Reduction of Defect for Imprinted UV Curable Resin including Volatile Solvents using Gas Permeable Mold Derived from Cellulose

Kento Mizui*, Kazuho Kurematsu, Shinya Nakajima, Makoto Hanabata, and Satoshi Takei

Department of Mechanical Systems Engineering, Toyama Prefectural University, Imizu, Toyama 939-0398, Japan
*t753012@st.pu-toyama.ac.jp

Nanoimprint lithography has recently attracted much attention in microfabrication technology due to its two benefits of high resolving power and decreased production cost. It is promising for the next generation microfabrication technology. However, voids generated between the master mold and transferred replica mold are one of the problems for nanoimprint lithography. We have been developing gas permeable molds derived from cellulose to reduce defects caused from these voids. This study demonstrates the applicability of gas permeable mold. Defects in line and space patterns of the UV-cross-linkable materials including 10 wt% of acetone, 10 wt% of 1-methoxy-2-propyl acetate (PGMEA) and 10 wt% of cyclopentane as volatile solvents were greatly eliminated by using a gas permeable mold. This approach is expected to expand the utility of non-liquid materials which need solvents that are currently not suitable for nanoimprint lithography.

Keywords: Nanoimprint lithography, Biomass, Gas permeability, Volatile solvent, Mass production, Raman spectra

1. Introduction

In recent years, attention has been focused on microfabrication technology because of rising demand for highly integrated semiconductor manufacturing. The mainstream of microfabrication technology is a photolithography [1,2]. Photolithography is a suitable process that can transfer geometric patterns to a film or substrate. However, due to the increasing cost to achieve high resolution, it reaches to the limitations. In this situation, imprint lithography (IL) has drawn much attention because of its high productivity and low cost. The IL is a processing method proposed by Prof. Chu et al. in 1995 [3,4]. It was reported that it is possible in transcription of 10 nm [5]. This technique has a high resolution, high throughput, high aspect ratio patterning, cost reduction, and large area patterning [6-10]. The applicability of IL has wide varieties of biosensor, optical materials, and compact discs. [11-13]. It is promising as the next generation microfabrication technologies.

A gas impermeable quartz mold used in conventional processes often causes air trapping and out gas accumulation between the mold and the transfer material. To solve the air trapping problem, the use of pentafluoropropane (PEP) was suggested [14].

In previous studies, we reported a gas permeable mold derived from cellulose reduces the void caused by the outgas from acrylic material including 4.9 wt% of acetone [15]. Figure 1 shows the comparison between the gas impermeable mold and the gas permeable mold in IL process. The pattern failures caused by the air trapping and the outgassing between the mold and the UV curing liquid material were removed because these gasses easily passed outside through the gas permeable mold.

However, due to adhesion between the gas permeable mold and the UV curing liquid material, it is limited to use only one time IL process, so productivity is problematic. IL mold should be used
multiple times to reproduce the desired pattern on one or more substrates. Thus, many deformations can result in imperfect patterning. In some experiments, the surface of the template is modified to enhance the reliability of the template. For example, a liquid release agent coating is deposited on the surface of the template prior to its use in an IL processes [16].

In this study, we developed a gas permeable mold with superior releasability using liquid release agent to improve productivity. In order to investigate the applicability of the gas permeable mold, mass productivity, Raman spectra, imprinted pattern containing three kinds of volatile solvents and repeatability property were investigated.

2. Experimental

2.1. Gas permeable mold material

Figure 2 shows the chemical structure of gas permeable mold material. This material was derived from hydroxyl propyl cellulose (Wako Pure Chemical Industries). Double bond was used as a crosslinking site and 2-methacryloyloxyethyl isocyanate (MOI) having a methacrylate group. Trimethylamine was used as a synthetic reaction initiator and 2-butanone was used as a solvent. A 3 wt.% solution of 2,2'-azobisisobutyronitrile (AIBN, Tokyo Chemical Industry) as the thermal initiator was added to the thermoset cellulose solutions in methyl ethyl ketone [17].

2.2. Mass productivity of gas permeable mold

A quartz master mold (NIPPON FILCON) was coated by fluorinated self-assembled monolayer DS-831TH (DURASURF, Harves). Surface finishing processes were applied by an ozone generator (LTOZ-180, Litho Tech Japan) for 300 seconds. The quartz master mold was immersed into the DS-831TH for 60 seconds and dried for 60 seconds at room temperature. The quartz master mold featured 2 µm line and 2 µm space patterns. Then it was rinsed for 60 seconds by DS-TH (DURASURF, Harves) and dried for 60 seconds.

Figure 3 shows thermal IL process of gas permeable mold imprinted from the quartz master mold. The process conditions were as follows; (1) The gas permeable mold material was coated on a silicon substrate. (2) The material was brought into contact with the quartz master mold 300 seconds and The imprint pressure was 0.86 MPa at vacuum chamber. Thermal polymerization reaction for the material was carried out at 130 °C for 300 seconds.

Fig. 1. Comparison of (a) gas impermeable mold and (b) gas permeable mold.

Fig. 2. Chemical structures of gas permeable mold.

Fig. 3. Thermal Imprint lithography process of gas permeable mold imprinted from the quartz master mold.
(3) After the quartz master molds were demolded, the gas permeable mold was obtained and observed by a confocal microscope (OPTELICS H1200, Laser Tec). Figure 3 steps (1) - (3) are repeated 100 times to evaluate mass productivity of the master quartz mold and the antifouling of gas permeable mold.

2.3. UV curing liquid material

Figure 4 shows the chemical structures of UV curing liquid material. Two specific trehalose and glucose derivatives with ultraviolet curable acryloyl groups were synthesized from biomass. (a) Trehalose derivatives 16.0 wt%, (b) Glucose derivatives 8.01 wt% having glucose ring, (c) Isobornyl methacrylate 70 wt% was used as a diluent for improving the coating property and (d) 2-hydroxyl-2-methyl-1-phenyl-propane-1-ol 5.45 wt% was used as a liquid radical initiator for UV curing reaction. The plant derived ratio of the UV curing liquid material was 24.1 wt%.

![Chemical structures of UV curing liquid material](image)

Fig. 4. Chemical structures of (a) Trehalose derivatives, (b) Glucose derivatives, (c) Isobornyl methacrylate, and (d) 2-Hydroxyl-2-methyl-1-phenyl-propane-1-ol used in UV-curing liquid resist material for IL.

2.4. Raman spectra of UV curing liquid material

The UV curing liquid material was dispensed on the glass substrate and UV irradiation was carried out by using a metal halide lamp system (Sun Energy, 200-650 nm peak, UV exposure dose: 200 mW/cm²) for 0, 30, 60, 120, 300 and 600 seconds respectively. Raman spectra has the efficacy as the bonding configuration analysis of acryloyl groups and carbonyl groups in the UV curing liquid material during UV irradiation. It was measured using Raman spectroscope Nano finder FLEX-532-TPU-T11 (Tokyo Instruments).

2.5. Imprint process using quartz master mold

Volatile solvents that causes outgas was added to UV curing liquid material by 10 wt% each of acetone, 1-methoxy-2-propyl acetate (PGMEA), and cyclopentane as a transfer material. Comparison of gas permeability and repeated transferability of gas permeable mold were evaluated by using quartz master mold and gas permeable mold.

Figure 5 shows processes of UV curing liquid imprint lithography using the quartz master mold. The experimental conditions were as follows;
(1) The UV curing liquid material was dispensed on the under layer-coated glass substrate. (2) The material was filled into the quartz master mold at 0.052 MPa for 60 seconds. (3) The polymerization in the UV curing liquid materials was carried out by using a metal halide lamp system (Sun Energy, 200-650 nm peak, UV exposure dose: 200 mW/cm²) for 60 seconds. (4) After demolding of quartz master mold from imprinted the UV curing liquid material, the patterned material was observed using confocal microscopes (OPTELICS H1200, Laser Tec).

2.6. Imprint process using gas permeable mold

Figure 6 shows processes of UV IL using the gas permeable mold imprinted from quartz master mold. Thermal and UV IL were performed utilizing an imprint test machine (LTNIP-5000, Litho Tech Japan). The experimental conditions were as follows;
(1) The gas permeable mold material was coated on a substrate. (2) The material was brought into
contact with the quartz master mold 300 seconds and the imprint pressure was 0.86 MPa at vacuum chamber. Thermal polymerization reaction of the material was carried out at 130 °C for 300 seconds. (3) After the quartz master mold was demolded, the gas permeable mold was obtained. (4) Gas permeable mold was coated with the liquid release agent chem lease 70 (Chem trend) by dipping for 24 hours. (5) The UV curing liquid material was dispensed on the under layer-coated glass substrate. (6) The material was filled into the gas permeable mold at 0.052 Mpa for 60 seconds. (7) The polymerization of the UV curing liquid materials was carried out by using a metal halide lamp system (Sun Energy, 200-650 nm peak, UV exposure dose: 200 mW/cm²) for 60 seconds. (8) After demolding of gas permeable mold from imprinted curing liquid material, the patterned material was observed using confocal microscopes (OPTELICS H1200, Laser Tec). The procedures of (5) - (8) were repeated to evaluate the repeatability of gas permeable mold for each volatile solvents.

3. Results and discussion

3.1. Mass productivity of gas permeable mold

Figure 7 shows micrographs of patterned 2 µm line and space in gas permeable mold by 1, 10, 30, 50, 80, and 100 times. Even when the number of imprinting times increased, the quartz master mold was no contamination, and no large change appeared in the gas permeable mold pattern. From this result, it is expected that the gas permeable mold material has superior mass productivity and antifouling property.

3.2. Raman spectra of UV curing liquid material

Figure 8 shows the time dependent Raman spectra of UV curing liquid material in the spectra range from 1600 to 1800 cm⁻¹. A peak at around 1635 cm⁻¹ which corresponds to C=C stretching vibration of ultraviolet curable acryloyl groups and also the peak at around 1730 cm⁻¹ which corresponds to C=O stretching vibration of carbonyl groups were observed in UV curing liquid material. Time-dependent Raman spectra of UV curing liquid material indicated an obvious decrease of both C=C stretching vibration of UV curing acryloyl groups and C=O stretching vibration of carbonyl groups. It is obvious that UV curing liquid material was polymerized by ultraviolet irradiation.

3.3. Comparison of quartz master mold and gas permeable mold

Figure 9 shows a confocal micrograph of line and space patterns of UV curing liquid material including acetone, PGMEA, and cyclopentane using quartz master mold and gas permeable mold. The repeatable properties of producing line and space pattern with 2 µm line patterns on the surface of master quartz mold and gas permeable mold were evaluated to observe the effect of reducing the defect numbers on the mold replication of imprint process cycles. When quartz master mold was used,
there were bubble defects after only one-time imprint process in the UV curing liquid material because of the gas volatized from acetone, PGMEA, and cyclopentane. In gas permeable mold process, there were no bubble defects in UV curing liquid material. We found that gas permeable mold process was much superior to gas impermeable process. UV curing liquid material in acetone using gas permeable mold is applicable to over 10 times imprint process. We can expect this is promising to mass production. UV curing liquid material in PGMEA using gas permeable mold was possible to 5 times imprint process cycle times and cyclopentane was possible to 3 imprint process cycle times. Both of gas permeable molds were adhered to UV curing liquid material and easily could be peeled off.

As a result of investigation of repeatability property of gas permeable mold, it was adhered to UV curing liquid material and was peeled off. It was considered that repeated imprinting process made volatile solvents remain on the surface of the gas permeable mold and the UV curing liquid material including the same volatile solvent were adhered each other.

We believe that the difference between the molecular structure of volatile solvents and the boiling point greatly influence the reason why the volatile solvents remain on the surface of the gas permeable mold surface. Figure 10 shows the image of volatile solvents causes adhesion to the gas permeable mold and the UV curing liquid material.

In the case of a UV curing liquid material including 10 wt% of acetone, it is estimated below: (1) The molecule of acetone penetrates deeply into the gas permeable porous mold. This means acetone did not rise up to the surface of the gas permeable mold. (2) Acetone has a relatively low boiling point of 56.5 °C, so evaporation occurred and did not remain on the surface of the mold. It is estimated that high repeatability was obtained, and further increase in the number of imprinting can be expected (Fig 10 (a)).

In the case of a UV curing liquid material including 10 wt% of PGMEA, it is estimated as follows: (1) The molecular chain of PGMEA was longer than that of acetone and molecules could not penetrate fully in the porous. (2) PGMEA has a higher boiling point of 146.4 °C, so evaporation does not occur easily and it tends to remain on the surface of gas permeable mold. We believe that these two differences caused adhesion (Fig 10 (b)).

In the case of a UV curing liquid material including 10 wt% of cyclopentane, we believe that the molecular structure of cyclopentane is larger than other volatile solvents and all of them remain on the surface without entering porous domain of the gas permeable mold (Fig 10 (c)).

In order to adopt all of volatile solvents, it is necessary to add heat treatment above the boiling point temperature during imprinting process to remove volatile solvents, or we need frequent cleanings of the gas permeable mold at every imprinting process.
In the next step, we will make trials of imprinting the UV curing liquid material including other volatile solvents using gas permeable mold and also investigate the surface condition of the gas permeable mold after releasing from the UV curing material.

4. Conclusion
The applicability of the gas permeable mold was investigated. Mass productivity of the gas permeable mold from quartz master mold was confirmed by replicating a large amount of gas permeable mold. Reproducibility was improved by coating liquid remover on the gas permeable mold. Even when the amount of acetone contained became two times higher than in our previous study, the gas permeability and repeatability were excellent. Imprinting performance was also kept when various volatile solvents other than acetone, such as PGMEA (Propylene Glycol Monomethyl Ether Acetate), cyclopentane were included in imprinted materials.

Acknowledgement
This project was supported by JSPS KAKENHI No. 16K04920, JSPS Bilateral Joint Research Projects 2017 in Belgium, JST program No. VP29117936791, Toyama Nanotech Cluster of Ministry of Education, Culture, Sports, Science and Technology, Japan, The Canon Foundation, The Amada Foundation, The Die and Mould Technology Promotion Foundation, The Murata Science Foundation, The Osaka Scientific Studies Grants Foundation, Advanced Machining Technology & Development Association, The Ogasawara Foundation, and Mazak Foundation.

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