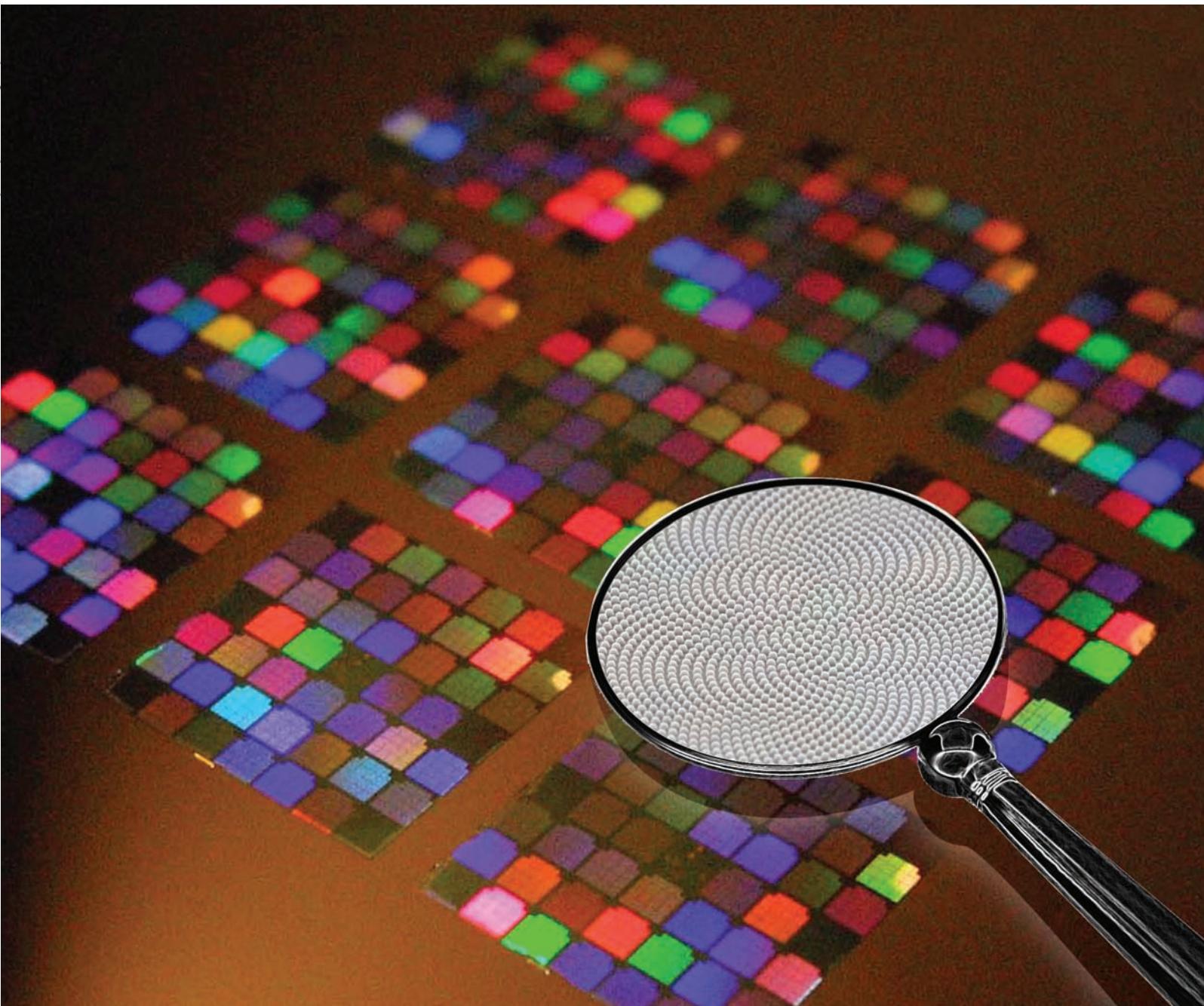


# Journal of Materials Chemistry

www.rsc.org/materials

Volume 17 | Number 34 | 14 September 2007 | Pages 3565-3656



ISSN 0959-9428

**APPLICATION**  
C. Grant Willson *et al.*  
Materials for step and flash imprint  
lithography (S-FIL<sup>®</sup>)

**COMMUNICATION**  
Wen-Kuang Hsu *et al.*  
Gas sensing improvement of  
carbon nanotubes by  $\text{NH}_4\text{OH}$ -flash  
treatment: a nondestructive  
purification technique



0959-9428(2007)17:34;1-X

RSC Publishing

# Materials for step and flash imprint lithography (S-FIL<sup>®</sup>)

Brian K. Long, B. Keith Keitz and C. Grant Willson\*

Received 10th April 2007, Accepted 31st May 2007

First published as an Advance Article on the web 15th June 2007

DOI: 10.1039/b705388f

Step and flash imprint lithography, or S-FIL<sup>®</sup>, was introduced in 1999 by The University of Texas at Austin (*Proc. SPIE-Int. Soc. Opt. Eng.*, 1999, **3676**, 379), and has progressed from an academic curiosity to commercialization in less than five years (*J. Microlithogr., Microfabr., Microsyst.*, 2005, **4**, 1). It has proven to be a cost effective, high resolution alternative to traditional optical lithography and has been placed on The International Technology Roadmap for Semiconductors (ITRS) as a potential candidate for 32 nm device fabrication ([http://www.itrs.net/Links/2006Update/FinalToPost/08\\_Lithography2006Update.pdf](http://www.itrs.net/Links/2006Update/FinalToPost/08_Lithography2006Update.pdf)). This article summarizes the efforts made towards the development of imprint materials for S-FIL and the obstacles that have yet to be overcome.

## Introduction

The lithographic industry is driven to produce ever smaller, faster, and cheaper microelectronic devices. As feature size steadily decreases, drastic changes in materials and tools are periodically necessary to meet consumer needs and standards outlined by the ITRS. Industry has pushed photolithography to exposure at 193 nm (immersion), 157 nm, and extreme ultra-violet (13.5 nm) wavelengths of light in attempts to meet these requirements. Each change, however, is accompanied by ever increasing costs associated with tool replacement and materials development. This economic stress has resulted in the exploration of disruptive lithographic techniques that might provide high resolution imaging at significantly lower cost.

Nanoimprint lithography (NIL) has emerged as a viable alternative to traditional optical lithography.<sup>1</sup> Thermal nanoimprint lithography, first described by Chou *et al.*,<sup>2</sup> uses a patterned template and high pressures to transfer an image into a heated thermoplastic material. This process, sometimes referred to as “hot embossing,” has shown impressive

resolution down to 5 nm.<sup>3–5</sup> Although this demonstration of resolution is attractive and the process is valuable for making some nanostructures, thermal imprint is not favorable for multi-layer device fabrication due to the repeated heating and cooling cycles associated with this process. This cycling of temperature can lead to decreased throughput and improper overlay of device layers and features due to differences in resist, substrate, and template coefficients of thermal expansion.<sup>6</sup>

To circumvent these disadvantages, step and flash imprint lithography, or S-FIL<sup>®</sup>, was introduced in the late 1990's as a room temperature, low pressure process applicable to multi-level device fabrication.<sup>7</sup> S-FIL uses a low viscosity prepolymer (monomer) solution that is dispensed onto a substrate and imprinted using a quartz template. Once the template features have filled with monomer solution *via* capillary action, the sample is irradiated to initiate photopolymerization of the monomer solution. After irradiation, the template is separated from the substrate, leaving behind an exact inverse replica of the template pattern (Fig. 1). The samples are irradiated with an inexpensive mercury-arc lamp through simple optics, making this a cost effective alternative to optical lithography.

Department of Chemistry, University of Texas, Austin, TX, 78712, USA. E-mail: willson@che.utexas.edu; Fax: +1 512-471-7222; Tel: +1 512-471-3975



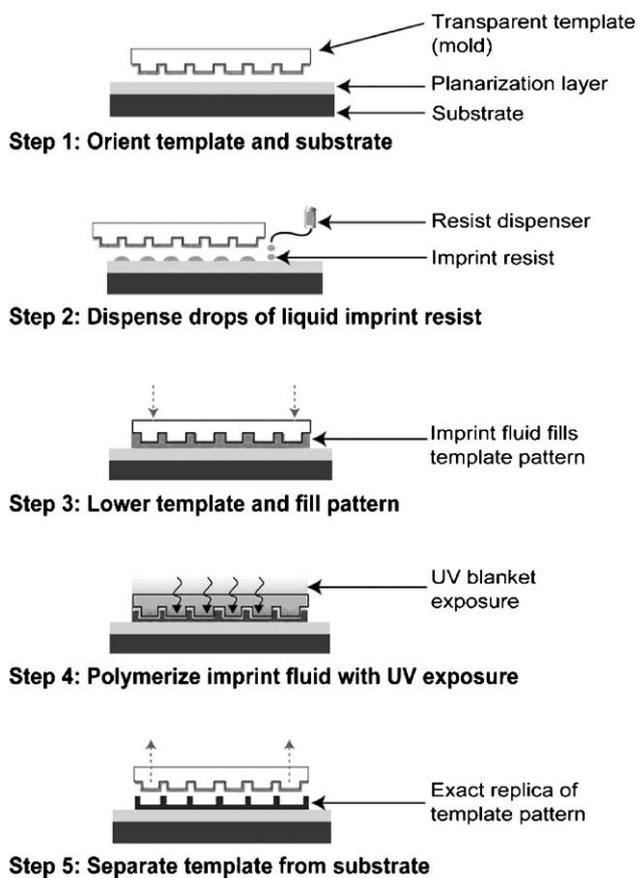
Brian K. Long

Brian K. Long earned his B.S. in chemistry from North Georgia College and State University (2003). Brian enrolled in the graduate program at the University of Texas at Austin in 2004 and is currently a graduate student in the labs of Professor C. Grant Willson. He is working towards the design and synthesis of new functional materials for microelectronics and new organic materials for non-linear optical applications.



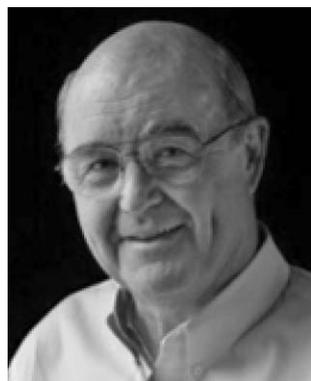
B. Keith Keitz

B. Keith Keitz is a senior undergraduate student working in the Willson research laboratory. He has worked in the group for 2 years and has participated in various research projects in both chemistry and chemical engineering. His research interests include thermally reversible cross-linked polymers and non-linear optical materials. Keith plans to graduate in May 2007 with a B.S. in chemical engineering.



**Fig. 1** Overview of the SFIL process. Reproduced with the permission of SPIE.<sup>6</sup>

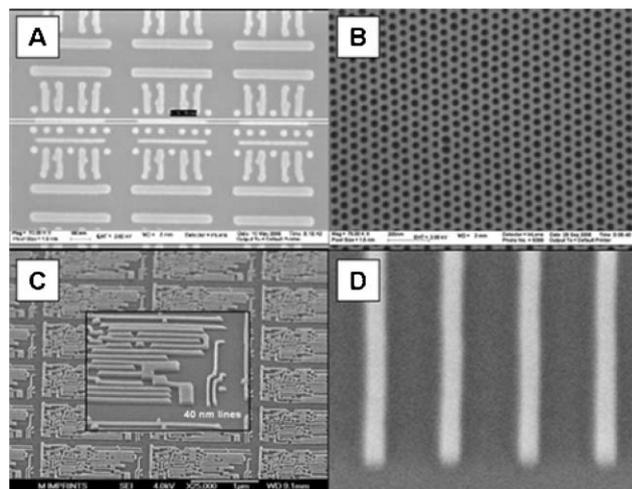
While traditional optical lithography has struggled to reliably produce sub 45 nm features, S-FIL has repeatedly shown resolution capabilities of 20 nm and below.<sup>6</sup> S-FIL's versatility and remarkable resolution potential were highlighted further when Rogers *et al.* used a variation of S-FIL to successfully imprint a mold of a single-walled carbon nanotube into a polyurethane prepolymer solution producing 2.4 nm



**C. Grant Willson**

*the Rashid Engineering Regents Chair. His research can be characterized as the design and synthesis of functional organic materials with emphasis on materials for microelectronics.*

*C. Grant Willson received his B.S. and Ph.D. in organic chemistry from the University of California at Berkeley and an M.S. degree in organic chemistry from San Diego State University. He came to The University of Texas from his position as an IBM Fellow and Manager of the Polymer Science and Technology area at the IBM Almaden Research Center. He is jointly appointed to the Departments of Chemistry and Chemical Engineering, where he holds*



**Fig. 2** Images produced using SFIL: a) 22 nm logic before etch, b) staggered 25 nm contact *via* holes with aspect ratio of approximately 3, c) 40 nm logic before etch, and d) 20 nm lines with aspect ratio of 2.5 and residual layer etched. Aspect ratios are height–width. All images courtesy of Molecular Imprints Inc.

wide features.<sup>8</sup> Such demonstrations of high resolution have only helped to cement NIL's incorporation into the ITRS roadmap as a potential candidate for the production 32 nm device features.<sup>9</sup> Examples of high resolution imprints with various architectures are shown in Fig. 2. The following sections will give an overview of the types of S-FIL materials being investigated to produce such features while maximizing throughput and minimizing cost.

## Materials for S-FIL

An imprint resist is typically a mixture of various polymerizable components, each adding desired characteristics to the final polymeric material. There are four main components to any S-FIL resist. The first is a bulk polymerizable monomer, which constitutes a large portion of the repeat units (30–50%) in each of the polymer chains. The second is a silicon- or siloxane-containing monomer, which provides the oxygen-etch resistance needed to transfer the pattern onto the underlying substrate. The third is a difunctional cross-linker, which is used to provide mechanical strength, and finally a photoinitiator is required to initiate polymerization.<sup>10</sup>

Several factors must be considered when selecting components for an imprintable S-FIL resist material. First, the prepolymer formulation must have low enough viscosity to be dispensed by an automated dispense system and its composition must not change significantly due to evaporation. Second, it must photopolymerize rapidly to maintain high throughput, and shrinkage due to polymerization must be minimal. Third, it must adhere to the substrate, be able to release from the imprint template, and still have sufficient mechanical properties and integrity to avoid feature collapse. Finally, it must be thermally stable to common temperatures associated with reactive ion etching, and must possess the high etch selectivity required to produce high aspect-ratio device features.<sup>11</sup> The following paragraphs will describe the two predominant S-FIL

formulations, which have been found to meet the above requirements.

### Acrylate formulations

Acrylates are the most widely studied monomers for S-FIL.<sup>1,6,7,11–13</sup> They provide a low viscosity prepolymer solution that can easily be dispensed while maintaining low volatility. They cure quickly upon photoinitiated radical polymerization, and a variety of silicon-containing monomers are readily available from various commercial sources avoiding time-consuming and ultimately expensive syntheses. An example of a widely used S-FIL formulation is given in Fig. 3. The bulk polymerizable monomer of the formulation is *t*-butyl acrylate (37.5%), while the remainder is composed of Darocur 1173 (product of Ciba Geigy) for photoinitiation, a siloxane monomer for etch resistance, and ethylene glycol diacrylate, which provides cross-links for mechanical strength and feature integrity.

Despite the many advantages of acrylates, there are several limitations inherent to radical-based photopolymerizations. The primary limitation is inhibition due to the presence of molecular oxygen in the imprint formulation and the surrounding atmosphere. Oxygen readily forms stable peroxy radicals during radical polymerizations,<sup>14</sup> which cause an induction period at the onset of irradiation and often produce a band of unpolymerized material at the periphery of the template.<sup>12,13</sup> This requires extended exposure times and ultimately decreases wafer throughput.

### Vinyl ether formulations

Vinyl ethers, which polymerize *via* a cationic pathway, are an attractive alternative to acrylates.<sup>15–17</sup> Cationic polymerization is accomplished by the incorporation of a photoacid generator (PAG) in place of the photo-induced radical initiators found in typical acrylate formulations. The omission of a radical mechanism avoids inhibition of polymerization due to atmospheric oxygen and hence, polymerization takes place with little to no induction period. Another advantage of vinyl ethers is that they are generally of lower viscosity (approximately 1 cP) than acrylate-based systems (commonly used acrylates are 3–4 cPs), facilitating dispense and spreading processes while maintaining adequate material properties.<sup>10</sup>

Although vinyl ethers offer certain advantages over acrylate formulations, they are not without limitations. In general, vinyl ethers have higher vapor pressures than acrylates, which can result in a change of prepolymer composition and

ultimately affect resist performance and stability. They also produce a separation force approximately twice that of acrylates, which can lead to template fouling, this will be discussed in detail later.<sup>10</sup> Finally, the limited selection of commercially available monomers, cross-linkers, and silicon-containing monomers has handicapped the incorporation of vinyl ethers into standard S-FIL resists.

### Functional materials for S-FIL and S-FIL/R

Many of today's microprocessors contain multiple ( $\geq 8$ ) levels of wiring that are interconnected through vias between wiring levels. To avoid certain limitations associated with the lack of effective plasma-etch processes for copper, researchers have instituted the use of a dual-layer patterning process referred to as "Dual Damascene." This process, when performed using traditional optical lithography, can take as many as 20 steps per wiring layer. S-FIL has been shown to reduce that number by more than half through the use of multi-tiered templates, which are imprinted just as described in Fig. 1, producing a via and wiring level in a single step.<sup>18</sup> A further improvement can be made if the imprinted material is a functional dielectric. These dielectric materials have to meet 5 key requirements to be implemented in the S-FIL process: they must 1) be thermally stable to 400 °C, 2) be liquids at room temperature, 3) be photocurable, 4) have a low dielectric constant, and 5) embody sufficient mechanical properties after curing to maintain feature stability.<sup>18,19</sup>

A material that is being extensively studied for "Dual Damascene" is based on functionalized polyhedral oligomeric silsesquioxanes (POSS) (Fig. 4). These materials have been used for dielectric materials in other semiconductor-manufacturing processes,<sup>20,21</sup> and provide an attractive basis for S-FIL as well.<sup>22</sup> It was determined that a mixture of functionalities is integral to achieving sufficient mechanical and thermal properties. This POSS material typically incorporates three methacrylate functionalities and five pendant benzocyclobutane (BCB) groups. The methacrylate groups efficiently cure *via* free-radical polymerization to provide initial feature integrity, while the BCB groups are cured through a thermal process, further improving mechanical properties and thermal stability with minimal shrinkage due to polymerization. The material has a dielectric constant of 2.89, which meets the requirement for upper level wiring ( $<3$ ) and has a Young's modulus of 1.8 Gpa, which is appropriate for S-FIL.<sup>19</sup>

These POSS materials, just as with typical acrylate and vinyl ether formulations, have a drawback concerning their high silicon content. If the material becomes imbedded within the

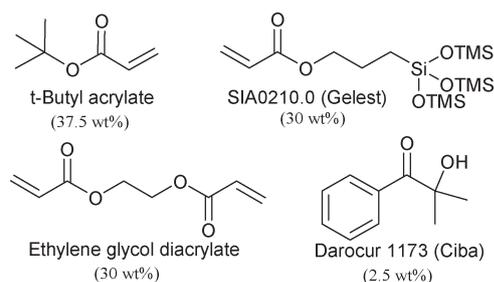


Fig. 3 Example of standard imprint resist formulation.

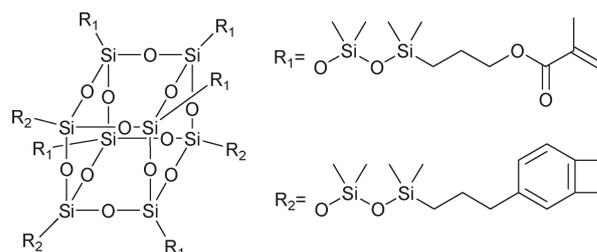


Fig. 4 POSS structure.

template features, the material can become difficult if not impossible to clean or remove without template degradation. Approaches that may help circumvent this template fouling will be discussed in the following sections.

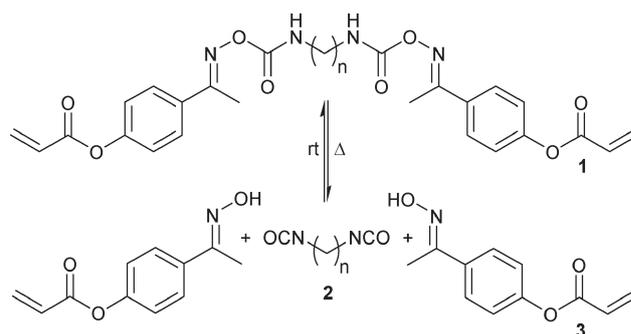
### Reversible materials to prevent template fouling

Template fouling is one of the more significant challenges facing S-FIL. Fouling occurs when portions of the polymerized, silicon-containing resist adhere and/or become lodged within the features of the imprint template. S-FIL requires that the template be a 1 : 1 scale, inverse mold of the features to be patterned due to its direct imprinting nature. Small feature sizes along with high silicon content and a large degree of cross-linking make any residual imprint polymer left on the mold almost impossible to remove from the template without damaging the expensive quartz template. The high cross-linker loading is needed to provide mechanical properties for the desired high aspect ratio features, but results in a material that is insoluble in any aqueous or organic solvent. Similarly, high silicon content is needed for etch resistance, but gives the material a quartz-like property when exposed to typical oxygen plasma cleaning processes, making removal of this material from a quartz template virtually impossible.

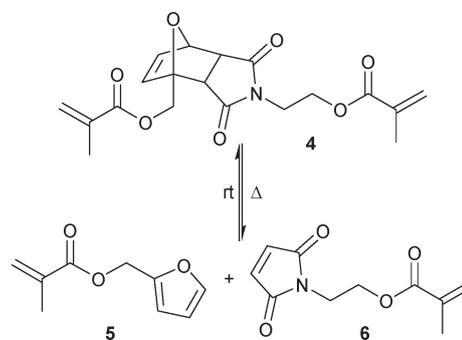
A number of solutions have captured the interest of researchers including the use of fluorinated self-assembled monolayers (FSAMs) as template-release layers, and the inclusion of reversible or degradable cross-linkers in place of ethylene glycol diacrylate or its divinyl ether analogue. Although surface treatments such as FSAMs are attractive solutions, preliminary research has shown that currently available surface treatments cannot exclusively prevent template fouling. Therefore, many researchers have chosen to focus their efforts toward the possible use of degradable and reversible cross-linkers instead. Theory suggests that the highly cross-linked, insoluble resist may become soluble in common organic solvents if the cross-links were to be broken, resulting in lower molecular weight linear polymer.<sup>23</sup> Thermally reversible cross-linking materials and acid labile cross-linking materials provide two attractive routes through which this theory could be tested.

#### Thermally reversible cross-linked resists

The first class of thermally reversible cross-linkers studied is based upon the reversible linkage referred to as a blocked isocyanate<sup>24</sup> (Scheme 1). Cross-linker **1** is readily synthesized by the formation of aromatic oximes, which are further reacted with diisocyanates. This diol structure can then be functionalized with pendant acrylates, methacrylates, or vinyl ethers completing the cross-linking structure. Compound **1** was found to revert back to its constituent oximes and diisocyanate at temperatures greater than 100 °C, making it a likely candidate for incorporation into S-FIL formulations. The reversible nature of this linkage was confirmed by solid state IR spectroscopic analysis and solution-state NMR spectroscopy. Unfortunately difficulties were encountered due to the low solubility of **1** in standard S-FIL formulations that prevented further studies.<sup>25</sup>



Scheme 1 Blocked isocyanate cross-linker reversibility.

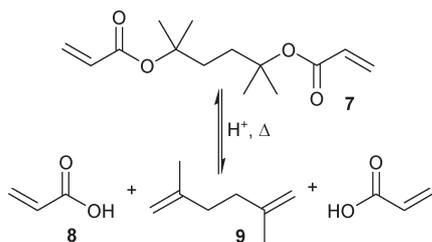


Scheme 2 Diels-Alder cross-linker reversibility.

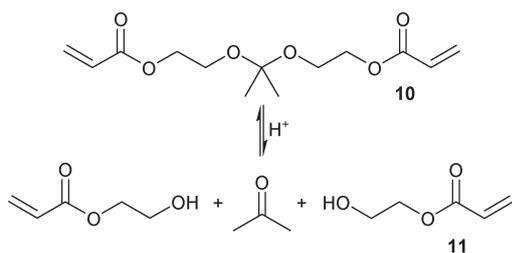
A second class of thermally reversible cross-linkers is based on the reversible linkage formed from the Diels-Alder reaction between substituted furans and maleimides. This reversible linkage was popularized by Wudl *et al.*<sup>26,27</sup> and has been extensively studied.<sup>28–32</sup> The reversible cross-linker **4** (Scheme 2) was synthesized *via* a Diels-Alder reaction between furfuryl alcohol and a hydroxyethyl-functionalized maleimide, which was then further functionalized with pendant acrylates or methacrylates providing the cross-linking structure. Model studies show that the cycloreversion of these Diels-Alder adducts occurs at temperatures above 80 °C in solution, making them excellent candidates for S-FIL. The Diels-Alder adduct **4** was easily incorporated into S-FIL formulations and provided adequate mechanical properties for feature integrity. Solid state <sup>13</sup>C-NMR data of poly(methyl methacrylate) cross-linked with compound **4** showed conclusively that upon heating, cycloreversion occurs. Despite this evidence, the polymer films could never be removed from silica substrates through immersion into hot organic solvents such as DMSO, NMP, toluene, DMF, *etc.* Research continues within our group to understand this surprising observation.

#### Acid-labile cross-linked resists

The first class of acid-labile cross-linkers studied was *t*-butyl ester cross-linkers that have been reported for various other applications.<sup>33–35</sup> Cross-linker **7** (Scheme 3) is known to readily decompose, upon addition of acid and mild heat, to products **8** and **9**. This allows the system to be decross-linked, rendering the remaining linear polymer soluble in the warm, acidic, organic media. Cross-linker **7** is readily soluble in common acrylate formulations and provides mechanical



**Scheme 3** *t*-Butyl ester cross-linker reversibility.



**Scheme 4** Ketal cross-linker reversibility.

properties suitable for the S-FIL process. Imprints containing compound **7** have been successfully stripped from their respective substrates upon introduction into warm acidic organic solvent demonstrating the utility of these reversible compounds. This demonstration gives promise that these *t*-butyl esters may be successfully incorporated into commercial prepolymer resists in the future.<sup>25</sup>

A second class of cross-linkers derived from acetal and/or ketal linkages have been investigated. Acetals and ketals are known to readily hydrolyze to their corresponding ketone and hydroxyl compounds upon treatment with wet, acidic, organic solvent.<sup>36–40</sup> Compound **10** was synthesized, and has been successfully incorporated into S-FIL formulations and imprinted. The imprints were successfully decross-linked (Scheme 4) and dissolved away after introduction into room-temperature, acidic organic media. One drawback of these ketal-type materials is they require a higher concentration in the prepolymer solution to obtain satisfactory mechanical properties,<sup>25</sup> but they do not require heat to reverse the linkages.

## Conclusions

Many challenges remain before S-FIL will be fully ready for commercialization. One problem is the need for an improved release layer for imprint-template coatings. The improvement of this release-layer chemistry may avoid many of the problems associated with template fouling and higher separation forces encountered when using previously mentioned vinyl ether formulations. There is also an urgent need to develop new dielectric and sacrificial imprint materials<sup>41</sup> (SIM) that may be patterned *via* imprint lithography. The development of these materials, specifically for the “Dual Damascene” process, may aid the acceptance and implementation of S-FIL as an effective alternative lithography.

A relatively unexplored area of S-FIL is the use of “fugitive” materials. These are materials that may be patterned *via*

imprint and remain as part of the device until all metal layers have been deposited. Once all levels of metal deposition are complete, the “fugitive” material is removed to leave free-standing metal structures separated by air. These so called air bridges take advantage of the extremely low dielectric constant of air, thereby providing further advances in the miniaturization of microelectronic device features.

From the time of its inception at The University of Texas at Austin in the late 1990's, step and flash imprint lithography has come from a demonstration of resolution, to having been placed on the ITRS Roadmap as a viable alternative lithography.<sup>9</sup> S-FIL has shown that it provides a low cost alternative to traditional optical lithography, with overlay and resolution capabilities that meet or exceed those required for 32 nm device fabrication and beyond.

## Acknowledgements

We gratefully acknowledge the National Science Foundation, Intel, Molecular Imprints Inc., and the National Institute of Standards and Technology Advanced Technology Program for financial support of this work. The authors would also like to thank Dr Gerard Schmid and Dr Michael Stewart for their help in the preparation of this manuscript.

## References

- B. D. Gates, Q. Xu, M. Stewart, D. Ryan, C. G. Willson and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1171.
- S. Y. Chou, P. R. Krauss and P. J. Renstrom, *Appl. Phys. Lett.*, 1995, **67**, 3114.
- S. Y. Chou, P. R. Krauss and P. J. Renstrom, *J. Vac. Sci. Technol., B*, 1996, **14**, 4129.
- M. D. Austin, H. Ge, W. Wu, M. Li, Z. Yu, D. Wasserman, S. A. Lyon and S. Y. Chou, *Appl. Phys. Lett.*, 2004, **84**, 5299.
- M. D. Austin, W. Zhang, H. Ge, D. Wasserman, S. A. Lyon and S. Y. Chou, *Nanotechnology*, 2005, **16**, 1058.
- M. Stewart, S. Johnson, S. V. Sreenivasan, D. Resnick and C. G. Willson, *J. Microlithogr., Microfabr., Microsyst.*, 2005, **4**, 1.
- M. Colburn, S. Johnson, M. Stewart, S. Damle, T. Bailey, B. Choi, M. Wedlake, T. Michaelson, S. V. Sreenivasan, J. Ekerdt and C. G. Willson, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1999, **3676**, 379.
- F. Hua, Y. Sun, A. Gaur, M. A. Meiti, L. Bilhaut, L. Rotkina, J. Wang, P. Geil, M. Shim and J. A. Rogers, *Nano Lett.*, 2004, **4**, 2467.
- See: [http://www.itrs.net/Links/2006Update/FinalToPost/08\\_Lithography2006Update.pdf](http://www.itrs.net/Links/2006Update/FinalToPost/08_Lithography2006Update.pdf).
- E. K. Kim, N. A. Stacey, B. J. Smith, M. D. Dickey, S. C. Johnson, B. C. Trinque and C. G. Willson, *J. Vac. Sci. Technol., B*, 2004, **22**, 131.
- D. J. Resnick, S. V. Sreenivassan and C. G. Willson, *Mater. Today*, 2005, **8**, 34.
- M. D. Dickey and C. G. Willson, *AIChE J.*, 2006, **52**, 778.
- M. D. Dickey, R. L. Burns, E. K. Kim, S. C. Johnson, N. A. Stacey and C. G. Willson, *AIChE J.*, 2005, **51**, 2547.
- G. Odian, in *Principles of Polymerization*, John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 4th edn, 2004, ch. 3, pp. 255–263.
- E. K. Kim, M. D. Stewart, K. Wu, F. L. Palmieri, M. D. Dickey, J. G. Ekerdt and C. G. Willson, *J. Vac. Sci. Technol., B*, 2005, **23**, 2967.
- E. K. Kim and C. G. Willson, *Microelectron. Eng.*, 2006, **83**, 213.
- H. Ito, F. A. Houle, M. W. Hart and R. A. DiPietro, *Proc. SPIE-Int. Soc. Opt. Eng.*, 2006, **6153**, 61531A–1.
- G. M. Schmid, M. D. Stewart, J. Wetzel, F. Palmieri, J. Hao, Y. Nishimura, K. Jen, E. K. Kim, D. J. Resnick, J. A. Liddle and C. G. Willson, *J. Vac. Sci. Technol., B*, 2006, **24**, 1283.
- J. Hao, F. Palmieri, M. D. Stewart, Y. Nishimura, H. L. Chao, A. Collins and C. G. Willson, *Polym. Prepr.*, 2006, **47**, 1158.

- 
- 20 M. Morgen, E. T. Ryan, J. H. Zhao, C. Hu, T. H. Cho and P. S. Ho, *Annu. Rev. Mater. Sci.*, 2000, **30**, 645.
- 21 J. L. Hedrick, R. D. Miller, C. J. Hawker, K. R. Carter, W. Volksen, D. Y. Yoon and M. Trollsas, *Adv. Mater.*, 1999, **10**, 1049.
- 22 M. D. Stewart, J. T. Wetzel, G. M. Schmid, F. Palmieri, E. Thompson, E. K. Kim, D. Wang, K. Sotoodeh, K. Jen, S. C. Johnson, J. Hao, M. D. Dickey, Y. Nishimura, R. M. Laine, D. J. Resnick and C. G. Willson, *Proc. SPIE-Int. Soc. Opt. Eng.*, 2005, **5751**, 210.
- 23 G. Odian, in *Principles of Polymerization*, John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 4th Edition, 2004, ch. 9, pp. 731–732.
- 24 A. W. Levine and J. Fech, Jr., *J. Org. Chem.*, 1972, **37**, 1500.
- 25 W. H. Heath, F. Palmieri, J. R. Adams, B. K. Long, J. Chute, T. Holcombe, S. Zieren, M. J. Truitt, J. L. White and C. G. Willson, *Macromolecules*, submitted.
- 26 X. Chen, F. Wudl, A. K. Mal, H. Shen and S. R. Nutt, *Macromolecules*, 2003, **36**, 1802.
- 27 X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran and F. Wudl, *Science*, 2002, **295**, 1698.
- 28 Y. L. Liu and C. Y. Hsieh, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **44**, 905.
- 29 M. L. Szalai, D. V. McGrath, D. R. Wheeler, T. Zifer and J. R. McElhanon, *Macromolecules*, 2007, **40**, 818.
- 30 R. Gheneim, C. Perez-Berumen and A. Gandini, *Macromolecules*, 2002, **35**, 7246.
- 31 Y. Imai, H. Itoh, K. Naka and Y. Chujo, *Macromolecules*, 2000, **33**, 4343.
- 32 J. R. McElhanon, T. Zifer, S. R. Kline, D. R. Wheeler, D. A. Loy, G. M. Jamison, T. M. Long, K. Rahimian and B. A. Simmons, *Langmuir*, 2005, **21**, 3259.
- 33 M. F. Montague and C. J. Hawker, *Chem. Mater.*, 2007, **19**, 526.
- 34 K. Ogino, J. S. Chen and C. K. Ober, *Chem. Mater.*, 1998, **10**, 3833.
- 35 L. Kilian, Z. H. Wang and T. E. Long, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3083.
- 36 R. R. De Clercq and E. J. Goethals, *Macromolecules*, 1992, **25**, 1109.
- 37 E. Ruckenstein and H. Zhang, *Macromolecules*, 1999, **32**, 3979.
- 38 E. Themistou and C. S. Patrickios, *Macromolecules*, 2006, **39**, 73.
- 39 N. B. Lorette and W. L. Howard, *J. Org. Chem.*, 1960, **25**, 521.
- 40 R. Jain, S. M. Standley and J. M. J. Frechet, *Macromolecules*, 2007, **40**, 452.
- 41 K. Jen, F. Palmieri, B. Chao, M. Lin, J. Hao, J. Owens, K. Sotoodeh, R. Cheung and C. G. Willson, *Proc. SPIE-Int. Soc. Opt. Eng.*, 2007, **6517**, 65170K.