

Internal Layered Structures of UV-Cured Thin Films after Sequential Vapor Infiltration Analyzed by X-ray Reflectivity Measurements

K. Chiba, T. Nakamura, S. Ito, M. Nakagawa
IMRAM, Tohoku University, Sendai, Miyagi 980-8577, Japan
masaru.nakagawa.c5@tohoku.ac.jp

Resist masks with high dry etching durability are required for high-aspect-ratio processing in UV nanoimprint lithography (UV-NIL). Organic-inorganic hybridization by sequential vapor infiltration (SVI) with trimethylaluminum (TMA) improves resistance of organic UV-cured films for dry etching.¹ We found that hydroxy-containing monomer-A (Fig. 1a) and hydroxy-free monomer-B (Fig. 1b) caused different aluminum (Al) distributions in respective UV-cured films after SVI by scanning transmission electron microscopy and energy dispersive X-ray spectroscopy (STEM-EDS).¹ In this study, three kinds of SVI-treated UV-cured spincoated films made with monomer-A, and monomer-B, and their mixture (NL-SU1) suitable for UV-NIL were prepared, and their internal layered structures arising from different Al distribution were analyzed by non-destructive X-ray reflectivity (XRR) measurements without volume shrinkage during the measurement.

UV-cured thin films of *film-A* (monomer-A), *film-B* (monomer-B), and *film-S* (monomer A+B; NL-SU1) were prepared by spincoating onto silicon substrates and UV exposure at 365-nm dose of 2 J cm⁻². Respective UV-cured films with 100 nm thickness were subjected to SVI comprising 100-cycle sequential doses of TMA and a final dose of H₂O in the same manner previously reported by us.¹

Figure 2 shows measured and calculated XRR curves of SVI-treated *film-A* (Fig. 2a), *film-B* (Fig. 2b), and *film-S* (Fig. 2c). It was obvious that the measured XRR curves were completely different among the SVI-treated films. The measured XRR curves were almost consistent with those calculated using the Fresnel equation. The calculated curves suggested that the film-A, B, and S had an internal structure of three layers (Fig. 3a), four layers (Fig. 3b), and two layers (Fig. 3c), respectively. The presence of the internal layered structures were also supported by STEM-EDS. High-density Al-rich layers were present near the surface and interface in case of *film-A*, while a high-density Al-rich layer was present near the middle of *film-B*. The mixture of monomer-A and B caused organic-inorganic hybridization to be homogenized. This suggested that the hydroxy-containing monomer-A was miscible with the hydroxy-free monomer-B in the UV-cured films. We led the conclusion that the mixing of monomers could be a positive way to homogenize Al distributions and densities of UV-cured films in organic-inorganic hybridization by SVI for the purpose of strengthening dry-etching resistance of organic resist masks.

¹M. Nakagawa et al., *J. Vac. Sci. Technol. B* **36**, 06JF02 (2018).

²T. Uehara et al., *Bull. Chem. Soc. Jpn.* **91**, 178 (2018).

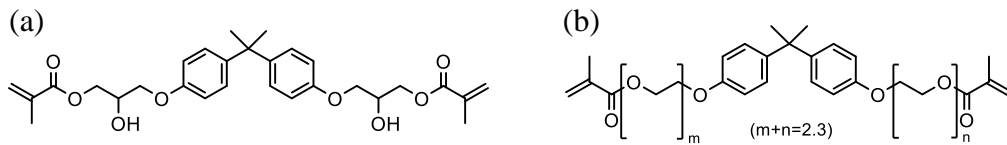


Figure 1: Chemical structures of (a) bisphenol A glycerolate dimethacrylate (hydroxy-containing monomer-A) and (b) bisphenol A ethoxylate dimethacrylate (hydroxy-free monomer-B).

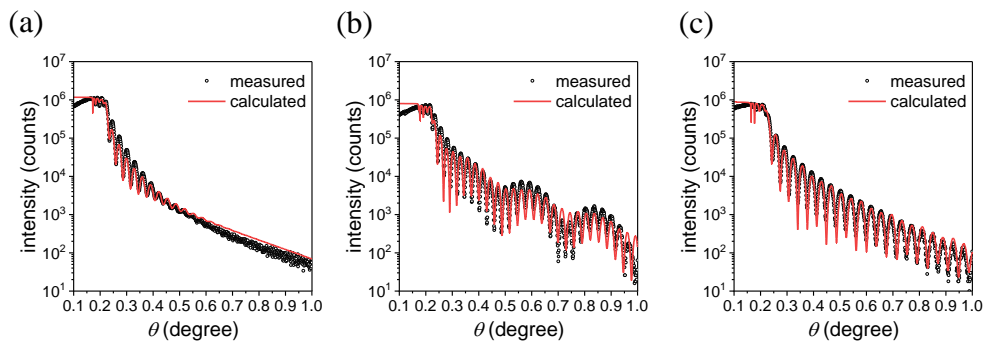


Figure 2: Measured and calculated XRR curves of SVI-treated (a) *film-A* (monomer-A), (b) *film-B* (monomer-B), and (c) *film-S* (monomer A+B) on silicon substrates with a native oxide layer.

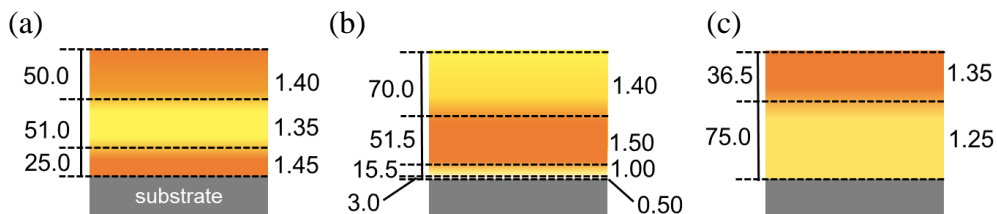


Figure 3: Illustrations of density-different internal layered structures of SVI-treated 100 nm-thick UV-cured films made with (a) *film-A*, (b) *film-B*, and (c) *film-S* on silicon substrates. The values on each left and right side indicate respective thicknesses (nm) and densities (g/cm^3) under rough calculation.