# Preparation of Novel Resin Mold for UV Imprint Lithography using UV Curable Monomers

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## Abstract

A novel resin mold for the UV imprint lithography was devised.    The resin mold was prepared by the method of duplication of the original quartz mold.    The surface of the UV cured resin mold was modified by photoreaction to form hydrophilic groups.    The resin mold with hydrophilic nature was used for UV imprint lithography without surface treatment by fluorine-containing compounds.    The resin mold consisted with a conventional multifunctional acrylate, a photoacid generating monomer, and a photoradical initiator. The formulation of the resin was studied in terms of the de-molding nature and durability of the resin mold.

## 1. Introduction

Since UV imprint lithography is a cost-effective high-resolution patterning technology that does not require expensive optical elements, UV imprint lithography has emerged as a promising technology which can be used in wide areas.    The imprinted patterns can be used in a variety of applications fields, e.g., data storage, MEMS, optronics, biotechnology, electronics, display, and so on.[1,2]    However, the quartz mold for UV imprint lithography is an expensive component and the mold is susceptible to contamination during the UV imprinting process and is seriously damaged.    Since UV imprint lithography uses photo-curable resins, it is almost impossible to remove the cured resins adhered to the surface of the quartz mold.    Recently, we reported a novel method to make a resin mold by the replication of original quartz mold.[3,4]    The replicated resin mold is very cheap and disposable.    A big concern is the de-molding property of the resin mold during the UV imprint process.    In this paper we report a novel method to enhance the de-molding nature of the resin mold by modifying the surface property.

## 2. Experimental

### 2.1. Materials

2,2-Dimethoxy-2-phenylacetophenone (DMPA), 3-methacryloxypropyltrimethoxysilane (γ-MPS), and diethylene glycol monomethyl ether methacrylate (DEGMM) were of reagent grade and used without further purification.    2,2,3,3,4,4,5,5-Octafluoropentyl acrylate (V-8F) was supplied from Osaka Organic Chemical Ind., Ltd.    Pentaerythritol triacrylate (PTA) and dipentaerythritol hexa-acrylate (DPHA) were supplied from Shin-Nakamura Chemical Co., Ltd.    Photoacid generating monomers, naphthylidene imino styrenesulfonate (NISS) and 3,6-dimethylphenacyl methacrylate (DMPMA) were newly prepared.
Structures of the chemicals used are shown in Figure 1.
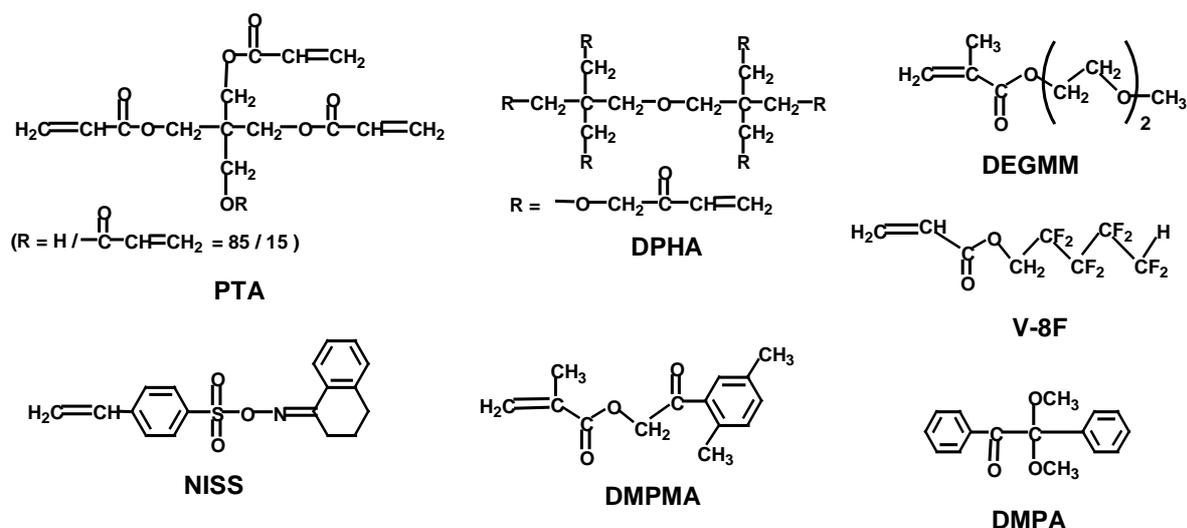
Figure 1.   Structures of chemicals used.

## 2.2. Synthesis of monomers

Naphthylidene imino styrenesulfonate (NISS) was prepared according to the method reported.[5]   3,6-Dimethylphenacyl methacrylate (DMPMA) was prepared as follows: 2,5-Dimethylphenacyl methacrylate was prepared form 2,5-dimethylphenacyl bromide and methacrylic acid.   2,5-Dimethylpnenacyl bromide was newly prepared form the bromination of 2,5-dimethylacetophenone.   2,5-Dimethylacetophenone (10.9 ml) and diethyl ether (25 ml)  were placed in a three-necked round-bottom flask fitted with an efficient magnetic stirrer and a thermometer.   Bromine (3.82 ml) was added dropwise over 15 min at room temperature under $N_2$ atmosphere and the reaction was continued for 30 min. After removal of diethyl ether at 45 $^o$C, a slightly greenish liquid was obtained (15.7g). This compound was used for the following reaction without further purification.   ^{1}H NMR ($CDCl_3$)**:** δ (ppm) 2.37 (3H, s, Ar-$CH_3$), 2.47 (3H, s, Ar-$CH_3$), 4.42 (2H, s, -$CH_2$-Br), 7.16~7.45 (3H, m, Ar).

Methacrylic acid (5.4 g), dimethyl formamide, and 2,6-di-t-butyl-p-cresol (68 mg) were placed in a three-necked round-bottom flask fitted with an efficient magnetic stirrer and a thermometer.   Triethylamine (10 ml) was slowly added at 5 $^o$C.   Then, 2,5-dimethylphenacyl bromide (16 g) was added dropwise over 20 min under $N_2$ atmosphere. The reaction was continued for 4h.   Ethyl acetate (200 ml) was added and the reaction mixture was washed with water and saturated NaCl aqueous solution.   The organic layer was dried over $MgSO_4$.   After removal of the organic solvent, slightly yellowish liquid was obtained.   The crude product was purified by column chromatography (silica gel, eluent: chloroform/hexane=4/6 (v/v)). Yield 43%: m.p. 46.2-48.1 $^o$C.   ^{1}H NMR ($CDCl_3$): δ (ppm) 2.01 (3H, s, $CH_3$), 2.37 (3H, s, Ar-$CH_3$), 2.47 (3H, s, Ar-$CH_3$), 5.24 (2H, s, -O-$CH_2$-), 5.67 (1H, s, =$CH_2$), 6.26 (1H, s, =$CH_2$), 7.15~7.43 (3H, m, Ar). ^{13}C NMR ($CDCl_3$): δ (ppm) 18.3, 20.6, 67.5, 126.6, 128.6, 132.0, 132.8, 134.5, 135.3, 135.6, 135.7, 166.8, 196.0.   IR (KBr): 1700 (C=O), 1719 (O-C=O), 1635 cm$^{-1}$ (C=C).

## 2.3. Preparation of replicated resin mold

The sample for the formation of replicated resin mold was a mixture of conventional UV curable resin, photoacid generating monomer, and photoradical initiator.   To improve the release property, the surface of the original quartz mold (2.5 x 2.5 cm) was treated with OPTOOL DSX (Daikin Industry) before use.   The depth of line patterns (20 μm width) of the quartz mold was 1 μm.   The process for the replicated resin mold consists of nine steps as shown in Figure 2: 1) dropping the reworkable UV curable resin on quartz plate, 2) placing the quartz mold and pressing the resin, 3) irradiating at 365 nm through the quartz mold to cure the reworkable resin, 4) releasing the quartz mold to obtain the patterns of reworkable resin on quartz plate, 5) dropping a conventional UV resin containing photoacid generating monomer on the imprinted patterns, 6) placing quartz plate treated with 3-methacryloxypropyltrimethoxysilane (γ-MPS) and pressing the resin, 7) irradiating at 365 nm and followed by irradiation at 254 nm through quartz plate, 8) stripping the quartz plate, and 9) dipping the sample in methanol to obtain the resin patterns on quartz plate (replicated resin mold).
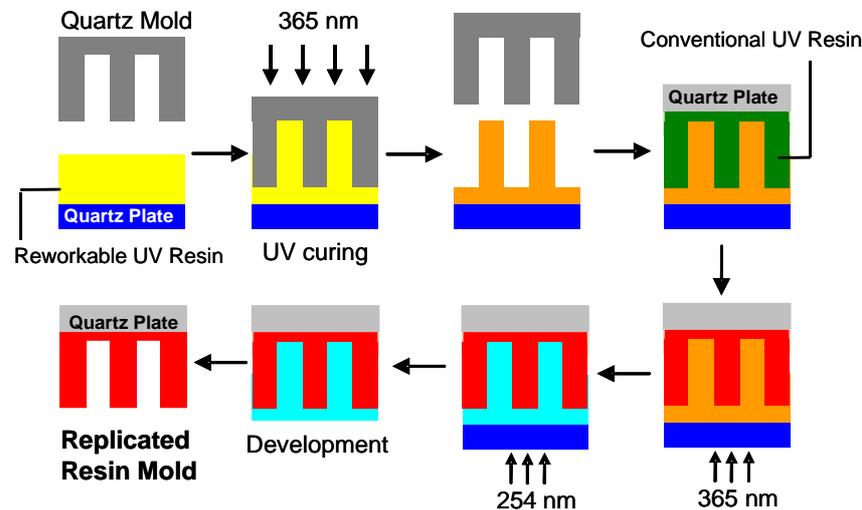


Figure 2.   Preparation process for replicated resin mold.

## 2.4. Measurements

The depth and height of line patterns of mold and imprinted patterns were measured using a Kosaka Surfcorder ET 3000i.   Degree of shrinkage was calculated from comparison of the depth/height ratio of line patterns of mold and imprinted resin.   UV imprint process was performed using Maruni MNI-1000HC.   $^1$H NMR spectra were observed at 400 MHz using a JEOL LA-400 spectrophotometer.   FT-IR measurements were carried out using a JASCO FT/IR-4200.   Water contact angle was measured using an Eruma M-2010A.

## 3. Results and Discussion

### 3.1 UV imprint process

A general UV imprint process is shown in Figure 3.   After dropping the UV curable monomers on substrate, a quartz mold was placed and the liquid sample was pressed at relatively low pressure (~1 MPa).   UV light was irradiated through the quartz mold to cure the sample.   After removing the mold, imprinted patterns were obtained on the substrate.

The liquid sample for UV imprint was generally a mixture of UV curable monomers and photo-initiator. The quartz mold was modified by fluorine-containing compounds to make the surface hydrophobic. The water contact angle of the mold surface was ca. 110 $^{o}$. On the other hand, the water contact angle of the UV cured acrylate resin was ca. 60 $^{o}$. Thus, to accomplish the good detachment between mold and cured resin, a difference in water contact angle between surfaces of the cured resin and mold must be larger than 50 $^{o}$. The large difference in the water contact angle can be accomplished by making a hydrophilic surface of the mold. According to this concept, we have designed the resin mold which has acid units on the surface.
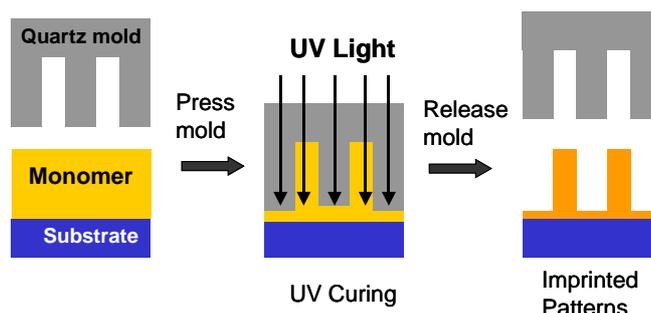


Figure 3.    General UV imprint process.

## 3.2 Surface properties of resin mold

The replicated resin mold was prepared according to the process shown in Figure 2. The formulation of the resin mold was a mixture of PTA, DEGMM, and NISS or DMPMA. The monomers NISS and DMPMA can generate sulfonic acid [6] and carboxylic acid [7] units, respectively, on irradiation at 254 nm as shown in Figure 4. Thus, the surface of the resin mold becomes hydrophilic.
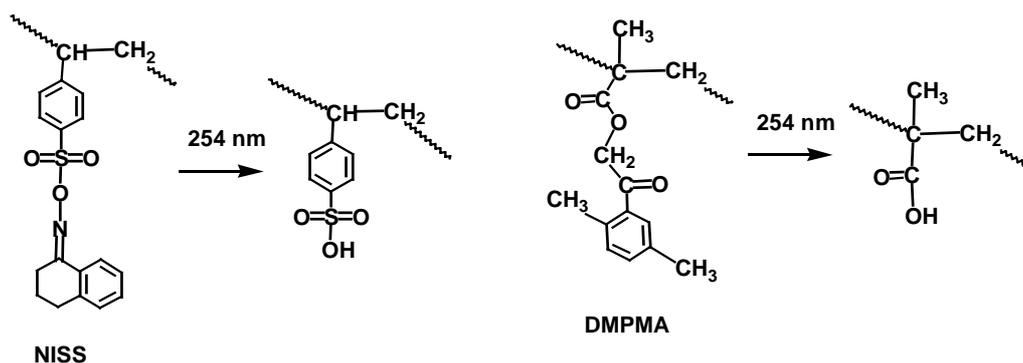


Figure 4.    Photo-induced acid generation at the mold surface.

The water contact angle of the mold surface decreased with irradiation at 254 nm because of the generation of acid units (Table 1). The increase of the content of the acid-generating monomers may increase the hydrophilic nature of the surface. However, the amount of the acid-generating monomers added was limited by their solubility to PTA.

Although DEGMM was used to enhance the solubility of the acid-generating monomers, DEGMM also worked to enhance the hydrophilic nature of the mold surface. The water contact angle of the mold surface was observed to be 25~33 $^{o}$. Since the water contact angle of the cured acrylic resin is about 60 $^{o}$, it is necessary to use the UV curable monomers with more hydrophobic nature compared to the conventional multi-functional acrylates.

Table 1. Surface property of resin mold.

| Mold | Monomer (wt/wt) | | | | Water contact angle ($^{o}$) | | Pencil hardness |
|------|-------|-----|------|-------|-------------------|------------------------|-----------------|
|      | DEGMM | PTA | NISS | DMPMA | Before irradiation | After irradiation[a) | |
| 1 | 40 | 50 | 10 | 0  | 57 | 33 | HB |
| 2 | 40 | 50 | 0  | 7  | 55 | 33 | HB |
| 3 | 40 | 50 | 0  | 14 | 58 | 25 | HB |
| 4 | 0  | 90 | 0  | 7  | 61 | 29 | 3H |

a) Irradiation dose: 1800 mJ/cm$^2$ at 254 nm.

The resin for the UV imprint is needed to have a water contact angle higher than 70~80 $^{o}$ for the system using the present resin mold. Thus, a mixture of DPHA and V-8F was used. Table 2 shows the water contact angle for the UV cured resin obtained by a mixture of DPHA and V-8F. The cured DPHA resin showed the water contact angle of 62 $^{o}$. The water contact angle increased with the content of V-8F.

Table 2. Water contact angle of UV cured DPHA / V-8F mixture

| Monomer feed ratio (wt/wt) | | Water contact angle ($^{o}$) |
|------|------|----------------------|
| DPHA | V-8F | |
| 100 | 0  | 62 |
| 95  | 5  | 78 |
| 90  | 10 | 84 |
| 80  | 20 | 92 |

### 3.3. UV imprint using replicated resin mold

The replicated resin mold was obtained according to the method described in Figure 2. UV imprint was performed using the resin mold by a conventional method as shown in Figure 3. No specific treatment of the resin mold surface was done without irradiation at 254 nm in air. Figure 5 shows the optical micrographs of the replicated resin mold No. 1 shown in Table 1 and the UV imprinted patterns. The line width of the mold patterns was 20 μm and the depth of the lines was 1 μm. Good UV imprinted patterns were obtained using a resin of DPHA/V-8F mixture with various DPHA/V-8F ratios. The deviation of the imprinted pattern size in z-direction was 1.2 and 2.1 % for DPHA/V-8F (80/20) and DPHA/V-8F (90/10), respectively. Furthermore, good imprinted patterns were obtained using DPHA/V-8F (95/5) with the size deviation of 2.0% in z-direction. However, no good patterns were obtained when DPHA was used without V-8F.

Figure 5.   Optical micrographs of replicated resin mold and imprinted patterns.
(a) resin mold No. 1 (DEGMM / PTA / NISS / DMPA = 40 / 50 / 10 / 1 (wt/wt)).
(b) resin: DPHA / V-8F / DMPA = 80 / 20 / 1 (wt/wt).
(c) resin: DPHA / V-8F / DMPA = 90 / 10 / 1 (wt/wt).

A similar result was obtained for the UV imprint using the resin mold No. 2. shown in Table 1.    However, the deviation of the imprinted pattern size in z-direction was 3.7 and 2.4 % for DPHA/V-8F (80/20) and DPHA/V-8F (90/10), respectively.    When DPHA/V-8F (95/5) was used, no good imprinted patterns were obtained due to the incomplete remolding. On the other hand, when the resin mold No. 3 shown in Table 1 was used, very nice imprinted patterns were obtained for DPHA/V-8F (90/10), DPHA/V-8F (95/5), and DPHA/V-8F (98/2) with the size deviations of 1.6, 1.9, and 2.4 %, respectively.

## 4. Conclusions

Novel replicated resin mold for UV imprint was developed based on the new concept. The surface of the resin mold had hydrophilic nature which was induced by the photoreaction of the photoacid-generating monomers incorporated into the resin components.    Using the resin mold with hydrophilic surface, the UV imprint was successfully accomplished for the resins composed of conventional multi-functional acrylate and fluorine-containing monomer. The resin mold was able to use for UV imprint repeatedly.

## References
[1] Chou, S. Y.; Krauss, P. R.; Renstrom, P. J., *J. Vac. Sci. Technol.*, **B14**, 4129 (1996).
[2] Heath, W. H.; Palmieri, F.; Adams, J. R.; Long, B. K.; Chute, J.; Holcombe, T. W.; Zieren, S.; Truitt, M. J.; White, J. L.; Willson, C. G.. *Macromolecules*, **41**, 719 (2008).
[3] Matsukawa, D.; Wakayama, H.; Mitsukura, K.; Okamura, H.; Hirai, Y.; Shirai, M. *J. Mater. Chem.,* **19**, 4085 (2009).
[4] Horii, S.; Matsukawa, D.; Okamura, H.; Shirai, M. *Proceedings RadTech Asia 2011*, pp.56-57 (**2011**).
[5] Shirai, M.; Hayashi, M.; Tsunooka, M.; *Macromolecules*, **25**, 195 (1992).
[6] Shirai, M.; Hayashi, H.; Tsunooka, M. *Eur. Polym. J.,* **28**, 379 (1992).
[7] Klan, P.; Zabadal, M.; Herger, D. *Org Lett.*, **2**, 1569 (2000).