A Consideration of Important Factor on Demolding Force for Various Molds

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The demolding forces for various molds are studied for thermal imprint process. Molds are fabricated by anisotropic KOH etching of (110) Si wafer and conventional plasma etching. Although the side wall roughness by the KOH etching is much smaller than that by the plasma etching, the demolding forces for the both molds are similar. The demolding forces for the molds with various cavity depths are measured, and it is found that the demolding force depends on the total side wall area. The demolding force for the mold with line and space pattern is about 50 times as large as that for the mold with no patterns. These results show that the demolding force from the side wall is dominant in the thermal imprint process.

Keywords: imprint, demolding force, adhesion, friction, Si mold

1. Introduction
Nanoimprint lithography (NIL) [1] is promising for cost effective nanofabrication. However, there still remain several issues for the industrial applications of this method. One of the significant issues is demolding. Since a mold usually adheres to the resist polymer, it has to be mechanically released from the resist. Fatal defects are sometimes induced in resist patterns during the demolding process. Thus, it is very important to examine the demolding force [2, 3]. At the top and bottom surfaces of the mold pattern, the adhesion force works as shown in Fig. 1. The additional force works at the side wall by the friction. The side wall of the mold pattern must be very important for the demolding force.

In this study, the extents of the demolding force induced by the top and bottom surfaces and by the side wall are explored. Si molds are fabricated both by the plasma etching (PE mold) and by the anisotropic etching of (110) Si wafer by KOH (KOH mold). When the KOH mold is used, its side wall is extremely smooth and the effects of the side wall roughness can be excluded. The molds with various cavity depths are fabricated and the relation between the demolding force and the cavity depth is examined. The dependence of the demolding force on the mold surface energy is also examined by controlling the anti-sticking treatment.

2. Experiments
Line and space pattern of 2 µm half pitch is fabricated on Si wafer of 10x10 mm by a conventional photolithography. The patterned region is 5x5 mm. The Si wafer and the pattern areas are $A_S=100 \text{ mm}^2$ and $A_P=25 \text{ mm}^2$, respectively. For the PE mold, (100) Si wafer is used. Cr pattern is fabricated on the Si wafer by the lift-off process and the Si wafer is etched by commercial ICP etcher (ULVAC, NE550). The modified Bosch process is used in order to suppress the side wall roughness. The one cycle of the process consists of short deposition step by $C_4F_8$ plasma ($\sim5$ s) and etching step by $Ar+SF_6+CHF_3$ plasma ($\sim8$ s). The cycle is repeated and the desired cavity depth is obtained. The details of the etching conditions were shown.
in the previous paper [4]. For the KOH mold, (110) Si wafer with 0.5µm SiO2 film is used. The SiO2 pattern is fabricated by CHF3 plasma etching and the wafer is dipped into 5 M/L KOH solution at 65 °C. After the etching, the fabricated mold is bonded to a graphite mold holder of 15 mm in diameter. The standard anti-sticking treatment (Daikin: OPTOOL DSX) is carried out to the mold [5]. In some experiments, the anti-sticking layer is degraded by the UV/O3 treatment [6]. The surface energy of the mold is controlled by changing the time of the UV/O3 treatment. After the anti-sticking treatment, the mold is pressed to PMMA film on Si wafer of 30 x 30 mm. The molecular weight of the used PMMA is 350 k. The press conditions are 170 °C, 10 MPa for 15 min. The sample is cooled to the room temperature, and the press pressure is released. Finally, the Si wafer is removed from the mold. The schematic view of the demolding tool is shown in Fig.2. The Si wafer is fixed to the sample holder and the mold holder is connected to a force gauge through the flexible joint. The sample holder is placed on the z moving stage, which is controlled by a computer, through the tilt stage. When the z stage is moved down, the mold is pulled upwards. The maximum pull force is defined as the demolding force. By the tilt stage, the direction of the pull force is adjusted perpendicular to the wafer surface.

3. Results and discussions
3.1. Fabricated molds
An example of the PE mold is shown in Fig.3. A pattern with vertical side wall is obtained. The line and cavity widths are 2.0 µm and the cavity depth is 3.2 µm. However, the side wall roughness can be observed in the high magnification SEM picture of Fig. 3(b). The roughness is about 10 nm. An example of the KOH mold is shown in Fig.4. The SiO2 mask is not removed. The line and cavity widths are 1.0

![Fig. 2 Used demolding tool. (a) is an explanation around sample shown by white circle in (b). (b) shows a picture of the tool.](image1)

![Fig. 3 SEM picture of PE mold at (a) low and (b) high magnifications, respectively.](image2)

![Fig. 4 SEM picture of KOH mold at (a) low and (b) high magnifications, respectively.](image3)
and 3.0 µm, respectively. The cavity depth is 4.2 µm. Since the fabricated line width is clearly narrower than the SiO₂ mask one, the undercut etching is induced because of the small misalignment between the resist line direction and (110) direction of the Si wafer. However, the mold pattern with extremely smooth side wall can be obtained. Molds with various cavity depths are fabricated for both the PE and KOH molds.

3.2. Demolding force for various molds

During the demolding, the adhesion force works at both the top and bottom surfaces of the mold pattern as shown in Fig. 1. The total of the sum of the top and bottom surface areas is equal to the Si wafer area of \( A_s \). Therefore, it is considered that the demolding force by the top and bottom surfaces is equal to the demolding force for the Si wafer with no patterns as the first approximation. Therefore, the demolding force by the top and bottom surfaces is named as “flat component” in the following discussion. On the other hand, both the adhesion and friction forces work at the side wall. The total side wall area, \( A_w \), can be estimated by the following simple equation.

\[
A_w = \frac{2H}{P} A_P
\]  

where \( H \) and \( P \) are the cavity depth and the pattern pitch which is the sum of the line and cavity widths, and \( A_P \) is the pattern area. The demolding force by the side wall is named as “side wall component” in the following discussion. The total contact area between the mold and PMMA surfaces, \( A_T \), is given by \( A_s + A_w \). Figure 5 shows the dependence of the demolding force on the total contact area for the KOH molds. It is considered that the demolding force is proportional to the contact area, but its dependence greatly deviates from the linear relation. Figure 6 shows the dependence of the demolding force on the total side wall area for both the KOH (shown by circles) and the PE (shown by squares) molds. A good linear relation between the demolding force and the total side wall area is obtained. This shows that the demolding force depends on

<table>
<thead>
<tr>
<th>UV/O₃ Time (min)</th>
<th>0</th>
<th>1</th>
<th>3.5</th>
<th>4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water droplet</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>Contact angle (deg)</td>
<td>114</td>
<td>100</td>
<td>70</td>
<td>25</td>
</tr>
<tr>
<td>Surface energy (mJ/cm²)</td>
<td>8.6</td>
<td>17.5</td>
<td>36.6</td>
<td>85.1</td>
</tr>
</tbody>
</table>

Fig. 7 Variation in the water contact angle and mold surface energy by changing UV/O₃ exposure time
the side wall area, and the “side wall component” is much larger than the “flat component”.

The demolding force for the KOH molds is almost same as that for the PE mold although the surface roughness of the KOH molds is much smaller than that of the PE mold. Thus, the demolding force must be insensitive to the roughness below 10 nm.

3.3. Flat component and side wall component

It is considered that the demolding force for the patterned mold is the sum of the “flat component” and the “side wall component”. The “flat component” is equal to the demolding force for the flat mold, which is the Si mold with no pattern. Therefore, when the demolding forces for both the flat mold, $F_1$, and the patterned mold, $F_2$, are measured under the same surface condition, the “side wall component” of the patterned mold can be estimated by their difference, $F_2 - F_1$. In this study, the surface condition is characterized by the surface energy. It is widely used that the surface energy is estimated from the contact angles for both pure water and diiodomethane [7, 8]. Since the anti-sticking layer is degraded by the UV/O$_3$ treatment, the surface energy increases, that is, the contact angle decreases as the time of the UV/O$_3$ treatment increases. Figure 7 shows the change in the contact angle for pure water when the time of the UV/O$_3$ treatment is varied. It is clear that the surface energy increases as the time of the UV/O$_3$ treatment increases. The surface energy has to be checked after the UV/O$_3$ treatment, because the values of the surface energy are often different even when its treatment time is same.

The demolding forces for both the flat and patterned molds are measured. The PE mold, whose cavity depth is 5 µm, is used as the patterned mold. Figure 8 shows the dependence of the demolding force on the mold surface energy for both the flat mold (shown by circles) and patterned mold (shown by squares). It is found that the values of the demolding force for the patterned mold are about 50 times as large as those for the flat mold. This shows that the “side wall component” is much larger than the “flat component”. This agrees to the results shown in the section 3.2. The demolding force can be expressed as the power law of the mold surface energy, that is, $(\text{mold surface energy})^b$. The values of $b$ are 1.2 and 0.83, respectively. This shows that the demolding force is approximately direct proportional to the mold surface energy.

4. Conclusions

The demolding forces under various mold conditions are studied for the thermal imprint process. First, both the KOH and PE molds with various cavity depths are used. It is found that the demolding force depends on the total side wall area. Next, the patterned and flat molds with various surface energies are used. The demolding force for the patterned mold is much larger than that for the flat mold. These results show that the demolding force by the side wall is dominant in the thermal imprint process.

References