Epoxy novolac resins are used as the base polymers of I-line (365 nm) photosensitive materials with sub-300 nm resolution limits because of high light absorption at wavelengths less than 300 nm.\(^1,2\) When compared with acrylic-base polymers of ArF (193 nm) in photosensitive materials with resolution capabilities of less than 100 nm, the epoxy novolac resins have better properties, such as etch resistance to carbon fluoride gases, better mechanical strength, better thermal stability, and lower swelling of resists.\(^3,4,5\)

This study was directed at expanding the resolution limits of epoxy novolac resins, which have enhanced etch resistance as one of their resist properties, using a specific ultraviolet (UV) nanoimprint lithography process with gas-permeable templates and volatile solvents in the resist materials. Previously, the applicability of epoxy novolac resins as resist materials in UV nanoimprint lithography was limited by their poor liquidity or non-liquid properties at room temperature.\(^6,7,8\)

Volatile solvents in resist materials are expected to decrease the viscosity of epoxy novolac resins, resulting in resist-solution fluidity for filling the template smoothly during the pre-exposure delay process before UV irradiation. However, the use of volatile solvents in nanoimprint resist materials has resulted in solvent trapping and pattern failure in UV nanoimprint lithography when using non-gas-permeable templates such as quartz and light-transparent plastic.\(^9,10,11\) At the same time, some techniques using gas-permeable templates have been reported in relation to material development.\(^12,13\) In our previous studies into nanoimprint resist design for high-volume manufacturing, cyclodextrin-based gas-permeable porous template materials were prepared to minimize solvent trapping, as such trapping would result in incomplete filling of the materials in the template during the imprint process.\(^15\) Using our previously developed cyclodextrin-based gas-permeable porous template materials, high-resolution patterning of epoxy novolac resins, with their many advantageous resist properties, was demonstrated for the expanded use of UV nanoimprint lithography instead of photolithography.

Figure 1 shows the chemical structures of (a) epoxy novolac resins having high etch resistance and mechanical strength, (b) a UV initiator for cationic polymerization of epoxy groups, (c) acetone as a volatile solvent to decrease the viscosity of the epoxy novolac resins for resist-solution fluidity in UV nanoimprint lithography, (d) cyclodextrin derivatives with methacryloxyalkyl groups as in the above gas-permeable template material,\(^16\) (e) a UV initiator for the radical polymerization of methacryloxyalkyl groups, (f) other novolac resins with hydroxyl and epoxy groups in our reported underlayer,\(^17\) (g) 1,3,4,6-tetrakis(methoxymethyl)glycoluril, and (h) pyridinium p-toluenesulfonate.

The epoxy novolac resin (Dow Chemical D.E.N. 431), used as one of the commercial resist-based components, is a general-purpose polymer and has high viscosity (1000–1500 mPa·s) at 50 °C and is non-liquid at room temperature. The viscosity of approximately 50 mPa·s was achieved by diluting 15 wt% acetone into the epoxy novolac resin for an acceptable UV nanoimprint-resist material. The viscosity was measured using a rheometer (Reorojika Visco Analyzer VAR100). The low viscosity of a nanoimprint-resist material can also enable filling of the topography of the template at low imprint pressure for defect reduction. The chromatograph (Tosoh Bioscience HLC-8320GPC EcoSEC) was equipped with three connected separation columns: two columns (Tosoh SuperAW3000) and one SuperAWM-H column (Tosoh Bioscience TSKgel\(^9\)). N,N-Dimethylformamide was used as the mobile phase. The column temperature was maintained at 40 °C. The solvent flow rate was set at 0.6 mL/min. The average molecular weights of the epoxy novolac resin were approximately 1000 relative to those in polystyrene standards (Tosoh PSTQuick Kit-H). The used nanoimprint
Resist material comprised 80 wt% epoxy novolac resin as shown in Fig. 1(a), 5 wt% additives and UV initiator as shown in Fig. 1(b), and 15 wt% acetone.

In order to confirm the cationic polymerization of epoxy groups in the epoxy novolac resin and minimize the irradiation time needed, a fine-demolding of the epoxy novolac resin nanoimprint-resist material from the gas-permeable template was performed. This stripping test has been used in sensitivity checks of nanoimprint materials.20–22) The above nanoimprint resist material was spun on silicon wafers at 5000 rpm for 120 s and polymerized using a metal-halide lamp system (Sun Energy, broad-band targeted for the 365 nm peak, irradiation intensity of 71 mW/cm²). The thickness of the resulting films, measured with a spectroscopic reflectometer (Fimetrics F20-UV), was found to be approximately 4 µm. After UV irradiation, acetone, cyclohexanone, propylene glycol monomethyl ether, and ethyl lactate were dispensed on the silicon wafer coated with the epoxy novolac resin, then held for 90 s, followed by spin drying at 1500 rpm for 60 s and at 5000 rpm for 120 s. The thicknesses of the nanoimprint resist material were measured again. The amount of stripping was determined by the difference between the initial and final thicknesses. The irradiation time in the formulation of the above nanoimprint-resist material was minimized at 20 s.

Figure 2 shows a flowchart of UV nanoimprint lithography using a gas-permeable template and epoxy novolac resin as one of the general-purpose polymers. UV nanoimprint lithography is divided into four processes, which can be designated as dispensing, imprinting, polymerizing, and demolding.

As a first step, our developed underlayer was coated on silicon wafers before dispensing the above resist material in the UV nanoimprint lithography process. This was done in order to avoid the resist peeling and to minimize defects. The underlayer was crosslinked at 130 °C for 300 s. The quartz master template was drawn using an electron-beam lithography system (Crestec CABL-8000TPU) and featured 70 nm line and 70 nm space dense patterns with 70 nm depth in an area of 5 mm².

Secondly, a gas-permeable template, including the cyclodextrin derivatives, was also prepared after removing the quartz master template. The average pore size of the β-cyclodextrin was approximately 0.7 nm and was considered to have little impact on the light transparency and resolution of the 70 nm line patterns. A gas-permeable template was prepared with a multipurpose stretching tester autograph (Shimadzu EZ Test EZ-L) using specific software (Shimadzu TRAPEZIUM). The nanoimprint force was maintained at approximately 100 N. UV polymerization of the gas-permeable template was performed using the above introduced metal-halide lamp system (irradiation intensity of 58 mW/cm² and irradiation time of 10 min). After UV irradiation, the gas-permeable template was maintained at 120 °C for 3 h under reduced pressure for drying and thermal polymerization.

Thirdly, sub-70 nm resolution patterning of the epoxy novolac resin, which included acetone as a volatile solvent, was performed in the above tool used in fabricating the gas-permeable template. The epoxy novolac resin was brought into contact with the gas-permeable template at 200 N for 90 s and then baked at 100 °C for 60 s to remove acetone from the nanoimprint resist material before being polymerized at 71 mW/cm² for 20 s. The UV-curable epoxy groups of the epoxy novolac resins underwent cationic polymerization in the imprinted area, and then the epoxy novolac resin was demolded from the gas-permeable template. A piece of gas-permeable template was repeatedly used in 5 cycles of UV nanoimprint lithography.

Figure 3 shows top-down scanning electron microscopy (SEM) images of the sub-70 nm resolution patterning of (a) the gas-permeable template, the (b1) first, (b2) second, and (b3) fifth cycle of nanoimprinted results using the epoxy novolac resins containing 15 wt% acetone.

\[ \text{Fig. 2. Flowchart of UV nanoimprint lithography using a gas permeable template for epoxy novolac resins.} \]

\[ \text{Fig. 3. Top-down scanning electron microscopy (SEM) images of sub-70 nm resolution patterning of (a) the gas-permeable template, the (b1) first, (b2) second, and (b3) fifth cycle of nanoimprinted results using the epoxy novolac resins containing 15 wt% acetone.} \]
devices. CF$_4$ etch selectivity of the resist materials was required as a property of resist materials for next-generation nanoimprint lithography processes. The result that one can nano-imprint a molded resin containing a volatile solvent is expected to be a breakthrough for nanofabrication techniques.

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Fig. 4. CF$_4$ etch selectivity of epoxy novolac resins, and the referenced materials.