Applied Physics Express **9**, 056501 (2016)
http://doi.org/**10.7567/APEX.9.056501**

Sub-70 nm resolution patterning of high etch-resistant epoxy novolac resins using gas permeable templates in ultraviolet nanoimprint lithography

Satoshi Takei* and Makoto Hanabata

Toyama Prefectural University, Imizu, Toyama 939-0398, Japan

*E-mail: takeis@pu-toyama.ac.jp

Received March 17, 2016; accepted March 31, 2016; published online April 15, 2016

This study aimed to expand the resolution limits of epoxy novolac resins that have enhanced etch resistance as one of the desirable resist properties for next-generation devices. Epoxy novolac resins have high etch resistance. However, because epoxy novolac resins are either solid or semisolid at room temperature, and because the use of volatile solvents in resist can be a cause of pattern failure in nanoimprint lithography, epoxy novolac resins have been of limited utility as resist. Excellent sub-70 nm resolution patterning can be achieved by diluting 15 wt % acetone in an ultraviolet nanoimprint lithography using gas-permeable templates. © 2016 The Japan Society of Applied Physics

Epoxy novolac resins are used as the base polymers of I-line (365 nm) photoresist 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 photoresist 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 resist.[3–5]

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.[6–8]

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.[9–13] At the same time, some techniques using gas-permeable templates have been reported in relation to material development.[14–17] 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.[18] 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.

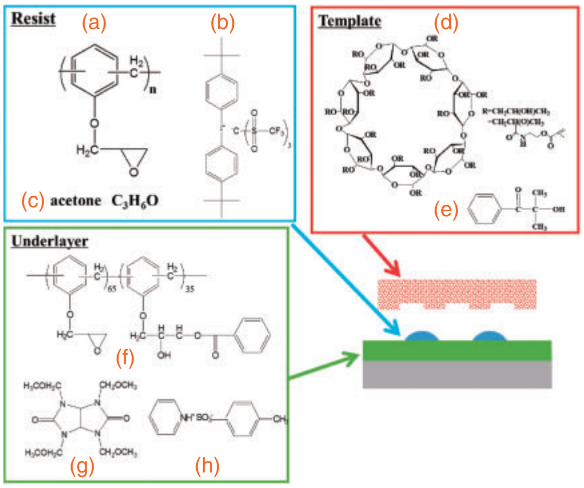

Fig. 1. Chemical structures of (a) epoxy novolac resins, (b) UV initiator, (c) acetone, (d) cyclodextrin derivatives, (e) UV initiator, (f) other novolac resins, (g) tetrakis(methoxymethyl)glycoluril, and (h) pyridinium *p*-toluenesulfonate.

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 methacryloyloxyalkyl groups as in the above gas-permeable template material,[18] (e) a UV initiator for the radical polymerization of methacryloyloxyalkyl groups, (f) other novolac resins with hydroxyl and epoxy groups in our reported underlayer,[19] (g) 1,3,4,6-tetrakis(methoxymethyl)glycoluril as a crosslinker to react with hydroxyl groups, and (h) pyridinium *p*-toluenesulfonate as a thermal initiator.

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®). *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

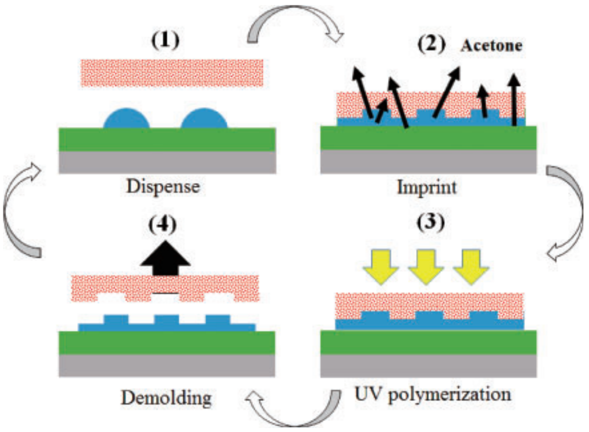

Fig. 2. Flowchart of UV nanoimprint lithography using a gas permeable template for epoxy novolac resins.

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/cm^2). 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 mm^2.

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 abovementioned metal-halide lamp system (irradiation intensity of 58 mW/cm^2 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.

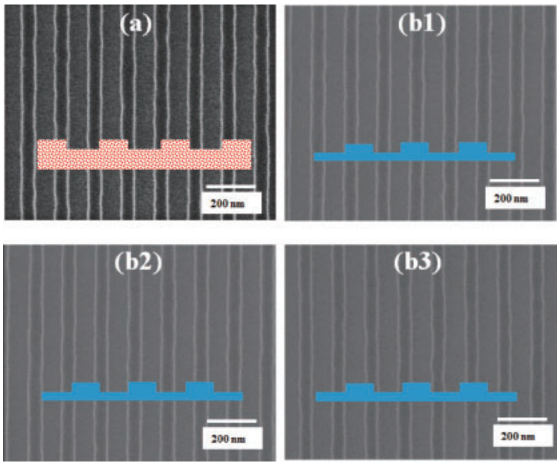

Fig. 3. Top-down scanning electron microscopy (SEM) images of sub-70 nm resolution patterning of (a) the gas-permeable template, the (b1) first, (b2) second, and (b3) fifth cycle of nanoimprinted results using the epoxy novolac resins containing 15 wt% acetone.

Thirdly, sub-70 nm resolution patterning of the epoxy novolac resins, 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/cm^2 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 and (b) the nanoimprinted results of the epoxy novolac resins including acetone from the (b1) first, (b2) second, and (b3) fifth cycles of UV nanoimprint lithography. These top-down SEM images were observed by the abovementioned electron-beam lithography system. Excellent sub-70 nm dense-line patternings of epoxy novolac resins were successfully demonstrated in our UV nanoimprint lithography using the gas-permeable templates and the epoxy novolac resins diluted with 15 wt% acetone. Without the lowered viscosity provided by the 15 wt% acetone, the poor liquidity of the epoxy novolac resins would cause pattern failure. The measured line widths of the gas-permeable template and the epoxy novolac resins of the (b1) first, (b2) second, and (b3) fifth nanoimprinted results were 68 ± 5, 71 ± 7, 68 ± 7, and 64 ± 8 nm, respectively. These measured

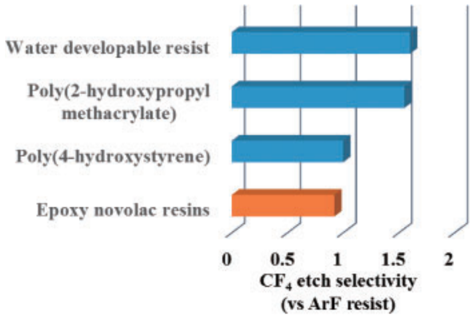

Fig. 4. CF_4 etch selectivity of epoxy novolac resins, and the referenced materials.

results were estimated to be within the variability of the linewidth roughness of the SEM images, and seemed consistent with a sub-70 nm line width. The aspect ratio of the width to the height of the lines of the gas-permeable template and the fifth nanoimprinted results (b3) were almost the same at approximately 1.0. It is proposed that the initial nanopatterning results using epoxy novolac resins in this study will become a pioneer in developing general-purpose polymers as the base component of nanoimprint resist materials for developing new applications at reduced manufacturing cost.

A more accurate evaluation of the results of high-resolution patterning of epoxy novolac resins is expected to be obtained by changing from these laboratory tools to mass production equipment and increasing the cycle of the UV nanoimprint lithography processes.

Etch resistance to fluorinated etch-gas systems was required as a property of resist materials for next-generation devices.[23] CF_4 etch selectivity of the resist materials was evaluated using a reactive ion etcher (Samco FA-1K). For comparison, ArF chemically-amplified positive photoresist (Fujifilm GARS8105G1), water-developable resist material derived from biomass, poly(4-hydroxystyrene) (Maruzen MarukalyncurM), and poly(2-hydroxypropyl methacrylate) (Sigma-Aldrich) as the reference polymers were spin-coated onto silicon wafers and then heated on the hot plate at 110 °C for 60 s.[24–26] The thickness was controlled to approximately 200 nm by diluting the material with solvents. The wafers with these different materials were blanket-etched to determine the plasma etch rate (nm/min). The film was etched using CF_4 gas (pressure of 1 Pa, flow rate of 20 sccm, time of 2–20 min, and RF-power of 100 W). The thickness of the films was measured after the etch process. The thickness reduction by the etch process was calculated as the difference between the initial and final thicknesses.

Figure 4 shows the CF_4 etch selectivity of epoxy novolac resins, and the referenced materials compared with the ArF chemically amplified positive photoresist. CF_4 etch selectivity of the epoxy novolac resins was approximately 10% less than that of standard ArF chemically amplified positive photoresist. The excellent etch resistance of epoxy novolac resins is reasonable to expect, based on the small Ohnishi parameter of epoxy novolac resins.[27–30] The CF_4 etch selectivity of materials is generally known to be inversely proportional to an Ohnishi parameter. The calculated Ohnishi parameters of epoxy novolac resins, water-developable resist material derived from biomass, poly(4-hydroxystyrene), and poly(2-hydroxypropyl methacrylate) are approximately 3.0, 6.0, 2.4, and 6.2, respectively. As compared with the effectiveness of all of the referenced materials, the effectiveness of the high-resolution lithography approach using epoxy novolac resins that have enhanced etch resistance as one of their resist properties was confirmed.

In summary, we successfully demonstrated the high-resolution patterning of generic epoxy novolac resins having specific desired processes using gas-permeable templates in UV nanoimprint lithography. The result that one can nanoimprint a molded resin containing a volatile solvent is expected to be a breakthrough for nanofabrication techniques.

Acknowledgments The authors are deeply grateful to Professor C. Grant Willson of the University of Texas at Austin for his encouragement and his technical advice in lithography. This work was supported by JSPS Grant-in-Aid for Scientific Research No. 16K04920, JSPS Bilateral Joint Research Projects No. 14039901-000025, and Regional Innovation Strategy Support Program, Toyama Nanotech Cluster 2014 of the Ministry of Education, Culture, Sports, Science and Technology, Japan. This project was also partially supported by the Shorai Foundation for Science and Technology and the Naito Taisyun Science and Technology Foundation.

---

1) M. Endo, M. Sasago, A. Ueno, and N. Nomura, J. Vac. Sci. Technol. B **7**, 565 (1989).
2) M. Hanabata, Adv. Mater. Opt. Electron. **4**, 75 (1994).
3) J. Yu, N. Xu, Z. Liu, and L. Wang, ACS Appl. Mater. Interfaces **4**, 2591 (2012).
4) M. Endo, M. Sasago, H. Nakagawa, A. Ueno, and N. Nomura, Jpn. J. Appl. Phys. **28**, 2035 (1989).
5) K. T. Hattori, T. Hattori, S. Uchino, T. Ueno, N. Hayashi, S. Shirai, N. Moriuchi, and M. Morita, Jpn. J. Appl. Phys. **31**, 4307 (1992).
6) S. Ito, M. Kuwamura, S. Sudo, M. Mizutani, T. Fukushima, H. Noro, S. Akizuki, and A. Prabhu, Proc. 47th Electronic Components and Technology Conf., 1997, p. 46.
7) S. Rimdusit and H. Ishida, Polymer **41**, 7941 (2000).
8) T. Jeevananda and S. Palaniappan, J. Appl. Polym. Sci. **74**, 3507 (1999).
9) H. Hiroshima, M. Komuro, N. Kasahara, Y. Kurashima, and J. Taniguchi, Jpn. J. Appl. Phys. **42**, 3849 (2003).
10) H. Hiroshima, Jpn. J. Appl. Phys. **45**, 5602 (2006).
11) D. Yoo, J.-M. Seok, and N. W. Kim, J. Vac. Sci. Technol. B **32**, 061602 (2014).
12) S. Matsui, H. Hiroshima, Y. Hirai, and M. Nakagawa, Microelectron. Eng. **133**, 134 (2015).
13) Y. Hirai, J. Photopolym. Sci. Technol. **23**, 25 (2010).
14) M. J. Hampton, S. S. Williams, Z. Zhou, J. Nunes, D. H. Ko, J. L. Templeton, E. T. Samulski, and J. M. DeSimone, Adv. Mater. **20**, 2667 (2008).
15) M. T. Demko, J. C. Cheng, and A. P. Pisano, ACS Nano **6**, 6890 (2012).
16) B. K. Lee, H. Cho, and B. H. Chung, Adv. Funct. Mater. **21**, 3681 (2011).
17) M. T. Demko, T. P. Brackbill, and A. P. Pisano, Langmuir **28**, 9857 (2012).
18) S. Takei and M. Hanabata, Appl. Phys. Lett. **107**, 141904 (2015).
19) S. Takei, T. Ogawa, R. Deschner, and C. G. Willson, Microelectron. Eng. **116**, 44 (2014).
20) S. Takei, Y. Horiguchi, T. Ohashi, Y. Mano, M. Muramatsu, M. Iwashita, K. Tsuchiya, and A. Samura, J. Micro/Nanolithogr. MEMS MOEMS **7**, 043005 (2008).
21) S. Takei, Appl. Phys. Express **3**, 025203 (2010).
22) S. Takei, T. Ogawa, R. Deschner, K. Jen, T. Nihira, M. Hanabata, and C. G. Willson, Jpn. J. Appl. Phys. **49**, 075201 (2010).
23) T. Bailey, S. Johnson, S. Sreenivasan, J. Ekerdt, C. Willson, and D. Resnick, J. Photopolym. Sci. Technol. **15**, 481 (2002).
24) S. Takei, T. Shinjo, and Y. Sakaida, Jpn. J. Appl. Phys. **46**, 7279 (2007).
25) S. Takei, Y. Horiguchi, T. Shinjo, Y. Mano, Y. Nakajima, M. Muramatsu, M. Iwashita, and K. Tsuchiya, Proc. SPIE **6519**, 651933 (2007).
26) S. Takei, A. Oshima, T. Wakabayashi, T. Kozawa, and S. Tagawa, Appl. Phys. Lett. **101**, 033106 (2012).
27) Y. Ohnishi, M. Itoh, K. Mizuno, H. Gokan, and S. Fujiwara, J. Vac. Sci. Technol. **19**, 1141 (1981).
28) H. Gokan, S. Esho, and Y. Ohnishi, J. Electrochem. Soc. **130**, 143 (1983).
29) Y. Sato, E. Shiobara, K. Matsunaga, T. Shibata, J. Abe, H. Hayashi, T. Ohiwa, M. Kasai, T. Hachiya, and Y. Onishi, J. Photopolym. Sci. Technol. **14**, 439 (2001).
30) S. Saito and T. Nakasugi, Microelectron. Eng. **78–79**, 528 (2005).