photoresist (dotted lines) and resist containing 6.7 % by mass TPS-PFOS photoacid generator (solid lines) as a function of entrance-grid bias from -50 V to -250 V. At -320 V, no signal is detected. The inset highlights the $\pi^*_{C=C}$ region which allows direct quantification of the triphenyl groups of the photoacid generator.

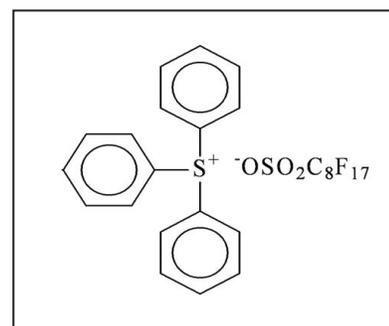


Figure 2. Triphenylsulfonium perfluorooctanesulfonate photoacid generator.