Improved etching resistance of UV-cured films with/without hydroxy groups by organic/inorganic hybridization through sequential infiltration synthesis and sequential vapor infiltration

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Sequential infiltration synthesis (SIS)[1,2] and sequential vapor infiltration (SVI)[3,4] methods enable organic/inorganic hybridization of organic polymers by infiltration of a reactive inorganic precursor. It was demonstrated that SIS was helpful in improving dry etching resistances of organic resist films in electron beam lithography[1] and block copolymer lithography.[2] We noticed the organic/inorganic hybridization methods to apply to ultraviolet nanoimprint lithography (UV-NIL). In UV-NIL, a resist residual layer formed underneath imprint patterns should be removed by dry etching such as oxygen reactive ion etching (O_2 RIE) under the condition of anisotropic etching that the pattern width of the resist mask is maintained.[5] Therefore, it is preferable to adopt UV-cured resist films made of aromatic segment-containing monomers rather than aliphatic segment-containing monomers based on Ohnishi parameter. In this study, we investigated whether SIS or SVI, using trimethylaluminum (TMA) as an inorganic precursor, strengthened etching resistance of UV-cured films toward O_2 RIE. Because TMA is a kind of Lewis acid, we compared etching rates between two UV-cured films made of either a monomer with or without hydroxy groups to discuss the difference in infiltration of TMA into the UV-cured films.

Two UV-curable *Resin A* and *B* composed of a bisphenol A-based monomer without and with hydroxy groups (Fig. 1), respectively, were prepared according to our previous reports.[6,7] UV-cured films of 0.1 μm thick were subjected to SIS or SVI procedures depicted in Fig. 2. O_2 RIE was conducted under conditions that we previously reported.[5] Figure 3 shows the changes in film thickness of the cured resins before and after modification through the SIS or SVI method as a function of O_2 RIE period. The etching rates were 31 nm min^{-1} for *Resin A* and 29 nm min^{-1} for *Resin B*. The 1- and 5-cycle SIS modification caused *Resin A* to be etched linearly at lower etching rates, whereas 5-cycle SIS-modified *Resin B* showed an increased etching rate with a decrease of film thickness. These results indicated that the monomer with hydroxy groups trapped TMA near the film surface and suppressed uniform organic/inorganic hybridization. Within 3 min, the 100-cycle SVI modification linearly and slowly decreased the film thicknesses of *Resin A* and *B*. These results suggested that the SVI method uniformly infiltrated TMA into the resin films rather than the SIS method, resulting in higher etching resistance. We will present elemental depth profiles of the hybridized resin films by X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM) combined with energy dispersive X-ray spectroscopy (EDS).

[1] Y.-C. Tseng, et al., *J. Mater. Chem*. **21**, 11722 (2011). [2] Q. Peng, et al., *Adv. Mater*. **22**, 5129 (2010). [3] B. Gong, et. al., *Chem. Mater*., **23**, 3476 (2011). [4] E. C. Dandley, et al., *Adv. Mater. Interfaces* **3**, 1500431 (2016). [5] T. Uehara, et al., *J. Photopolym. Sci. Technol*. **29**, 201 (2016). [6] T. Uehara, et al., *Chem. Lett.* **42**, 1475 (2013). [7] T. Uehara, et al., *Bull. Chem. Soc. Jpn.* (2017), doi: 10.1246/bcsj.20170280.

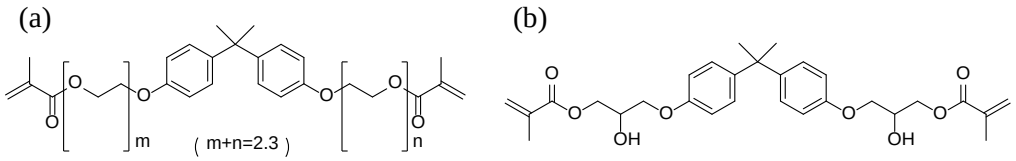

Figure 1: Chemical structures of (a) bisphenol A ethoxylate dimethacrylate and (b) bisphenol A glycerolate dimethacrylate.

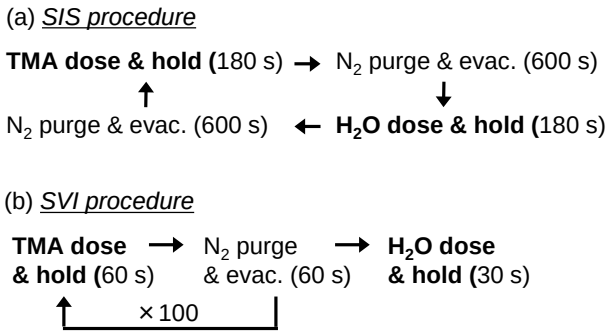

Figure 2: Flowcharts of (a) SIS and (b) SVI procedures.

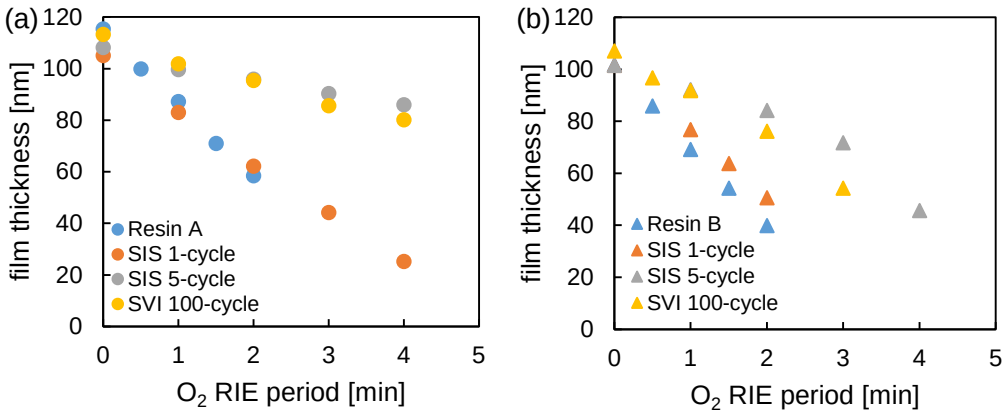

Figure 3: Changes in film thickness of (a) *Resin A* and (b) *B* films as a function of O_2 RIE period; (blue) no treatment, (orange) 1-cycle SIS modification, (gray) 5-cycle SIS modification, and (yellow) 100-cycle SVI modification.