Novel Fluorinated Compounds that Improve Durability of Antistick Layer for Quartz Mold

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In recent years, the reduction in pattern size is driving the rapid adoption of nanoimprint lithography (NIL). Since nanoimprinting is contact printing, high separation forces might damage the master and/or the imprint tool, either of which degrades pattern quality. One of the biggest concerns in NIL utilization is the mold-release characteristic of the master and the resin. Although Optool DSX (DAIKIN Ind. Ltd.) is a defacto standard as mold anti-sticking reagent, there is a problem with its UV-NIL durability. Accordingly, we focused on developing new fluorinated low molecular weight compounds to enhance the mold-release characteristic of the resist. This paper reports that resists containing these fluorinated compounds offer improved durability as anti-stick layers for quartz molds even under repeated UV-NIL exposure.

Keywords: Nanoimprint, Resist, Fluoropolymers, UV-NIL, Fluorine lyophobic resist, Fluoroalkyl acrylate copolymer, Contact angle, Release material, Perfluoropolyether

1. Introduction

The emergence of lithographic fabrication by nanoimprinting in 1995 [1] was followed by its rapid adoption due to its significant advantages. Examples are include non-reflection films for FPD to the improve brightness of LEDs. Nanoimprinting takes two forms: thermal-nanoimprinting and UV-nanoimprinting. The former needs high temperature and pressure and so is mainly used for glass processing of small areas. The latter, on the other hand, has a wide application range because it offers large areas and can form small pitch patterns easily; it has become the mainstream nanoimprint technology. The processing size has reached 2X nm - 1X nm and it is being considered to produce Bit-Map pattern HDD and NAND flash memory [2-5]. Various nanoimprint lithography (NIL) techniques have been presented for producing semiconductors. NIL generally uses quartz or Si wafers as the imprint master molds, and attention has recently been placed on dispensing the UV-curable resist material by ink-jet. This process uses a quartz master mold and iterated X-Y stage movement during printing. One advantage of this method is that it can reduce the residue layer by optimizing the quantity of the UV-curable material and conventional device technology can be used. As is also true for contact printing, high separation forces can damage the master mold and imprinting tool, leading to degradation in pattern quality. Particular problems are pilling defects and pattern clash defects. Fortunately, the separation force can be reduced by applying a release agent to the
master mold. Optool DSX (DAIKIN Ind. Ltd.) a well-known release agent for quartz master molds provides a perfluoropolyether (PFPE) chain and silane-coupling moiety [6]. However, to advance further we have to move beyond the idea that only the quartz master mold should be treated for better release. Because low viscosity is required for ink-jet deposition, resin-type nanoimprint UV-curable materials are being replaced by monomer-type equivalents. The latter has high hydrophobicity, so treating only the release properties of the quartz master mold is insufficient. Furthermore, PFPE is cleaved by the radicals formed by photon exposure. We have developed a method that turns just the surface of the resist lyophobic [7]. Our strategy is to enhance the release properties of both the quartz master mold and the surface of UV-curable material (resist) through the use of fluorne containing compounds and have been improving their performance [8-10]. In this paper, we report that release force can be decrease by adding fluorinated compounds to nanoimprint resist, furthermore, improvements in the durability of a PFPE antistick layer for quartz molds under repeated UV-NIL exposure.

2. Experiment
All materials were obtained from commercial suppliers and used without further purification, unless otherwise noted.

2.1. Synthesis method of fluorinated compounds
The synthesis procedures were carried out under nitrogen at 60~70 ºC in bulk. The fluorinated epoxides (1.0 mmol) were combined with polyethyleneglycol derivatives (1.0 mmol) at r.t. and dried at 60 ºC. BF3 ethereal (0.01 mmol) was added to the reaction mixture and maintained for 1hr. The compounds were used without further purification.

2.2. Characterization
The structures and compositions of the fluorinated compounds were determined from NMR spectra. Namely, 1H and 19F NMR spectra were obtained at room temperature in acetone-d6 or CDCl3 on a Bruker AC-300P FT-NMR spectrometer. These structures were also confirmed by FT-IR spectra as captured by a PERKIN ELEMER 1760X FT-IR spectrometer.

2.3. The measured of solubility fluorinated copolymer to resist monomer

The 1.0 mass% (vs. resist monomer) fluorinated compounds was added to resist monomer, and stirred for 1 to 12 hr. at room temperature. The authors determined that we dissolved when solution was transparent. Then it’s repeated this procedure to disappear the residue of fluorinated compound.

2.4. Resist materials
The base resist monomer was C-TGC-02 (TOYO GOUSEI CHEMICAL K. K.). 1.0~3.0 mass% (vs. resist monomer) fluorinated compound was added to the 10.0 mass% solution C-TGC-02 in Propylene glycol monomethyl ether acetate (PGMEA), and stirred for 1 hr. in the dark at room temperature. To this mixture was added 4.9 mass% Irgacure907 (BASF JAPAN Ltd.). The resist was spin-coated on 6 inch silicon wafers and baked at 80 ºC for 120 S.

2.5. Repeated UV-NIL procedure
The quartz mold was treated with Optool DSX as antistick layer. The antistick layer was deposited by the liquid-phase method as follows. The quartz was cleaned by oxygen reactive ion etching (RIE) and then exposed to UV-ozone for 60 min. It was submerged in the antisticking agent for 10 min. To settle the antisticking agent onto the mold surface, it was exposed under 100% relative humidity at 75 ºC for 1 h and rinsed with fluorne solvent, perfluorohexane or Optool HD-TH ( Daikin Industries Ltd.) in an ultrasonic bath for 5 min to wash away any extraneous antisticking agent. Water contact angles of the antistick agent on the mold surface were then determined. Step and repeat UV nanoimprinting, 6.5 mm pitch, was carried out on 6-in. silicon wafers and 15 imprint steps were made both in the lateral and longitudinal directions, so that 225 imprints were formed on each wafer. A certain amount of UV curable resist was deposited on the wafer and spin-coated at 3000 rpm for 30s. it was then prebaked at 80 ºC for 120 s to evaporate the solvent. Approximately 10 N of imprint pressure, which is equivalent to 0.3 MPa, was applied and held for 2-3 seconds in each imprint step. The mold was illuminated by UV light, 375 nm wavelength, from a UV LED lamp. The energy of the UV light at the imprint interface was approximately 1800 mJ.
3. Results and Discussion

3.1. Preparation results of fluorinated compounds and resist

The fluorinated compounds mainly consisted of perfluoroalkyl (Rf), C₆F₁₃ and C₄F₉ chain. The alkylene oxide chains are shown in Table 1. The fluorinated compounds are easily synthesized in bulk. Because the fluorinated compound did not cause micro phase separation, it was completely dissolve to resist monomer [9].

Table 1 The synthesis result of fluorinated compounds

| RUN   | Rf   | C₆F₁₃ | C₄F₉/C₆H₁₃ combination | C₄F₉ | X         |
|-------|------|-------|-------------------------|------|-----------|
| DSN-4030 | C₆F₁₃ | Mw=400 | -                        | -    | RF and OH |
| 1     | *    | Mw=200 | -                        | -    | RF and OH |
| 2     | *    | Mw=1000 | -                       | -    | RF and OH |
| 3     | C₄F₉ | Mw=200 | -                        | -    | RF and OH |
| 4     | *    | Mw=400 | -                        | -    | RF and OH |
| DSN-4034 | C₆F₁₃ | Mw=350 | -                        | -    | OCH₃      |
| 5     | *    | Mw=400 | -                        | -    | RF and OH |
| 6     | *    | Mw=1250 | -                       | -    | RF and OH |
| 7     | *    | Mw=350 | -                        | -    | OCH₃      |
| 8     | *    | -      | Mw=200                  | -    | RF and OH |
| 9     | *    | -      | Mw=400                  | -    | RF and OH |

(Rf=CH₂CHCH₂-O-(RO)n-X)OH

The solubility of the fluorinated compound in C-TGC-02 was shown in Table 2. Most of them dissolved to the level of 1.0~5.0 mass% in C-TGC-02.

Table 2 Solubility of Fluorinated compounds to C-TGC-02

| RUN    | Rf   | Solubility (mass %) | 1.0 | 3.0 | 5.0 |
|--------|------|---------------------|-----|-----|-----|
| DSN-4030 | C₆F₁₃ | ○                   | ○   | ○   | ○   |
| DSN-4034 | C₄F₉ | ○                   | ○   | ○   | ○   |

3.2. Impact of fluorinated compounds on release force

We choose DSN-4030 as the antisticking reagent, because of the result of our fundamental study about release force reduction effect [10]. The release force fell dramatically, when the DSN-4030 charge was raised from 1.0mass% (1pts) to 3.0mass% (3pts). These results are shown in Fig. 2. The fluorinated compound became segregated on the surface of the resist under room conditions due to the surface free energy. The fluoride content of DSN-4030 is low compared to other fluorinated polymers and fluorinated monomers [9]. 3.0 mass% is needed so that fluorine molecules can fully cover the resist surface.

Fig. 3 Relationship between the amount of DSN-4030 and the number of imprint steps

The antistick layer is indispensable when using quartz molds. As stated previously, Optool DSX is a de facto antistick material, but its durability is insufficient [7]. Our strategy is to improve the release performance of both the quartz master mold and the surface of the UV-curable resist (likely Topcoat-less resist) by the use of fluorine containing compounds. We are currently improving the repulsion force between the contacting surfaces. Our nanoimprint experiment
showed a significant improvement in durability of the antistick layer (Fig.3). Because, a blue line (added 3.0 mass% DSN -4030 vs C-TGC-02) is compared with a dotted line (no additive) as shown by Fig. 3, the fall of the water repellence on the surface of a quartz mold of a blue line is loose. Moreover, change of release force is not seen, either shown by Fig. 2. Since the surface of the resist is fully covered with the fluorinated compound, it is thought that it blocks the radicals generated by UV exposure from attacking the mold antistick layer.

4. Conclusion

We synthesized several novel fluorinated compounds, and measured their solubility in resist monomer C-TGC-02. All compounds showed high solubility. This fundamental study showed that adding a small quantity of the fluorinated compounds to the nanoimprint resist dramatically improves release performance. Furthermore, an experiment on repeated nanoimprinting confirmed the improved durability of the antisticking layer for the quartz mold.

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