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Tsuyoshi Ogawa
Daniel J. Hellebusch
Michael W. Lin
B. Michael Jacobsson
William Bell
C. Grant Willson

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Tsuyoshi Ogawa
University of Texas at Austin
Department of Chemistry
1 University Station A5300
Austin, Texas 78712
and
Central Glass Co. Ltd.
Chemical Research Center
2-17-5, Nakadai, Kawagoe
Saitama 350-1159, Japan
E-mail: tsuyoshi.ogawa@cgco.co.jp

Daniel J. Hellebusch
Michael W. Lin
B. Michael Jacobsson
William Bell
C. Grant Willson
University of Texas at Austin
Department of Chemistry and Chemical Engineering
1 University Station A5300
Austin, Texas 78712

Abstract. One of the major concerns with nanoimprint lithography is defectivity. One source of process-specific defects is associated with template separation failure. The addition of fluorinated surfactants to the imprint resist is an effective way to improve separation and template lifetime. This study focuses on the development of new reactive fluorinated additives, which function as surfactants and also have the ability to chemically modify the template surface during the imprint process and thereby sustain a low surface energy release layer on the template. Material screening indicated that the silazane functional group is well suited for this role. The new reactive surfactant, di-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silazane (F-silazane) was synthesized and tested for this purpose. The material has sufficient reactivity to functionalize the template surface and acceptable stability (and thus shelf-life) in the imprint formulation. Addition of F-silazane to a standard imprint resist formulation significantly improved template release performance and allowed for significantly longer continuous imprinting than the control formulation. A multiple-imprint study using an Imprio® 100 tool confirmed the effectiveness of this new additive. *© The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI.* [DOI: 10.1117/1.JMM.12.3.031114]

Subject terms: nanoimprint; step and flash imprint lithography; surfactant; silazane; ultraviolet.

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1 Introduction

Step and flash imprint lithography (S-FIL) has many advantages over traditional optical lithography in terms of procedural simplicity,[1,2] low cost,[3,4] and high-fidelity pattern transfer[5–7] as well as the ability to directly pattern multilevel structures.[8–10] However, effective use of S-FIL requires management of the template separation process (Fig. 1).

The materials and the interfaces must be engineered so that the cured resist material separates from the imprint template while maintaining tenacious adhesion to the underlying substrate. Adhesive failure at the substrate interface is obviously unacceptable. Cohesive failure of the cured polymer can also occur, which results in significant patterning defects. Both adhesive and cohesive failure must be controlled. The common method for minimizing such defects involves the use of surface treatments as shown in Fig. 2. An adhesion promoter is applied to the substrate prior to dispensing the imprint fluid. A variety of adhesion promoters has been developed to aid in adhesion of resist to oxide and other surfaces commonly encountered in microelectronic device manufacturing. The template is typically treated with a release layer such as fluorinated self assembly monolayer (F-SAM).

The classical adhesion promoter layers work effectively in most cases as each area of the substrate is only imprinted once during the patterning process. Considerably, more is required of the release layer as the template must perform numerous imprints without interruption. Covalent surface treatments such as perfluoroalkylchlorosilanes[11,12] slowly degrade during imprinting, leading to separation failure (Fig. 3). Several mechanisms for this degradation have been proposed, but a definitive mechanism is not currently agreed upon.[13–16]

Addition of surfactant to the imprint formulation is one method to limit separation failure. We recently reported the behavior of the fluorinated surfactant shown in Fig. 4.[17] X-ray photoelectron spectroscopy (XPS) studies indicated that the surfactant migrates to the interface of the imprint fluid and template, presumably because of the low surface energy of the F-SAM treated template and similar polarity. This reduces adhesion to the template,[17] thereby reducing the likelihood of cohesive failure.

With an intact monolayer, migration continues over multiple imprints. However, if the surface treatment degrades, the template becomes sufficiently hydrophilic to disrupt this surfactant migration process and defects begin to occur. As such, the use of a conventional surfactant does not represent a permanent solution to separation failure. In this study, a reactive fluorinated surfactant was added to the imprint formulation. The material was designed to serve both as a surfactant and reagent that functionalizes any silanol sites that are created during imprinting.[18]

2 Self-Replenishing Release Layer

Templates were initially treated with F-SAM to form the nominal release layer as shown in Fig. 5. Additionally, a small amount of reactive surfactant was added to the imprint fluid. During the imprint process, this material is believed to react with exposed areas of the template surface, replenishing the fluorinated monolayer. This allows for continuous

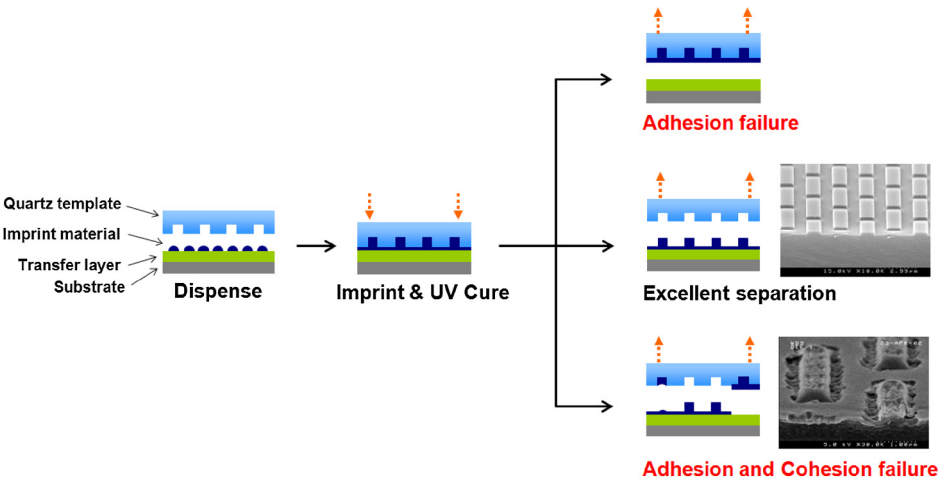


Fig. 1 Three possible outcomes of template separation.

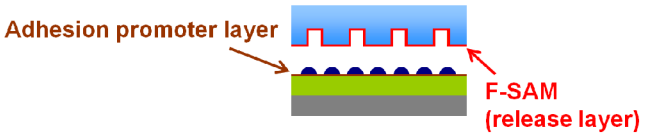


Fig. 2 Current method to improve separation.

imprinting as the requisite hydrophobicity is maintained without periodic cleaning and treatment of the template.

There are three requirements that the surfactant must meet in order to be effective. First, it must readily associate or react with the hydrophilic template surface. Second, it must be unreactive toward other components of the imprint formulation. Third, the structure must produce a surface energy similar to that generated by F-SAM treatment.

3 Material Screening

Several functional groups were auditioned to find a suitable reagent. Figure 6 lists the five candidates: a chlorosilane (Gelest Inc., Morrisville, PA) that is commonly used to form the F-SAM template release layer, N,N-dimethylaminopentamethyldisilane (DMAS) obtained from Gelest Inc., Morrisville, PA, hexamethyldisilazane (HMDS) (Acros Organics, Geel, Belgium), a reagent commonly used to treat surfaces in the semiconductor industry, and alkyl iodides IO and F-IO, which were obtained from Aldrich, St. Louis, MO.

3.1 *Effect on Surface Energy*

The effect on template surface energy was investigated as illustrated in Fig. 7. Glass plates were cut into 1×1 in. squares and cleaned with piranha (H_2SO_4: 30% H_2O_2 = 2:1) for 30 min, which generated a hydrophilic surface. The plates were immersed in 20 wt. % toluene solutions of the respective surfactants for 100 min. After rinsing the plates with toluene and isopropyl alcohol, the water contact angles were measured by goniometry (ramé-hart NRL model 100-00, ramé-hart Inc., USA). Measurements were taken at five different points on the plates and averaged.

The results are listed in Fig. 8. The control sample was only exposed to piranha solution. Without additional treatment, the surface was extremely hydrophilic, with a water contact angle of 11.2 deg. F-SAM gave the highest contact angle (106.7 deg). Both materials having Si-N bonds (DMAS and HMDS) showed high values (93.1 and 91.2 deg, respectively), whereas the alkyl iodides (IO and F-IO) generated much lower values (57.9 and 49.0 deg). F-SAM, DMAS, and HMDS appear to meet the surface energy criteria.

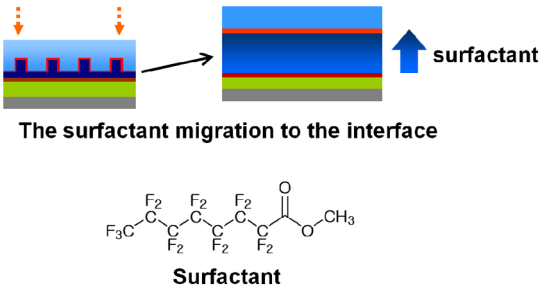


Fig. 4 Addition of surfactant reduces separation defects.

3.2 *Stability in Resist Formulation*

The shelf life of formulations containing the candidate materials was evaluated by gas chromatography-mass spectrometry

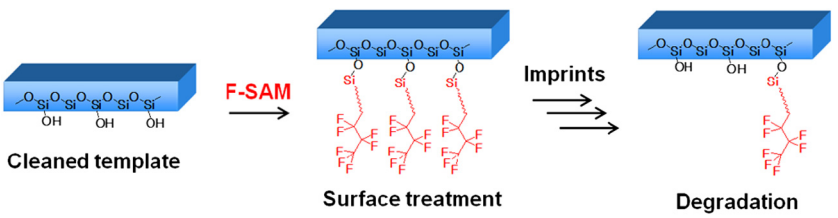


Fig. 3 Fluorinated self assembly monolayer (F-SAM) treatment and degradation during continuous imprinting.

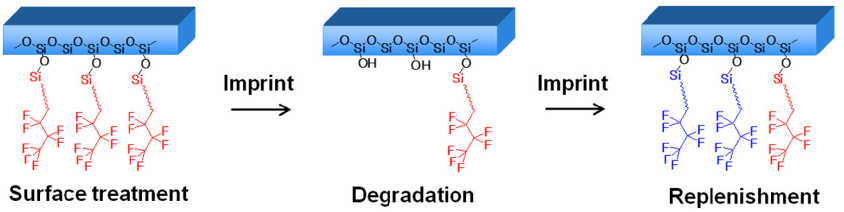


Fig. 5 Replenishing the release layer.

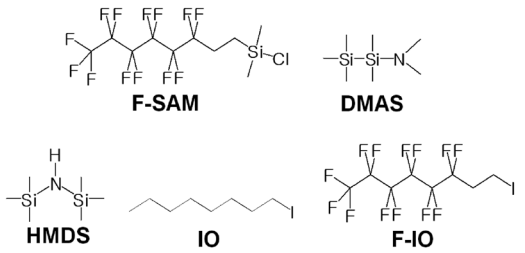


Fig. 6 Materials used in initial screening.

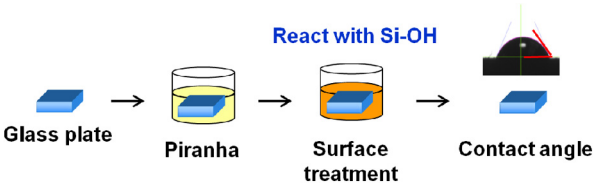


Fig. 7 Procedure for surface energy experiments.

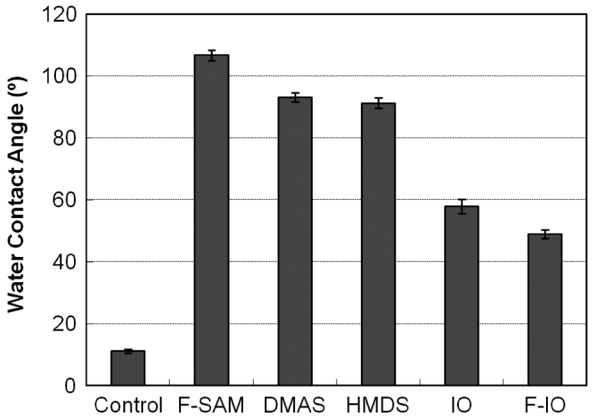


Fig. 8 Effect on surface energy.

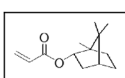
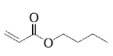
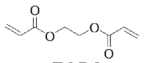
 IBA	 nBA	 EGDA	F-SAM, DMAS or HMDS
33 %	33 %	17 %	17 %

Fig. 9 Formulations for stability experiments.

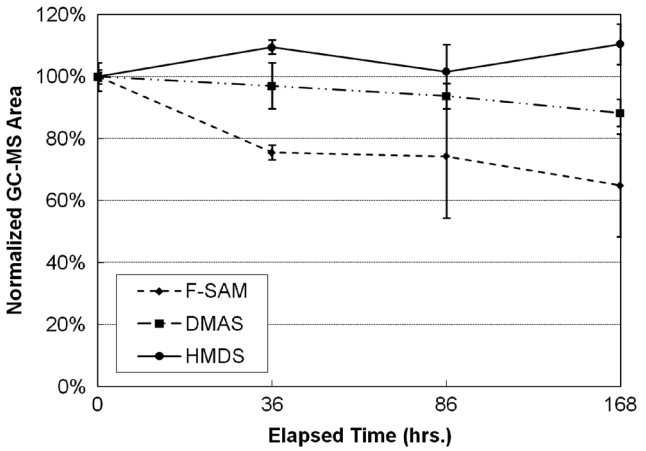


Fig. 10 Stability in imprint formulation.

(GC-MS), Agilent Technologies 6890 N equipped with an Agilent HP-5MS capillary column. Formulations consisting of 33 wt. % of isobornyl acrylate, 33 wt. % *n*-butyl acrylate, 17 wt. % of ethylene glycol diacrylate and 17 wt. % of one of the three additives (F-SAM, DMAS, or HMDS) were tested as a function of time. Aliquots were taken for 38, 86 and 168 h after addition of the additives and their concentrations were compared to those of the initial formulations (Fig. 9). Xylene was used as an internal standard in the gas chromatographic analysis.

The chlorosilane degraded rapidly, falling to 65% after 168 h. The solution also became turbid upon addition of F-SAM, even though the sample was prepared under nitrogen. The GC-MS data for the DMAS and HMDS formulations suggest considerably greater stability than the F-SAM (Fig. 10). Both solutions remained clear and colorless after 168 h. Based on these results, it was concluded that materials such as DMAS and HMDS show potential for use as reactive surfactants.

4 Fluorinated Silazane as a Reactive Surfactant

F-silazane (Fig. 11) was donated by Central Glass Co. Ltd., Japan. F-silazane is a colorless liquid that readily mixes with imprint formulations. The material is a reactive surfactant.

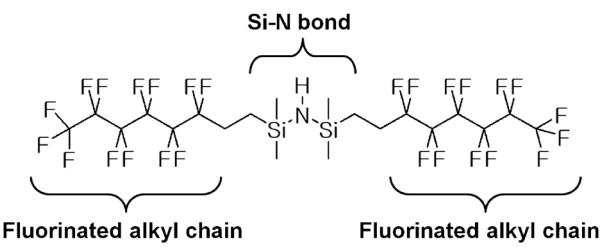


Fig. 11 Chemical structure of F-silazane.

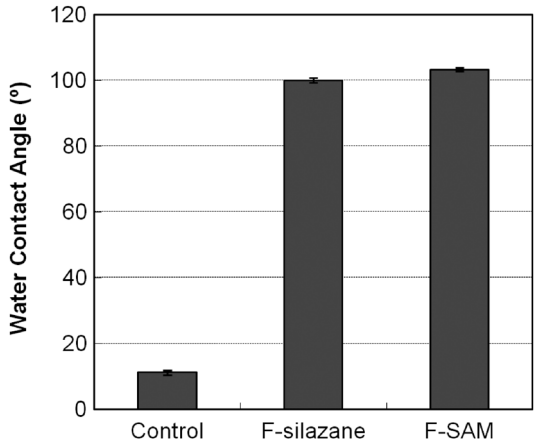


Fig. 12 Effect on surface energy of F-silazane.

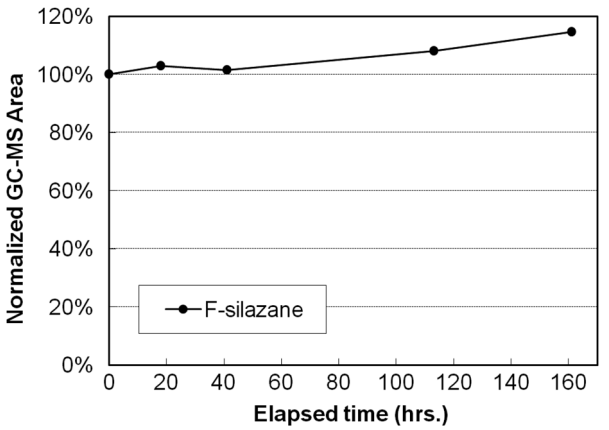


Fig. 13 Stability of F-silazane in imprint formulation.

4.1 *Evaluation of F-Silazane*

F-silazane was tested in the same manner as previous materials. The water contact angle was 100 deg, a value comparable to F-SAM (Fig. 12). No degradation was apparent by GC-MS, and the sample solution remained clear (Fig. 13).

4.2 *Multiple Imprint Study with F-Silazane*

A multiple imprint study was carried out to evaluate the performance of F-silazane as a reactive surfactant. Imprinting was performed with an Imprio 100® installed at The University of Texas at Austin using unpatterned templates (25×25 mm^2 mesa). The substrates were 8 in. silicon wafers coated with BT20 adhesion promoter (Brewer Science, Rolla, MO). The templates were cleaned and treated with F-SAM to form the initial release layer prior to imprinting. Each wafer was imprinted ~16 times and then the water contact angle was measured at five different points on the template surface and the values were averaged. A new substrate was prepared and imprinting was then resumed without cleaning the template. This was repeated for a total of 100 imprints. Table 1 shows the two formulations used in this study. One is a common imprint fluid, whereas the other contains 5 wt. % F-silazane.

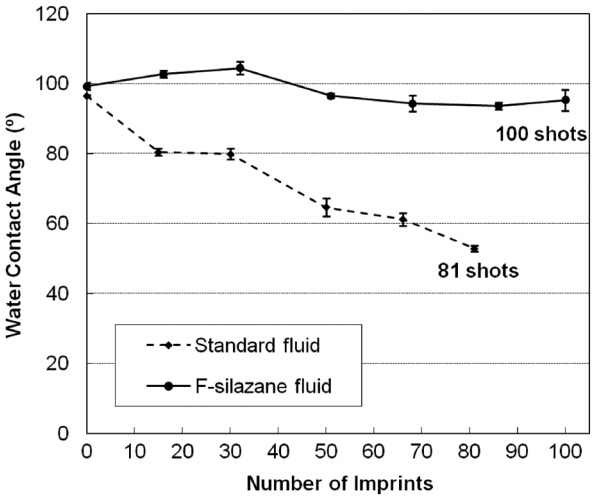


Fig. 14 Results of the multiple imprint study.

As shown in Fig. 14, imprinting with the conventional formulation leads to rapid degradation of the surface treatment; the water contact angle decreased significantly after patterning a single substrate. Due to severity of the defects, imprinting with this formulation was discontinued after 81 imprints. When the formulation that included the F-silazane, the template surface energy remained essentially constant even after 100 imprints. No separation failure was observed.

These results suggest that F-silazane allows for longer template life. Further analysis of the template surface and cured imprint material is necessary to better understand the release mechanism. XPS or electron spectroscopy for chemical analysis is two different methods that can be used to study the migration of a surface treatment. In the multiple imprint study, a nonpatterned template was selected to measure the water contact angle on the template after a set number of imprints. An imprint study using a patterned template also needs to be carried out. Thousands of imprints are necessary to fully investigate the effectiveness of F-silazane for industrial applications.

5 Conclusion

This study focused on the development of reactive fluorinated surfactants for use in imprint lithography. Initial experiments suggest that materials such as silylamines and silazanes are sufficiently reactive toward the template surface

Table 1 Formulations used in the multiple imprint study.

	Isobornyl acrylate (IBA)	Ethylene glycol diacrylate (EGDA)	*n*-butyl acrylate (nBA)	Darocure 1173	F-silazane
Standard fluid	38.2%	19.8%	38.0%	4.0%	0.0%
F-silazane fluid	35.4%	19.8%	35.4%	4.0%	5.4%

to replenish the degraded monolayer, yet stable in the imprint formulation. One of the materials tested, a perfluoroalkyl silazane (F-silazane) showed an effective combination of reactivity and stability. Multiple imprints were carried out with F-silazane on a commercial imprint tool (Imprio® 100). When the imprint fluid contained F-silazane, it was imprinted 100 times without any significant defects, whereas the conventional formulation began to suffer from increasing surface energy and ultimately suffered separation failure after 81 imprints. We conclude that F-silazane shows great potential for the use as a reactive surfactant in imprint lithography that could reduce defects and extend template life. Further study of this material is clearly warranted.

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Biographies and photographs of authors are not available.