Design of Release Interface for UV-NIL Material

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Release interface between UV-NIL resists and quartz mold was investigated focusing on surface energy and elastic modulus of resist film in order to improve release property of UV-NIL process. The resist with fluorine monomer and with non-reactive fluorine anti-sticking agent were compared by separation force measurements and surface analyses of release interface. The results indicated that resist design has the capability to both reduce the separation force and maintain a clear mold surface. The mold release agent decomposed with increasing number of imprint shots, but the low release force resist with non-reactive anti-sticking agent was able to control the degradation of mold release agent and thus improve release property endurance. In addition, resists with various acrylate monomer structures and formulations were studied in terms of elastic modulus of UV cured resist film. It is found that the separation force can also be controlled by resist elastic modulus without depending on the effect of anti-sticking agent.

Keywords: imprint, UV-NIL, resist, separation force, anti-sticking agent, release agent, elastic modulus, surface energy

1. Introduction
Nano-imprint lithography (NIL) is a promising technique for nano-pattern fabrication of future magnetic and semiconductor devices [1-4] because it can easily transfer sub-20nm scale structures at room temperature. Acrylate-based formulations are widely investigated as NIL resists [5-9] because a polymerization of acrylate is very fast and many acrylate compounds are commercially available.

However, the biggest challenge in UV-NIL is still to achieve defect-free separation of the mold and the imprinted resist layer. Release property is crucial during separation of resist and mold in preventing resist damage and mold contamination. Because there are two interfaces in the substrate/resist film/mold structure, one each between the mold and resist film and between the resist film and substrate, the adhesion forces of the interfaces must be suitably controlled to enable separating the mold at its interface with the resist film [10,11]. Furthermore, the strength design of the polymerized resist film is significant in preventing resist breakage.

The separation force between mold and resist is a current topic of great interest. In the early stage of UV-NIL study, mold surface treatment by perfluoroalkyl silane compound was proposed as a means of decreasing the surface energy of the mold surface [1]. However, several reports indicate that the release force does not depend on the mold surface energy [12] and that repeated imprinting rapidly reduces the amount of release agent on the mold [12,13]. Although it has been argued that radical attack from a radical initiator [12] or strong release force causes release agent decomposition, the reason for this is not yet clear.

In addition to reducing the surface energy of mold surface, many other approaches have been proposed to resolve the problem of
release agent degradation. Release agent on the mold surface was improved by changing the main chain part from a perfluoroalkyl chain to a perfluoroalkyl polyether chain to reduce release force [14]. The functional group of the release agent was also changed to improve adhesion to mold surface [15]. Resist release property was also improved by adding to the resist an anti-sticking agent such as fluoroalkyl silane (which is the same as the mold release agent) [16], fluorine surfactant [7,17,18], and fluorine monomer [18,19]. It was also found that reducing the elastic modulus is effective in reducing release force [20]. With these approaches, the resist design must include consideration of the pot life, chemical contamination on the mold, adhesion to substrate, and etching resistance. Yet despite the approaches listed above, there is no report of success in achieving mold life that can provide the shot number required for industrial use. For example, in the field of patterned hard disk media, though 100 million shots are needed for manufacture, only 100 shot imprints have so far been reported [15,17].

Recently, a new approach using condensable gas as ambient gas of UV imprint has been proposed [21]. A typical condensable gas used in the approach is 1,1,1,3,3-pentafluoropropane (PFP). It was reported that PFP can reduce the viscosity and separation force of UV curable resins and 20,000 repeated imprints with a single mold by UV imprint using PFP were successfully demonstrated [22]. However, influence of mixing of PFP and resist material should be discussed in terms of etching resistance of cured resist film.

Based on the above background, the most common approaches to improve release property are to reduce surface energy and to control mechanical property of resist. Theoretically, an adhesion force between two elastic plates depends on both surface energy and elastic modulus as following equation [20, 23]. This equation also indicates that release property should be improved by a surface energy of release interface and an elastic modulus of resist film.

\[
F = \left( \frac{3}{2} \pi \gamma KR^3 \right)^{1/2} \tag{1}
\]

where \( \gamma = \gamma_1 + \gamma_2 - \gamma_{12} \) (\( \gamma_1 \) and \( \gamma_2 \) are surface energies of the two surfaces and \( \gamma_{12} \) is the interface energy between \( \gamma_1 \) and \( \gamma_2 \)), \( R \) is the effective radius of interface, and \( K \) is the composite Young’s modulus.

\[
\frac{1}{K} = \frac{3}{4} \left( \frac{(1 - \nu_1^2)}{E_1} + \frac{(1 - \nu_2^2)}{E_2} \right) \tag{2}
\]

where \( E_1, E_2, \gamma_1 \) and \( \gamma_2 \) are Young’s modulus and Poisson’s ratios of the two elastic materials.

In this study, design of release interface between mold and resists were investigated by the measurement of separation force employing the example of an acrylate-type NIL resist currently under development in our laboratories. Regarding low surface energy, both mold release layer and resist with anti-sticking agent have been examined. Regarding mechanical property of resist, the elastic modulus of UV cured resist film was optimized by monomer structure and formulation.

2. Experimental

2.1. Materials

A newly developed NIL resist was investigated in this study. The resist was a mixture of acrylate monomer, fluorine acrylate monomer, additive and initiator. Both monomers were synthesized by FUJIFILM Corporation. The fluorine monomer was added to improve release from the mold, i.e. the release property. The fluorinated monomer had an acrylate group that reacts with the acrylate resin upon UV radiation. To study the release property, a fluorine anti-sticking agent was used instead of a fluorine monomer [24-26]. Several kinds of acrylate monomer were used to investigate the elastic modulus of the resist. An adhesion agent for a resist was also synthesized by FUJIFILM Corporation.

2.2. Imprint Process

The resist was coated onto 4 inch silicon wafers or 6 inch Quartz wafers by an ink-jet process using the FUJIFILM Dimatix DMP-2831 materials printer. Resist was dispensed in a grid pattern. Before resist dispensing, an adhesion agent was coated on wafers by spin coating. MEMS heads for drop
volumes of 10 pl (FUJIFILM Dimatix DMC-11610) was used for ink-jetting. Droplet density was determined so that resist thickness would be 60 nm for a blank imprint on silicon and quartz wafers. When a mold with a pattern formed on the surface was used, the residual layer thickness on the silicon wafer was set up to be from 15 to 20 nm.

The 6 inch quartz mold had a pattern with 90nm or 125 nm pitch with 1:3 line-to-space ratio and 60 nm depth. After cleaning the surface of the mold with ozone, the mold was coated with the release agent (Daikin OPTOOL HD2010) by dip coating. The surface free energy of the mold was 15 mN/m.

2.3. Measurement and Analysis

The elastic modulus of UV-cured resist film was measured by atomic force microscopy (AFM). Flat resist films with thickness of 60nm were prepared by blank imprint method and used for the AFM measurement.

Figure 1 illustrates the release force measurement apparatus. The UV cured stack was set in the release force measurement system. While holding the edge of substrate, the mold was pulled down at a constant speed from 0.1 mm/sec to 5.0 mm/sec. The separation force was measured by the strain gage (SG) during the separation. Because the frequency range of the SG was up to 30 Hz, the SG cannot detect the fast phenomena caused by the separation. Therefore, the acoustic emission sensor (AE) with upper frequency range of 100 kHz was mounted on the backside of the mold to monitor the dynamic separation progress. The AE has enough frequency response to detect the crack and vibration during the separation. Both signals were acquired by A/D converter and processed by frequency analysis method.

Figure 2 illustrates the step and repeat-type stamping tool. A 10 mm square size quartz plate was used as a mold. The resist was dispensed on the silicon substrate by dispenser and stamped at 0.1 MPa in air atmosphere. The thickness of resist film was approximately 2 μm after stamping.

The pattern width and height were measured by critical-dimension scanning electron microscope (CD-SEM), TEM, and AFM. The surface chemical composition of the mold and resist were evaluated by XPS and TOF-SIMS.

3. Results and Discussion

3.1. Understanding the separation by SG and AE signal analysis

The separation process was studied by the release force measurement apparatus shown in Figure 1. Figure 3 shows a typical measured SG and AE signals during fast separation with 5mm/sec. A 6inch quartz mold and 4inch silicon wafer were used for the measurement. Just after the test was started, SG signal gradually increased and showed the peak at 0.12 sec. Then SG signal gradually decreased and dropped at 0.24 sec. The AE signals were observed from 0.1sec to 0.24 sec. The strong peaks were observed at 0.1 sec and 0.23 sec. The result indicates that the separation process comprises three stages.

The first stage is the initial stage (0-0.1 sec in Figure 3), in which the silicon wafer was pulled down, but the separation did not start. Therefore, no AE signal was observed. The rim of quartz mold was bent and the entire under the wafer was being fixed to the holder by a vacuum. The SG signal increased with increasing of the distortion of quartz mold.

The second stage is progress of separation
The first AE peak at 0.1 sec indicates the beginning of separation around the outer edge of resist film, and then the release interface advanced toward the center of cured stuck. The weak AE signals followed by the first peak suggest many cracks were made at release interface as the separation progressed. During separation, the SG signal gradually decreased because of relaxation of quartz distortion.

The third stage is the completion of separation (0.23-0.25 sec). The biggest AE signal peak and the SG signal drop at 0.24 sec indicate the release point. Given that the mold was released at the center point of it, the separation stress of release interface was extremely high at the release point.

In the case of Figure 3, the separation was completed in 0.14 sec and gave the release force of 25 N. It is thought that there are several important measurement values to investigate the separation. For example, the peak value of SG signal as the maximum release force, the cumulative SG signal as release energy, the peak value of AE signal and the cumulative AE signal. In this study, the maximum value of SG signal as release force was used to evaluate of release property of resist materials, because the peak value of SG signal has a good repeatability and this study does not need to discuss detail regarding the separation stress of resist film with AE analysis.

3.2. The improvement of release property by addition of anti-sticking agent

Cured resist films were obtained by blank imprinting method using a quartz mold without surface coating. The migration of anti-sticking agent was then characterized by XPS. The results shown in Figure 4 indicate that both the fluorinated monomer and the fluorinated non-reactive anti-sticking agent are localized in the surface region of the cured films.

Figure 3. Typical SG (force) and AE signal chart during separation (upper graph) and schematic diagram of separation process for supplementary explanations (lower drawings).

Figure 4. Fluorine depth profiles of the resist films. The resist films were etched in a XPS chamber. Fluorine contents were measured by XPS at each measuring depth. The end points of resist film were detected at the point where Si-2p signal form molds were saturated.
surface after imprint show that non-reactive anti-sticking agent easily removes from the cured film surface and transfers onto the mold surface. In contrast, fluorinated monomer is fixed in the surface region of cured film and does not transfer onto the mold surface. This suggests that fluorine monomer is favorable for maintaining a clean mold.

In order to understand release property, a model compound was synthesized by changing the acrylate group of the fluorinated monomer to a non-reactive end group. This was done because separation force is strongly dependent on the structure of the anti-sticking agent. Figure 5 shows the separation force curves of each of the resists. Addition of fluorinated monomer could reduce by only 10% the force required to separate from the resist compared to without anti-sticking agent. Addition of non-reactive anti-sticking agent, however, could reduce the separation force by 50%. This is as low as provided by the combination of fluorinated monomer in the resist and release agent on the mold (OPTOOL from DAIKIN). These results indicate that either transfer of anti-sticking agent onto the mold surface or release agent coating onto the mold surface is needed to achieve low separation force. It was found that the surface treatment is needed to use the fluorinated monomer.

Figure 5. Separation force curves for three types of NIL resists. 4 inch wafer and 6inch Qz blank mold were used. Separation speed was 0.1 mm/sec.

The mold surface after multiple imprints was analyzed to study contamination from resist using the step and repeat type imprint test system shown in Figure 2. No release agent was coated on the mold surface. Figure 6 shows the chemical composition of the mold surface measured by XPS after 220 imprints. Si and O from the substrate slightly decreased and C from contamination increased with imprint number. F from the fluorine anti-sticking agent in the resist was less than 1atm%. There were no remarkable changes in the composition of each resist. This suggests that mold contamination from non-reactive anti-sticking agent is not a factor in this case.

Figure 6. The change of the mold surface chemical composition after multiple imprint shots as analyzed by XPS. Qz blank mold without release agent was used.

In the next step, the combination of anti-sticking agent in the resist and release agent on the mold was examined. Figure 7 shows the change in mold surface chemical composition over 880 imprints using the

Figure 7. The change of the mold surface chemical composition after multiple imprint shots as analyzed by XPS. The OPTOOL coated Qz mold was used for the test. The SEM photograph shows the resist pattern at 1000 imprints.

In the next step, the combination of anti-sticking agent in the resist and release agent on the mold was examined. Figure 7 shows the change in mold surface chemical composition over 880 imprints using the
combination of resist with fluorinated monomer and OPTOOL coated mold. OPTOOL exhibited a clear and rapid decrease with repeated imprints and then disappeared after 200 shots. This is consistent with studies that report OPTOOL degradation. Yet, despite this degradation, successful transfer of the resist pattern continued even after 880 imprints. Resist contamination was not observed by optical microscope or SEM. Consequently, controlling degradation of the mold release agent can be expected to improve release property.

![Figure 8. Separation force curves for NIL resists. Non-coated Qz mold or the OPTOOL coated Qz mold was used for the tests. Separation speed was 0.1 mm/sec.](image)

Another approach using the resist with non-reactive anti-sticking agent was investigated. New resist was formulated with the non-reactive anti-sticking agent that was improved over the model compound used in Figure 5 and Figure 7. The anti-sticking agent has a weak interaction with the mold surface. Figure 8 shows the separation force and Figure 9 summarizes the change in mold surface chemical composition over 880 imprints. Both figures are for the combination with the OPTOOL coated mold. It was found that the new resist in combination with OPTOOL coated mold has drastically reduced separation force. This resulted in an F ratio on the mold that did not change even after 220 imprints. From the fact that the resist composition was similar to the resist used in Figure 6, this result indicates that OPTOOL degradation in repeated imprints is caused by a high release force and not by radical attack from the initiator. In addition, it is thought that, because the increase in C content was relatively small, the contamination from resist was controlled in this case. However, as imprinting continued up to 880 shots, the F ratio and C ratio decreased, the F ratio drastically so, suggesting that the release agent on the mold gradually decomposed with increasing number of imprints.

These results indicate that the resist design makes it possible to manage both reducing the separation force and maintaining a clear mold surface. Moreover, the combination of low separation force resist and mold release treatment can control the degradation of mold release agent. Further improvements to release property, i.e. a lower release force and chemical stability, will require resist improvement and a new mold release agent.

3.3. Drawback of resist anti-sticking agent and mold release agent

The improvement of release property by the addition of anti-sticking agent and the coating of release agent was discussed in the previous section. Both anti-sticking agent and release agent can make the surface energy lower at release interface. A lower surface energy gives a lower separation force theatrically as the equation (1). In addition, it gives the resist a low affinity for the adhesion layer or mold surface. Therefore drawback to resist spreading issues must be discussed when resist anti-sticking agent or mold release agent is used.
The resist contact angles on the adhesion layer coated silicon wafers were summarized in Figure 10. The upper results in Figure 10 are for the resist with fluorinated non-reactive anti-sticking agent and the lower results are for the resist with non-fluorinated anti-sticking agent. The resist with fluorinated anti-sticking agent showed higher contact angle on the wafers. The contact angle increased with increasing contents of anti-sticking agent. Resists with a lower affinity for the adhesion layer will give slower spreading time of resist. Slower spreading time causes higher non-filled defect density. Therefore, it is thought that there is an essential trade-off relationship between release property and throughput. A fluorinated non-reactive anti-sticking agent and fluorinated release agent must be chosen with great care to ensure that the best throughput and defectivity are achieved.

3.4. The improvement of release property by optimization of elastic modulus of resist

There is another approach to improve release property by optimization of elastic modulus of resist film. Given that reducing surface energy of release interface has a draw back to defectivity, the optimization of resist elastic modulus should be an important consideration. In order to study potential effect of the elastic modulus, several kinds of acrylate monomer were prepared. The elastic modulus of UV cured resist film was controlled by acrylate monomer structure and formulation. Two series of resist formulation were used in this test. The first series was with fluorinated non-reactive anti-sticking agent and the second series was without fluorinated non-reactive anti-sticking agent. The mold without release agent was used for this test.

Figure 11 shows the relationship between the elastic modulus of cured resist film and the measured release force for the two series of resist. It is again confirmed that addition of anti-sticking agent into resist is effective to reduce release force by comparing the two resist series. The test condition was the same as Figure 3. The elastic modulus was calculated as relative value to the typical formulation without release agent which was used in Figure 3. The closed circle in the graph represents that no pattern collapse was observed, and the open circle represents that pattern collapse was observed. The release force linearly decreased with decreasing elastic modulus of resist film. But lower elastic modulus gave negative impact on pattern fidelity. The resists with elastic modulus less than 0.72 showed pattern collapse. Therefore it is obvious that the separation force can also be controlled by resist elastic modulus without depending on the effect of anti-sticking agent. Optimization of elastic modulus is quite important for resist formulation.
4. Conclusion

The release interface of UV-NIL resists was investigated focusing on the surface energy and the elastic modulus of resist film. The resist with fluorine monomer and with non-reactive fluorine anti-sticking agent were compared. The results indicated that resist design has the capability to both reduce the separation force and maintain a clear mold surface. The mold release agent decomposed with increasing number of imprint shots, but the low release force resist with non-reactive anti-stacking agent was able to control the degradation of mold release agent and thus improve release property endurance. However the resist with fluorinated anti-sticking agent showed higher contact angle on the mold surface, an essential trade-off relationship between release property and throughput must be discussed in further studies. On the other hand, the investigation on the UV cured resists with various acrylate monomer structures and formulations gave the conclusion that the separation force can also be controlled by resist elastic modulus without depending on anti-sticking agent. These two approaches from resist materials should be considered in designing release interface of UV-NIL process.

References
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