Evolution of Optical Properties of EUV Photoresists and Underlayer Materials upon Irradiation at 13.5 nm

Grace H. Ho (鄭秀英)[1], Fu-Hsiu Kang (康富修)[1], Yu-Hsien Shih (施郁嫻)[1], Wan-Ping Ku (古宛平)[1], Yu-Sheng Cheng (鄭宇勝)[1], Pei-Jung Wu (吳沛融)[1], Hok-Sum Fung (馮學深)[2], and Huang-Wen Fu (傅皇文)[2]

[1]Department of Applied Chemistry, National University of Kaohsiung, Kaohsiung, Taiwan
[2]National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Optical properties of refractive index (n), photoabsorption coefficient (k), and the thin-film thickness (T) are needed information for optimization of EUV resist patterning. The optical properties of several EUV model resists have been determined by a specular EUV reflectivity (SEUVR) method at the Advanced Light Source (ALS). A specular X-ray reflectivity (SXR) method is a more convenient technique for deriving the n, k, T, and density values; on the other hand, the actinic 13.5 nm light exposes the thin-film sample, and at the same time it monitors the evolution of thin-film properties *in situ*, which cannot be achieved with the SXR method. Optical properties, including refractive index, photoabsorption coefficient, and film thickness, are derived with a specular extreme ultraviolet reflectivity (SEUVR) method at 13.5 nm. The review of previous SEUVR and SXR studies and the SEUVR measurement of this work can be found elsewhere.

Figure 1 shows the reflectivity curves of a novolac-type underlayer (UL) sample and polymethyl-methacrylate (PMMA) upon 13.5 nm irradiation with different exposure doses. This UL sample maintains its thin-film integrity, whereas some of the thin-film properties ofPMMA change easily upon irradiation at 13.5 nm.

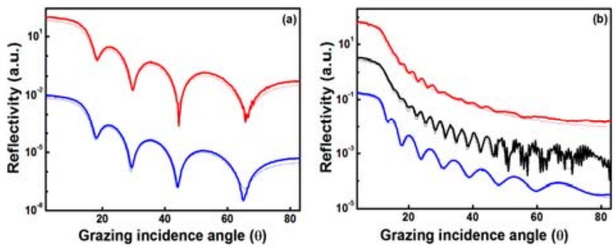

Fig. 1: Reflectivity curves evolve of (a) a novolac-type underlayer sample. (b) PMMA. (-): first exposure, (-) after extensive exposure, (-), first exposure with a reduced light intensity; dotted lines: simulations by X'Pert (Panalytical) software.

The SEUVR method is able to monitor the change of optical properties of photoresist materials actinic and *in situ*. Figure 2 illustrates the film integrity of the round robin resist (RRR) and three other UL samples of different types. The EUV radiation damage to samples can thus be determined. The refractive index and density of most samples that we measured do not change with an experimental significance. The evolution of the reflectivity curves is thus attributed to a change of the thin-film thickness. Figure 3 summarizes the thickness loss of more than forties samples measured by this work. The thickness loss is dependent on a structural metric, σ_{abs}/double-bond equivalent per carbon (DBEPC), which means it is EUV photoabsorption and polymeric structure dependent. The thickness loss is also thickness dependent, the loss of RRR and PMMA of 125 nm in thickness few times greater than that of UL samples of 30 nm in thickness.

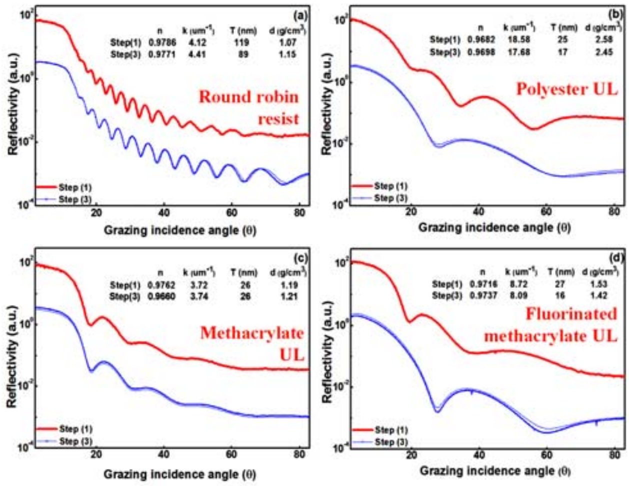

Fig. 2: Thickness loss of photoresist materials upon extensive EUV irradiation.

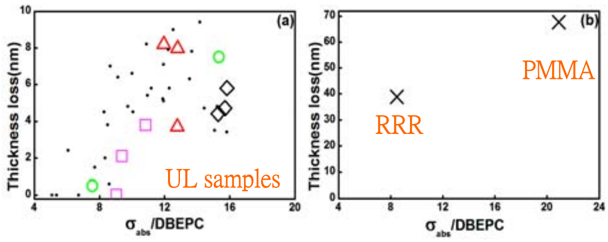

Fig. 3: Thickness loss of as a function of σ_{abs}/DBEPC. (a) UL samples, and (b) photoresists RRR and PMMA.

We have successfully constructed the structural metric to predict the relative extent of ionic outgassing and pressure rise for 12 UL samples, RRR, and PMMA [1]. In this work, we show that the absolute thickness loss and film integrity of photoresist materials can be predicted by the structural metric. This result can help resist vendor to formulate photoresist materials with stronger EUV radiation resistance.

[1] G. H. Ho *et al.*, J. Photochem. Photobiol. A: Chemistry (2010, accepted).

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