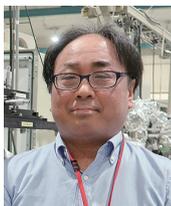


Development of Resonant Soft X-Ray Scattering Spectroscopy for Photoresists

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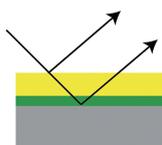
For further miniaturization of semiconductors, the era of EUV (13.5 nm) exposure has arrived, down from the 197 nm of the conventional ArF laser. This reduction in wavelength to less than one-tenth requires further thinning of the photosensitive materials (photoresists), leading to active development efforts of photoresist industry.

Since the depth of focus decreases in proportion to the wavelength, EUV exposure requires a thickness of only a few tens of nanometers, compared to conventional photosensitive materials of around a few hundred nanometers. To preserve the 10-nm pattern, a thin base layer between the silicon substrate and photoresist is essential. The EUV exposure technology utilizes a two-layer polymer film that is several tens of nanometers thick.

Resonant soft X-ray reflectivity is a technique that can determine the film thickness of different chemical species by utilizing the difference in X-ray resonance energy. We conducted experiments on a bilayer polymer film of PMMA (40 nm thick) and PVPh (70 nm thick). Figure 1 shows a schematic diagram of the sample.

The complex permittivity in the X-ray region is written as $(1-\delta(\text{h}\nu)) - i\beta(\text{h}\nu)$, where $(1-\delta)$ and β correspond to the refractive index and absorptivity, respectively. In the X-ray region, δ and β are much smaller than 1. Furthermore, δ and β are related by the Kramers-Kronig (KK) relation. Thus, $\beta(\text{h}\nu)$ is measured *via* the XAFS absorption spectrum. Figure 2 shows the refractive index δ calculated from each absorption spectrum using the KK transformation. Just as the pre-edge structure of the absorption spectrum differs depending on the molecular species, the refractive index δ also has a complex structure at the absorption edge that depends on the chemical

(a) At non resonant energies



Due to similar refractive index,
photons can not distinguish two layers

(b) At resonant energies

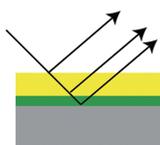


Figure 1. Schematic of (a) nonresonant and (b) resonant scattering of two polymer layers.

species. Near the core absorption edge, selecting the resonance energy allows scattering contrast between chemically distinct species, even if their electron densities are nearly identical.

Figure 3 shows reflectivity measurements at both non-resonant and resonant energies. At non-resonant energy, a single period is observed, indicating a film thickness of 110 nm. The bilayer film appears as a single film. At resonant energy, a complex vibrational structure appears, reflecting the properties of a bilayer film. Details are still under analysis; according to these results, a method for analyzing multilayer polymer films using resonant soft X-ray reflection is being developed.

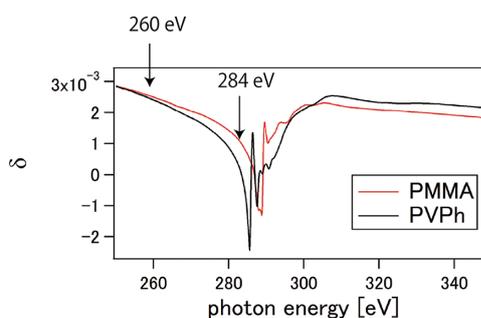


Figure 2. X-ray energy dependence of the refractive index δ of PMMA and PVPh polymers.

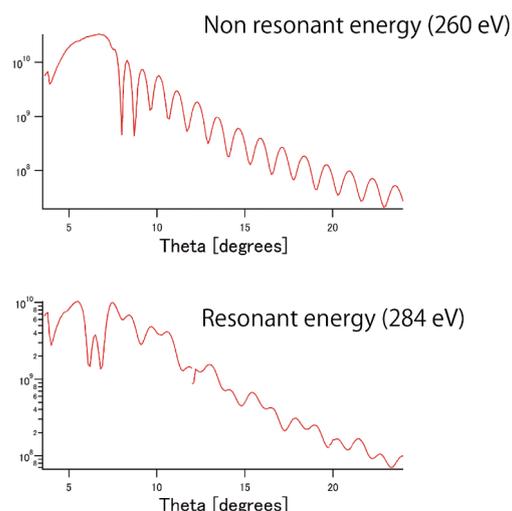


Figure 3. Reflectance spectra of (PMMA, PVPh) two-layer polymer film at off-resonance and resonant energies.