Mold Surface Treatment for Imprint Lithography


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An adhesion problem is one of the most significant problems in nano imprint lithography. A mold should be released from a resist polymer without adhesion. We investigate a surface coating of a mold by fluorine polymers to reduce surface tension and making it easy to release the mold from the resist polymer. Evaporation of a FEP polymer in vacuum atmosphere and surface treatment for a mold by a silane-coupling agent with perfluoropolyether (PFPE-S) is examined. The releasing characteristics of molds are quantitatively evaluated by a contact angle for a water droplet. Durability of the fluorine polymers is also evaluated by continuous imprinting and the abrasion examinations.

Keywords: imprint lithography, mold, surface treatment, contact angle, adhesion

1. Introduction

Nano-imprint lithography is one of the promising technologies for fabricating nano-scale integration system. It is finding wide application today in various fields for fabricating fine patterns in a large area.

There have been proposed some different kinds of imprint lithography[1][2]. The most typical method are the following two method. Chow et al., proposed the method that a fine mold was pressed in a polymer film which overheated beyond glass transfer temperature and release it after cooling down to room temperature[1]. They demonstrated 10nm holes fabrication by pillared mold. On the other hand, Colburn et al., proposed that the optical sensitive polymer was hardened by UV exposure through quartz mold[3].

In any method, the mold is pressed into polymer and released from the polymer as shown in Fig.1. In this process, the polymer often adheres to the mold. It causes transfer process errors. This error is significant problem for nano imprint lithography.

While the polymer must adhere to the substrate, it should be exfoliated from the mold. These are contradictory requirements to each other.

Fig.1. Schematic diagram of the nano imprint lithography.

Received April 11, 2001
Accepted May 25, 2001
Figure 2 shows scanning electron microscopy (SEM) images of imprinted polymer patterns by SiO₂ mold. Most part of the imprinted polymer film is peeled off.

We demonstrated surface treatment of a Si mold by hydrogen termination using diluted HF⁴. But the result was not perfect because the surface tension of hydrogen terminated Si surface is thought to be not sufficiently low for exfoliating the mold from the polymer. Haisma et al., used γ- methacryloxypropyltrimethoxysilane as a release layer, but the effect and durability are not discussed in detail[2].

To avoid the adhesion problem, surface treatment to reduce the critical surface tension of the mold is the most promising approach[5][6]. The fluoropolymers such as polytetrafluoroethylene (PTFE, γₛ = 18.5 [mN/m]) or fluorinated ethylene-propylene copolymer (FEP, γₛ = 17.8 [mN/m]) are well-known material, which has low critical surface tension. There are several methods to coat fluoro polymers on a mold surface. For example, reactive sputtering of PTEF films in CF₄ gas plasma[7] or microwave plasma deposition from a CF₄/H₂ discharge[8] had been demonstrated. However, durability is thought to be poor because it is not easy to adhere to the mold surface because the fluoropolymers have low surface tension.

On the other hand, Bailey et al., reported chemical treatment for the mold surface by a fluorine plastic containing silane-coupling agents[9]. By using silane-coupling agents, fluorine polymer is chemically reacted with mold surface and strong chemical bonding is formed. They employed chlorine groups for silane-coupling agent and demonstrated fine imprint results. They dipped the mold into tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (CF₃-(CF₂)₅-CH₂-CH₂-SiCl₃) for 1h at 90 °C. The silane-coupling agent using chlorine groups is strong bonding energy so that the reagent easily reacts with moisture in an atmosphere. It should be treated in an inert gas atmosphere and required exhaust gas treatment system.

In this paper, we newly examined two types of surface treatments taking the durability into consideration.

2. Background of Adhesion

Young and Dupre derived the classical thermodynamic terms about adhesion[5]. The conditions for equilibrium at solid-liquid interface like that in Figure 3 as

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \theta, \quad (i)$$

where $\gamma_S$ and $\gamma_L$ are surface energies of the solid and $\gamma_{SL}$ is interfacial energy between liquid and solid.

![Energy equilibrium at solid-liquid-gas interface.](image)

The work of adhesion $W_A$ between solid and liquid is

$$W_A = \gamma_S + \gamma_L - \gamma_{SL}. \quad (ii)$$

Combination of Eqs. (i) and (ii) yield the well-known Young-Dupre equation

![Low magnification SEM image.](image)  
![Enlarged image of the fault area.](image)

Fig. 2. SEM image of the resist peeling portion after release process. The imprinted resist is 0.3 µm PMMA on Si substrate. The line width is 0.5 µm and length is 200 µm.
\[ W_A = \gamma_A (1 + \cos \theta), \]

where \( \theta \) is a contact angle between solid-liquid-gas interface.

Large contact angle \( \theta \) makes it easy to release the polymer from the mold. The critical surface tension \( \gamma_c \) is associated with the wattability \( W_A \) of a surface.

In this paper, we measured the contact angle for water droplet to evaluate the release ability of the mold from the polymer.

3. Vacuum evaporation of FEP

First, we evaluated fluoropolymer coating on a mold surface by a vacuum evaporation of FEP. The schematic view of the coating system is shown in Fig.3. A FEP tip is heated in the melting pot. The temperature of the pot is around 555°C and the vaporized pressure is \( 2.8 \times 10^{-2} \) Torr. The deposition rate is about 0.03 nm/s.

The contact angles for water droplet of the coated surface are demonstrated in Fig.4. It depends on the thickness of the FEP film. The contact angle for water droplet on 20nm thick fluoropolymer is about 140 degree, which exceeds the physical characteristics of FEP (normally 110 degree). We have not done qualitative analysis about the chemical structure of the coated film but we predict that the polymer is modulated from pure FEP, which is decomposed over 270°C.

Figure 5 shows the scanning electron microscopy (SEM) image of mold with 5nm surface coating. The surface is excellently fine and smooth.

![Vacuum Chamber](image)

Fig.3. Schematic diagram of a vacuum evaporation system for a fluorine polymer.

![Water droplets on FEP evaporated surfaces](image)

Fig.4. Water droplets on FEP evaporated surfaces. The contact angles are 140° on 20nm FEP-like film and 108° on 5nm FEP-like film.

As for the coated film, good adherent is required to the mold. Figure 6 shows the changes in the contact angles for vaporized conditions. A plane mold is pressed into PMMA (polymethylmethacrylate) film at 160MPa, 170°C and released it at 60°C. The adherent of the coated film to the mold surface is enhanced by heating of the mold (200°C) during evaporation.

![Adhesively of the evaporated FEP films on SiO2 molds](image)

Fig. 6. Adhesively of the evaporated FEP films on SiO2 molds. The FEP thickness is 5nm. (160MPa, 170°C)

Figure 7 shows the imprinted patterns using the FEP evaporated mold. Fine pattern is successfully formed over large area without fatal defects.

As discussed above, FEP evaporation is a convenient method to solve the adhesion problem.
3. Surface treatment by PEPE-S

To form a molecular layer of a fluoropolymers on the mold surface, a silane-coupling agents with fluoropolymers is examined. Silane-coupling agents react with mineral surface and form a molecular layer on mineral surfaces.

A general structure is X₃Si-R, where X is a hydrolyzable group of halogen, alkoxy, acyloxy or amine that forms Si-OH groups in water or may react directly with mineral hydroxide groups M-OH to form oxane bonds M-O-Si [6][10].

We newly use l-trymethoxysilyl-3,3,4,4-tetrafluoro-4-(ω-fluoropolyperfluorooctane)-butane (C₃F₇-(OCF₂CF₂CF₂)₃OC₂F₄C₂H₄-Si(OCH₃)₃), which has methoxy hydrolyzable group with perfluoropolyether and shows excellent water repellent characteristic[11]. The critical surface tension of a perfluoropolyether is reported to be 13.0[mN/m].

Figure 8 shows a process flow of a surface treatment by silane-coupling agent. The mold is cleaned by H₂SO₄/H₂O₂ boiling and UV-ozone exposure to remove organic contamination.

Then, the mold is dipped into the 0.1 w% perfluoropolyether-silane (PEPE-S) diluted by perfluorohexane (C₆F₁₄) for 1 min at room temperature in air atmosphere.

After dipping into the PEPE-S, the mold is left in the high humidity atmosphere (65°C,95%) for 1 h. In this process, the perfluoropolyether molecular layer is formed on the mold surface by M-O-Si-R bond. Also, it forms multiple linking layer by layer. To remove the multiple layers, the mold is rinsed by perfluorohexane for 10min or more.

![Figure 8: Process flow of the surface treatment by a PEPE-S](image)

Fig.9 Water droplet on surface treated through silane-coupling agent by PEPE-S. The contact angle is about 114 degree.
Figure 10 shows SEM images of the SiO$_2$ mold surface treated by a PEPE-S with and without rinse. The trench depth of the mold is 270nm. Without rinse, sludge are remained in the trenches as shown in Fig.11(a). With rinse, the sludge are removed and fine mold is obtained.

4. Durability of the fluorine polymers

As discussed above, releasing problem of the mold is solved by both FEP evaporation and PEPE-S treatment, but the durability of the polymer has not been evaluated.

First, we evaluate the changes in the contact angles by continuous imprinting. The plane mold is repeatedly pressed into 300nm PMMA on Si by 160MPa at 170°C. Once the mold is imprinted, the contact angle is measured and the mold is cleaned by acetone for 5 min in a supersonic wave.

Figure 12 shows the changes in the contact angles for FEP evaporated and PEPE-S treated molds. The imprint examinations are proceeded 6 times. While the examination proceeds, the contact angles are almost kept constant for both molds.

![Fig. 10 SEM images of the SiO$_2$ mold surface treated by a PEPE-S with and without rinse. The trench depth is 270nm](image)

![Fig. 11 SEM images of the imprinted PMMA pattern by the rinsed mold after PEPE-S treatment. (200nm/250nm Line & Space, 300nm PMMA on Si, 90MPa, 170°C)](image)

It takes much time to continue the durability examination by the continuous imprint experiments. To examine the durability more efficiently, we employ an abrasion test using the Martindale abrasion-testing machine based on Japan Industrial Standards (JIS) L1096, which evaluates durability for fibers.

Figure 13 shows the schematic diagram of Martindale abrasion-testing machine. The mold is set to the sample holder. The sample holder moves on the standard texture fiber along a Lissajous figure. The pressure is alternated by the weight. Polyester is used as a texture fiber based on JIS-L0823.

Figure 14 shows the evaluation results of the durability for both mold. The contact angles for FEP coated mold decreases as the examination proceeds, while that of PEPE-S treated mold hardly change. The molecular fluorne layer formed by a silane-coupling agent is excitingly strong and shows excellent durability due to...
chemical bonding.

Acknowledgements

This work is partially supported by a Development of Basic Optical Information Technology, Joint-Research Project for Regional Intensive, in Osaka Prefecture.

The authors also thank to Mrs. T. Arase and T. Shimizu at DAIKIN INDUSTRIES Ltd. for helpful comments and suggestions about fluorine polymers.

References

6. Conclusions

Two kinds of mold surface treatments for imprint lithography are investigated to avoid the adhesions. By evaporating FEP, fine surface of the mold and fairly good releasing ability are obtained while the durability is relatively poor. On the other hand, surface treatment by silane-coupling agent using PEPE-S realizes excellent durability and releasing ability but it needs careful mold surface cleaning and rinsing.