Filling Behavior Observation on UV Nanoimprint Lithography

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Next-generation fine patterning requires a high throughput cost-effective process for the mass producing of various devices, which has a nanometer-scale pattern over a large area. UV nanoimprint lithography (UV-NIL) is a major breakthrough in this field because it is considerably simpler than the conventional techniques and the equipment cost of a NIL system is inexpensive. However, there are some technical challenges to be solved from a practical application standpoint. In particular, the elucidation of the filling behavior of UV photo-curable resin into the mold is very important to produce an exact replicated pattern. In order to observe the filling behavior, the midair structure mold with or without the release agent was employed because this mold needs not consider the air bubble defects. As a result, the filling behavior of UV photo-curable resin into the midair structure mold was observed clearly with scanning electron microscope and it is confirmed by this method that the release agent encumbered the filling of UV photo-curable resin in the nano-scale pattern. This phenomenon was appeared prominently in the finer pattern.

Keyword: Nanoimprint, UV photo-curable resin, filling behavior, release agent

1. Introduction

In the next generation, a strong need exists for nano-scale patterning technology, which has a high throughput and a cost-effective process. Nanoimprint lithography (NIL) is a major breakthrough method for next-generation lithography (NGL) because of its high resolution and simpler process compared to conventional technology [1]. In particular, ultraviolet (UV)-NIL technique utilizes high sensitive photo-curable resin, so theoretically it makes possible to implement high-speed pattern transfer such as step and repeat process [2]. Moreover, the three dimensional replicated pattern is obtained in only one shot [3]. This primary feature of UV-NIL technique will reduce the manufacturing cost drastically [4]. Now therefore, UV-NIL is one of techniques with the great potentiality as a new manufacturing process.

However, there are some technical challenges to be solved from a practical application standpoint. The shortage of the replicated pattern’s height compared to the mold’s depth is one of the key issues. Especially, the replication defect caused by air bubble is well known problem called “the bubble defect” [5]. The bubble defect is generated due to holding the air in the concave pattern of the mold, when the mold reaches to the photo-curable resin film which is formed on a substrate. Accordingly, the
replicated pattern will be shorter than the mold pattern or get chipped partially, especially the corner of the replicated pattern. In addition, the investigation of release agent properties with a normal NIL mold in air is interrupted by the bubble defect because it is difficult that we discern the bubble defect from the influence of a release agent. Therefore, we fabricated the midair structure mold to observe the filling behavior of the UV photo-curable resin at atmospheric pressure. This mold needs not consider the bubble defects. As a result, the filling behavior into the mold pattern in air was observed clearly with scanning electron microscope (SEM). Moreover, it is confirmed by this mold that the release agent encumbered the filling of UV photo-curable resin in the nano-scale pattern.

2. Experimental Setup

2.1. Fabrication of the midair structure mold

The midair structure molds were fabricated by control of acceleration voltage electron beam lithography (CAV-EBL) [6]. Hydrogen silsesquioxane (HSQ) was employed as a negative-type electron beam resist. ERA-8800FE (Elionix Co.), which is SEM customized for the delineate task, was used for the CAV-EBL system with 6 pA of beam current. The CAV-EBL process was as follows (figure 1).

![Figure 1. The fabrication process of the midair structure mold.](image)

First, HSQ was spin-coated at 3000 rpm on a cleaned Si substrate and baked at 180°C for 5 minutes, resulting in a 300 nm film. In order to investigate the surface state of HSQ film, the contact angle between PAK-01 and the HSQ surface, with or without the release coat, was measured by using a contact angle measurement system (FTA125, First Ten Angstroms, Inc.). Then, EBL was carried out at a high accelerating voltage of 30 kV to delineate line patterns. Subsequently, a second EBL was carried out at a low acceleration voltage of 3 kV to delineate up lines in a direction at right angles to the first one. Finally, the HSQ film was developed in tetramethylammonium hydroxide (TMAH 5%) for 180 s. The acceleration voltage changes the projection range of the electron beam; in this case, the EBL carried out at 30 kV to form trough beams and 3 kV to form bridges, result in the midair structure (figure 2). Glassy carbon (GC) was also employed as a substrate.

![Figure 2. The SEM image of the fabricated midair structure mold.](image)

2.2. UV-NIL process

In order to observe the filling behavior, UV-NIL was carried out at atmospheric pressure using fabricated midair structure molds. The advantage of using the midair structure mold is that free channels exist under the bridges that allow any air to escape at the beginning of the process; therefore, the bubble defect does not occur and the adjacent two bridges were considered as the both open ends HSQ channel. We prepared midair structure molds with and without release agent (Daikin Co., Optool DSX 0.1%). The midair structure mold without release agent was post-baked at 350°C for 30 minutes. PAK-01 (Toyo Gosei Co., Ltd.) was employed as the UV photo-curable resin. One drop of PAK-01 is put on the mold around the HSQ midair structure. The size is approximately...
0.13 mm$^3$. The transferred substrate was glass slide. Transfer pressures were 0.2 MPa, 0.5 MPa, and 0.8 MPa and the hold time was 60 s, which was sufficient to complete the formation of the PAK-01 pattern. After the hold time, UV radiation with an energy density of 4 J/cm$^2$ was focused to the midair structure mold. Then, the mold was retracted, leaving behind a PAK-01 pattern. At this time, the midair HSQ structure was also released from the substrate in some cases. However, we assume that the contact angle, which is developed between the liquid PAK-01 and solid mold side walls, was frozen during UV exposure and it expressed the filling behavior. So, we observed the PAK-01 pattern and the midair structure mold on the glass slide after UV-NIL process with SEM.

3. Results and Discussion

3.1. The measurement of the contact angle between HSQ film and PAK-01

Figure 3 shows the contact angle between HSQ film formed on Si substrate and PAK-01. Without release agent, the contact angle was 43° and it increase to 66° by release agent Optool DSX, which is fluorine-silane coupling agent. In contrast, the contact angle of HSQ film was decreased to 11° after post-bake at 350°C because the organic constituent in the HSQ film was desorbed.

The release agent leads to a low surface energy and the higher contact angle of a mold tended the easier release of the mold from the transferred substrate. In order to clear the distinction of contact angles, the post-baked mold was used as the mold without release agent.

3.2. Fabrication of the midair structure mold

Figure 4 shows the SEM image of the fabricated midair structure mold. The through beam lines and bridge lines are delineated at 30 kV, 175 μC/cm$^2$ and 3 kV, 100 μC/cm$^2$, respectively. The thickness of the bridge, which was considered as the both open ends HSQ channel length, was approximately 100 nm. The aperture shape of the midair structure mold was square, 1000 nm on a side.
3.3. The characteristics of the filling behavior of PAK-01 into the midair structure mold

Figure 5 shows the PAK-01 shape, which is patterned on the glass slide by the midair structure mold with or without release agent. The transfer pressure and the aperture size were 0.2 MPa and 1000 nm, respectively.

![SEM image of the filling behavior](image)

Figure 5. The SEM image of the filling behavior of PAK-01 on glass slide (a) with release agent, (b) without release agent.

Figure 5 (b) shows that PAK-01 was overflowed in adjoining aperture, since the PAK-01 was filled completely into the HSQ channel. In contrast, with release agent, PAK-01 was not overflowed and the patterned height of PAK-01 without release agent was shorter than one without release agent. This means that the release agent encumbered the filling of PAK-01 into the squared aperture of the HSQ channel.

The force, which is encumbered the filling of PAK-01, is constant ($P_c$) and the pressure against to $P_c$ is required to fill PAK-01 into the aperture of the midair structure mold. $P_c$ is represented as following expression [7] [8]:

$$P_c = \frac{4\gamma \cos \theta}{a}$$

(1)

Here, $a$ are lengths of the channel sides, and $\gamma$ is the liquid surface energy, $\theta$ is contact angle in the channel.

For experimental determination of $P_c$ with or without release agent, the filling behavior with respect to each transfer pressure was examined. Figure 6 shows the characteristics of the filling behavior of PAK-01 into the midair structure mold which has 1000 nm aperture.

![Characteristics of filling behavior](image)

Figure 6. The characteristics of the filling behavior with respect to each transfer pressure.

The patterned height of PAK-01 without release agent was shorter than the initial HSQ thickness because of the post-bake. Compared 0.5 MPa to 0.2 MPa with release agent, the patterned height was drastically increased. However, the patterned height without release agent was maintained almost constant throughout a range of pressure. This means that $P_c$ of the midair structure mold, which had 1000 nm aperture with release agent, was approximately 0.5 MPa and $P_c$ without release agent was less than 0.2 MPa. Consequently, it is confirmed that $P_c$ increased by release agent results in the encumbrance of the filling of UV photo-curable resin.

3.4. The $P_c$ dependency of the aperture size

In order to investigate the $P_c$ dependency of the aperture size, the midair structure mold
with release agent, whose length of the aperture side was 470 nm, was also examined. Figure 7 shows the PAK-01 shapes on the glass slide, which were patterned by midair structure molds with 1000 nm and 470 nm aperture. The transfer pressure was 0.5 MPa.

![Figure 7](image)

Figure 7. The $P_c$ dependency of the aperture size (with release agent).

In spite of same transfer pressure, the height, which is patterned with 470 nm aperture, was shorter than half of the height with 1000 nm. This shows that $P_c$ was increased due to the reduction of $a$. As a result, the finer aperture size of the midair structure mold tended to increase $P_c$.

Figure 8 shows the patterned PAK-01 in the midair HSQ structure with release agent on the glass slide using GC substrate. The transfer pressure was 0.9 MPa. The midair HSQ structure was detached from GC substrate because of the weak adhesion force. However, the contact angle was maintained since PAK-01 had been frozen by UV radiation. Therefore, the contact angles $\theta$ of the PAK-01 in the midair HSQ structure were able to observe.

![Figure 8](image)

Figure 8. The SEM image of the contact angle in the midair HSQ structure (with release agent) (a) 260 nm aperture, (b) 440 nm aperture, (c) 620 nm aperture.
The patterned heights of PAK-01 protruded from the midair HSQ structure were higher in accordance with the larger aperture size \(a\) and the observed contact angles appeared to be over 90°. Hence, the direction of each \(P_c\) value was faced to the edge of PAK-01 as the encumbrance force. The detailed investigation will be obtained by the cross section.

4. Conclusion

The filling behavior of UV photo-curable resin was examined using the midair structure mold with SEM. As a result, it was clear that following: First, the release agent encumbered the filling of PAK-01 into the midair HSQ channel as shown figure 9 (a). This force was represented by \(P_c\) and obtained by the observation of the contact angle \(\theta\) and aperture size \(a\) in the midair HSQ structure. Without release agent, the contact angle was not able to observe since the HSQ channel was filled completely. Therefore, we consider that the attraction capillary force is generated as shown figure 9 (b) by the channel, whose \(\theta\) was less than 90°.

![Figure 9](image)

Figure 9. The schematic model of the HSQ channel (a) \(\theta > 90°\), (b) \(\theta < 90°\).

In order to observe the contact angle without release agent, the midair structure mold, which has the larger \(a\), was demanded to decrease the reduction of the attraction capillary force. Secondly, the smaller aperture size tended to be larger \(P_c\). Accordingly, the transfer pressure above \(P_c\) was necessary to fill the PAK-01 into the midair HSQ channel. The same is true of usual NIL mold. Thus, it appears that the required transfer pressure, which is sufficient to fill the photo-curable resin completely into the mold with release agent, was greater than the previously thought. The enlargement of the transfer pressure will be more prominent in the finer mold pattern.

Consequently, the elucidation of the surface state in the NIL mold pattern with release agent is very important to be successful in the fine NIL process. Our observation method using the midair structure mold is very useful for this purpose. Additionally, the shrinking of the UV-photo curable resin at UV radiation was also needed to consider. The further elucidation of both phenomena will bring in an exact replicated pattern with UV-NIL, compared to the mold pattern.

References