A Study of the Demolding Force in Nano Imprint Lithography for Different Surface Treatments

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ABSTRACT

In the Nano Imprint Lithography (NIL) process, polymer flow and the arising of large demolding forces are important problems for the process productivity and final product features. This demolding force can cause fractures and deformation of the polymer patterns and the mold. The demolding forces, which originate from the mold-polymer contact areas, consist of micro/nano scale adhesion and friction forces. These forces are affected by the structure of the surface and the subsequent surface energy state. In this study, the characteristics of the demolding forces derived from the mold-polymer contact areas were investigated for different surface energy states, and the results were compared to friction signals measured with a surface treated AFM tip.

Keywords: atomic force microscopy, friction, demolding force, self-assemble monolayer, surface treatment

1 INTRODUCTION

Nano imprint lithography (NIL) is the most promising fabrication technology due to its high resolution, fast throughput, and cost effective fabrication in science and the micro/nano manufacturing industry [1, 2].

The NIL process can be divided into two steps: the pressing and demolding stages. In the pressing stage, micro/nano scale patterns on a mold are transferred to a polymer resist. During this stage, there are some issues of polymer flow between the mold and the substrate [3].

In the demolding stage after the pattern transfer stage, the demolding forces, which originate from the contact area between the mold and the polymer resist, are an important parameter for reliability in the reproducibility of the pattern shapes and for the process productivity. The occurrence of these demolding forces can cause serious fractures in the polymer patterns and mold [5].

The demolding forces consist of micro/nano scale adhesion and friction forces. These forces are difficult to measure due to the lack of equipment and have different tendencies compared to those on a macro scale [4, 5].

In this study, the surface of an AFM tip and mold were modified by hydrophilic or hydrophobic treatment, and these modified surface energy states were confirmed by the measurement of the water contact angle. The modified AFM tip was used to investigate the micro/nano scale friction signals, which showed different characteristics for each surface energy state. In addition we performed imprinting experiments using the surface modified Si mold, and the results were compared to the friction signals measured with the surface treated AFM tip.

2 EXPERIMENTAL METHOD

2.1 Materials

A poly(methyl methacrylate) (PMMA, 495 kg/mol, MicroChem, USA) was used as a polymer resist. PMMA is a commonly used polymer resist in NIL and has good optical clarity. A PMMA film was spin-coated on Si substrates at 4000 rpm for 40s resulting in a layer thickness of 500nm, and then pre-baked at 150℃ for 90s to remove any residual solvent.

The mold was fabricated by reactive ion etching (RIE) with a size of 25 x 25 mm. The line width of the mold patterns was 1000 nm, and depth was 300 nm. We prepared two sets of mold; one set had micro patterns on it, and the other set had a flat surface without patterns. Thus, we were able to observe the effect of the micro patterns on the demolding forces. The SEM and AFM image of the micro-patterns are shown in Figure 1.

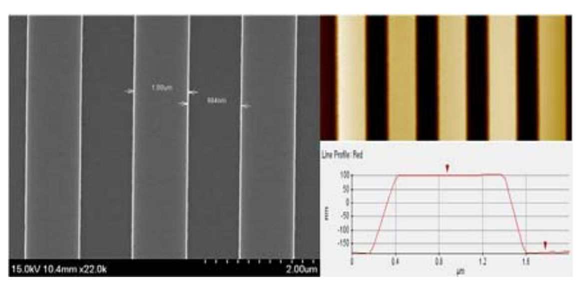

Figure 1: The SEM and AFM image of the micro-patterns.

2.2 Surface Treatment

The surfaces of the AFM tip and mold both made with Si were modified by the following treatments: a hydrophilic surface were formed by O_2 plasma treatment (MY-PL150, APP, Korea), and a hydrophobic surface was achieved by the formation of a self-assembled-monolayer. The water contact angles as a result of each surface treatment are shown in Table 1.

Surface Treatments	O_2 Plasma	Untreated	SAM(FOTS)
Contact angles	6.2°	17°	106°

Table 1: The results for the water contact angle.

For the O_2 plasma treatment, Argon (Ar) was used as a base gas, and Oxygen (O_2) was used as a reaction gas. Before the plasma exposure, specimens were rinsed with IPA and DI water and dried in a flow of nitrogen (N_2). Specimens were exposed to plasma for 60s. After the O_2 plasma treatment, hydroxyl groups (-OH) formed on the surface, causing it to become hydrophilic.

A hydrophobic self-assembled monolayer (SAM) of trichloro (1H,1H,2H,2H-perfluorooctyl) silane 97% (FOTS, Sigma Aldrich, US) was deposited on the surface of the mold and AFM tip using a vapor phase-coating technique, and then annealed in a convection oven at 573K for 90min. It has been shown that SAM suffers from a loss of hydrophobicity over time; however, annealing can significantly improve the hydrophobic stability of the FOTS monolayer that originates from the densification of the monolayer upon annealing [6].

Figure 2: The FOTS layer was deposited on the surface of the specimens in a vaccum chamber (L) and annealed in a convection oven (R).

2.3 Friction Signal Measurement

Atomic force microscopy (AFM XE-150, Park Systems, Korea) with the lateral (frictional) force mode was used to investigate the friction signals. In the lateral force measurement, a cantilever (PPP-CONTSCR, Nanosensors, USA) twisted laterally because of the surface-tip interaction, and AFM detected twisted displacements of the cantilever with laser sensor. Thus, this twisted displacement signal is directly proportional to the friction force, and friction can be compared with each surface from various specimens.

Prior to the friction measurement, the spring constant of the cantilever was calibrated [7]. The measured normal spring constant value obtained was 0.5 N/m, which was significantly different from the cantilever information received from the manufacturer. The tip radius of the cantilever was below 10nm. The SEM image is shown in Figure 3.

For the lateral force measurement, we scanned 5μm x 5μm areas, and the lateral (friction) signal was collected from all specimens, which were prepared for 10 samples for each surface treatment. The trace-retrace signals coming from the lateral force measurement was averaged for the scan areas. The differences between the averaged trace and retrace signals indicate the magnitude of the friction force; thus, these differences were compared to each surface treated specimen.

Figure 3: The images of the AFM (L) and cantilever (R).

2.4 Demolding Force Measurement

We performed the imprinting experiment using the surface modified Si mold and measured the forces between the mold and PMMA films during the demolding stage. The imprinting conditions are shown in Figure 4.

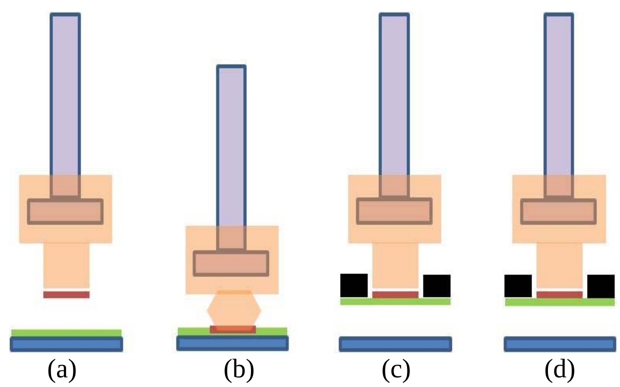

Figure 4: The imprinting and demolding conditions: (a) Ready, (b) Imprinting- 130℃, 30bar, 5 min (c) Cooling – from 130℃ to room temperature, (d) Demolding – measurement of the demolding forces.

The demolding force measurement was done in four steps. First, we produced the structure of the "T" shaped elastomer made with polydimethylsiloxane (PDMS, Dow Corning, Korea), which was connected to the Universal Test Machine (UTM, Lloyd Instruments, USA). PDMS has a good elastic property that can improve the degree of alignment, and prevent direct contacts between the mold and the UTM; thus, the destruction of the mold can be avoided. Second, the mold was attached to the PDMS, and then imprinted to the substrate on which the PMMA film was coated. The size of the mold was 25 x 25 mm, and the applied pressure was controlled at 30bars for 5 min by the UTM. During the imprinting stage, the process temperature was maintained at 150℃, which was well above the bulk glass transition temperature. During the third step, the mold and substrate were lifted and cooled down to room temperature. Finally, the substrate was fixed, and then the demolding force was measured by the UTM lifting the mold at a constant rate.

3 RESULTS

The O_2 plasma treatment increased the lateral force (friction) signals by 20%, and FOTS monolayer decreased signals by 70%. The measured results are shown in Figure 5.

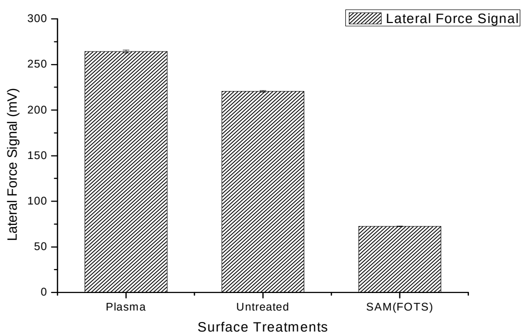

Figure 5: The lateral (frictional) force signals for the different surface treatments.

The demolding force measurements were performed using each surface treated mold, and we prepared two sets of molds with or without micro-patterns. A representative load profile is shown in Figure 6. The measured force increased, as the mold was lifted, and reached a maximum load at the moment of separation. This maximum load was defined as the demolding force.

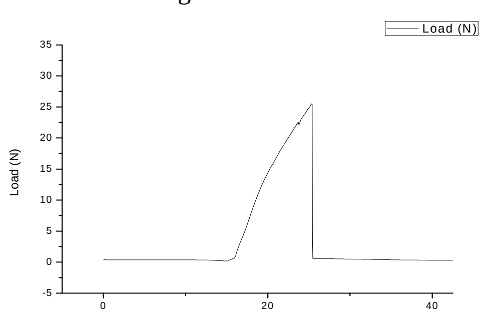

Figure 6: The representative load profile for the demolding force measurement. The measured maximum load was defined as the demolding force.

The measurement results are listed in Table 2.

(a)	Load (N)	Ratio
O_2 Plasma	24.1	1.399
Untreated	17.3	
SAM(FOTS)	3.11	0.18

(b)	Load(N)	Ratio
O_2 Plasma	31.2	1.62
Untreated	19.3	
SAM(FOTS)	4.56	0.24

Table 2: The results of the demolding force measurements: (a) mold with micro patterns, (b) without micro patterns.

The O_2 plasma treatment increased the demolding force, but the FOTS layer decreased the demolding force. In addition, the demolding force increased in all the surface treated cases in which micro-patterns were on the mold.

In order to observe the effect of the demolding forces on generating defects on the polymer resist, the resulting patterns on the PMMA resists after the demolding stages are shown in Figure 7.

Figure 7: The images of the polymer resist on the substrate after the demolding process.

4 DISCUSSION

The results for the water contact angle show that each surface treatment can effectively modify the surface of the mold, and these modified surfaces have different surface energy states. O_2 plasma treatment makes the surface of the mold hydrophilic, and the FOTS monolayer makes the surface hydrophobic.

In the AFM measurement, we found that the surface, in a different energy state, affected the micro/nano scale friction; O_2 plasma treatment increased the lateral force (friction) signals by 20%, but the FOTS layer decreased the signals by 70%. These results are in good agreement with previous research [8].

The demolding force measurement showed a similar tendency with the micro/nano scale friction signal, and the FOTS layer especially showed a similar reduction rate in friction and demolding force; thus, we conclude that the friction force is an important component of the demolding force.

In addition, the results indicate that the micro-patterns on the mold affected the demolding forces for all surface treatments. The comparison of demolding forces between

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the mold with micro-patterns and the flat mold are shown in Figure 8.

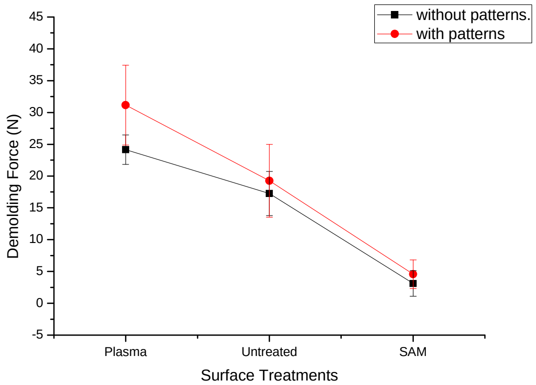

Figure 8: The demolding forces for the different surface treatments: mold with micro patterns (circle), without micro patterns (square).

The micro patterns on the mold also increased the demolding forces due to an increased contact area. The influence of the micro-patterns on the demolding force appears to be relatively larger in the plasma treatment since O_2 plasma treatment increases the friction forces between the mold-polymer contact areas. On the other hand, the FOTS layer decreases the friction forces; thus, the influence of the micro-patterns on the demolding force is relatively small; therefore, we can conclude that the function of the FOTS layer for anti-sticking is to provide most of the friction reduction at the mold-polymer contacts.

Figure 7 shows that the O_2 plasma treatment, from which a large demolding force originated, caused large defects on the PMMA resist, and polymer film peeled off. However, Figure 7 shows that the PMMA resist remained perfect without any defects when the mold was coated by FOTS.

5 CONCLUSION

The experimental results indicate that O_2 plasma treatment increased the friction signals and the FOTS layer decreased the signals drastically, and a similar trend was also observed when measuring the demolding forces. These results show that the demolding forces were strongly affected by the micro/nano scale friction, and the function of the FOTS layer for anti-sticking is to provide most of the friction reduction at the mold-polymer contacts. Micro patterns on the mold also increased the demolding forces due to an increased contact area, and this appeared to be less effective in the mold with the FOTS layer. Through additional research, it is expected that a new model for the demolding process can be derived.

6 ACKNOWLEDGEMENTS

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