

# Vinyl ethers in ultraviolet curable formulations for step and flash imprint lithography

E. K. Kim, N. A. Stacey, B. J. Smith, M. D. Dickey, S. C. Johnson, B. C. Trinque, and C. G. Willson<sup>a)</sup>

*Department of Chemical Engineering and Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712*

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Until now, acrylates have been the monomers of choice for use for step and flash imprint lithography (SFIL) etch barrier formulations, in part because of the commercial availability of silicon-containing acrylates (necessary for etch resistance), together with their low viscosities and capability for rapid photopolymerization. However, despite many desirable properties, the polymerization of acrylates via radical chain propagation causes some potential issues in the SFIL process as a result of the inhibition of these processes by oxygen. Vinyl ethers are prime candidates to replace acrylates. Their curing proceeds by a cationic mechanism, which is insensitive to oxygen and very rapid, while the vinyl ether group contribution to viscosity is significantly lower than that of an acrylate, silicon-containing vinyl ethers are not widely commercially available, and so were synthesized for this study. As expected, formulations based on these vinyl ethers were lower viscosity and faster curing than the acrylate etch barrier formulations presently employed, while the tensile strength of cured vinyl ether formulations were found to be higher than their acrylate counterparts. In spite of about twice higher template separation force compared with acrylates, the tensile strength of vinyl ether etch barrier formulations is about five times higher than that of acrylate formulations. Therefore, these vinyl ether-based formulations were used to pattern down to 50 nm features using the SFIL process. © 2004 American Vacuum Society. [DOI: 10.1116/1.1635849]

## I. INTRODUCTION

Essentially all semiconductor devices are made today using optical lithography as the method of feature patterning. Since the resolution of optical lithography is primarily limited by the wavelength of the light source and the numerical aperture of the lens, the patterning of ever smaller features in order to maintain processor speed and memory density advances requires shorter wavelength light sources and more complex optical components.<sup>1</sup> This relationship has resulted in a Moore's law-type (exponential) relationship in exposure tool prices over the last two decades.<sup>2</sup> Of more concern is the apparent escalation of this trend as we push toward 50 nm and beyond with next-generation lithography alternatives such as extreme ultraviolet, where both sources and optics become highly complex and difficult to fabricate. To escape these issues, other methodologies are being actively considered for integrated circuit patterning.

One such alternative, step and flash imprint lithography (SFIL), is an inherently relatively low cost and potentially high throughput process,<sup>3</sup> which has been demonstrated to be capable of generating patterns as small as 20 nm. The SFIL process is depicted schematically in Fig. 1. The key steps are as follows: (a) the template and substrate are aligned; (b) an organosilicon photocurable liquid, called an etch barrier, is dispensed onto the substrate; (c) the template is lowered onto the substrate to produce a contiguous contact so that the liquid fills the template-substrate gap, and the material is

then illuminated by UV to cure the liquid; (d) the template is separated from the cured etch barrier; and (e) the residual layer is etched by CF<sub>4</sub> and O<sub>2</sub> plasma, and then the pattern is transferred through the transfer layer by O<sub>2</sub> plasma etch to achieve high aspect ratio features.

It is clear that in such a process, the etch barrier must satisfy several design requirements. These include: (1) low viscosity, to dispense small amounts uniformly and deliver thin residual layers in short process times; (2) rapid photocuring to high conversion; (3) low separation force between cured etch barrier and the template; (4) high strength to maintain printed feature integrity; and (5) high silicon content to provide oxygen etch selectivity compared with the transfer layer. Acrylate-based formulations are presently used as the etch barrier formulations because their polymerization, via radical propagation, is very fast and many silicon-containing acrylates are commercially available. However, the acrylate formulations have some drawbacks. Oxygen inhibits radical polymerization.<sup>4</sup> In the SFIL process this manifests itself in two ways. On the periphery of the imprint, where the monomer is in contact with air, the polymerization is permanently inhibited, which results in an uncured edge. This is a potential defect generating source. In the bulk of the imprinting material, dissolved oxygen causes an induction time before the start of polymerization can begin, which will reduce throughput. Furthermore, difunctional acrylate monomers, necessary to increase the modulus of the etch barrier in order to maintain feature fidelity, are somewhat viscous (>3.0 cPs). Therefore, the stiffness cannot be enhanced without sacrificing viscosity in these formulations.

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: willson@che.utexas.edu

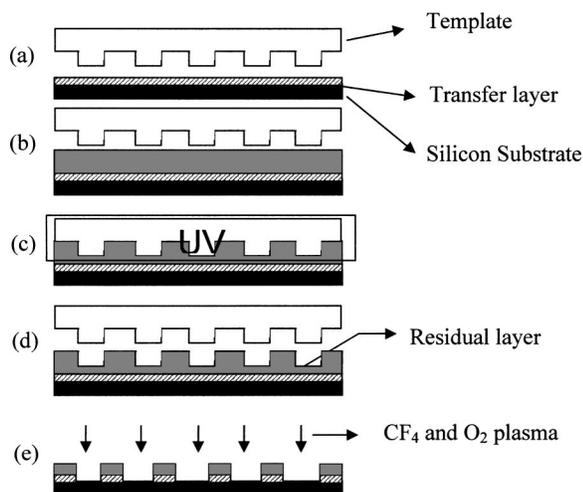


FIG. 1. Step and flash imprint lithography process.

Oxygen inhibition can be overcome with nitrogen purging, but this is experimentally inconvenient and complex to achieve in a manufacturing environment. A simple way to overcome this issue is to adopt a chemistry/propagation mechanism that is insensitive to oxygen, such as cationic polymerization. Vinyl ethers and epoxides are two widely industrially used chemistries that are cured by cationic polymerization. In addition, cationic photoinitiators are available in the form of photoacid generators (PAGs), which are already used for chemically amplified resists to make semiconductor devices. Epoxies are well known as structural polymers because of their excellent mechanical properties, but the polymerization rate is typically much slower than vinyl ethers.<sup>5,6</sup> Vinyl ethers are known to be very reactive cationic curable monomers, and their UV curing rates have been well studied.<sup>6,7</sup> Moreover, the viscosity of vinyl ethers is very low. For example, ethyl acrylate (0.55 cPs at 25 °C) is substantially more viscous than the equivalent vinyl ether, ethyl vinyl ether (0.25 cPs at 20 °C), which indicates that the ether functional group contributes less to the viscosity than the acrylate. One drawback of vinyl ethers for this application is the lack of commercially available silicon-containing monomers in this class, so that silicon-containing vinyl ethers for this work had to be synthesized (see Fig. 2).

The imprint performances of etch barrier compositions are strongly related to the material properties of the etch barrier. Therefore, both the synthetic method and the material properties are investigated in this article.

## II. EXPERIMENT

### A. Materials

*t*-Pentyl vinyl ether, cyclohexyl vinyl ether, and ethylene glycol divinyl ether were purchased from the Aldrich Company and used without further purification. The photoacid generator (4,4'-bis-(*t*-butylphenyl) iodonium tris-(trifluoromethanesulfonyl) methide) was kindly provided by the 3M Company.

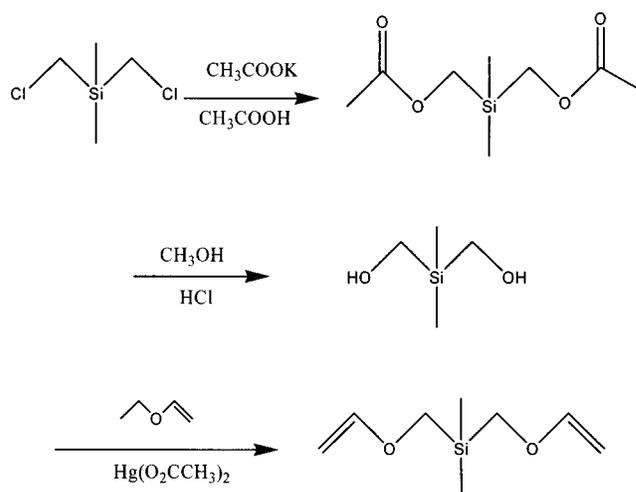


FIG. 2. Synthetic scheme of silicon containing vinyl ethers.

## B. Synthesis of silicon-containing vinyl ethers

### 1. Bis-(acetoxymethyl)-dimethylsilane<sup>8,9</sup>

To a 500 mL round bottom flask equipped with a stir bar and condenser was added 50.5 g (0.321 mol) of bis-chloromethyl-dimethylsilane, 78.8 g (0.803 mol) of potassium acetate, and 70 ml of acetic acid. The reaction mixture was heated to reflux for 24 h, after which time it was cooled to room temperature, poured into a 1 L separatory funnel containing 400 mL of saturated sodium carbonate, slowly, and the resulting mixture was extracted three times with diethyl ether (200 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and the solvent was removed by rotary evaporation. 65 g (99%) colorless liquid was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.011 (*s*, 6H), 2.00 (*s*, 6H), 3.79 (*s*, 4H).

### 2. Bis-(hydroxymethyl)-dimethylsilane<sup>8,9</sup>

To a 500 mL round bottom flask equipped with a stir bar and condenser was added 400 mL methanol, 20 g (0.098 mol) bis-acetoxymethyl-dimethylsilane, and 1 ml concentrated hydrochloric acid. The reaction mixture was heated to reflux for 24 h, after which time it was cooled to room temperature and 1 g sodium bicarbonate was added, and the solvent was removed by rotary evaporation. Vacuum distillation (72–82 °C, 1 mm Hg) afforded 9.29 g (79%) of a colorless liquid that was 99% pure by GC. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.046 (*s*, 6H), 3.06 (*bs*, 2H), 3.44 (*d*, 4H).

### 3. Dimethyl-bis-(vinylloxymethyl)-silane

To a dry, 1 L round bottom flask equipped with a stir bar, condenser, and nitrogen inlet was added 700 mL ethyl vinyl ether, 26.693 g (0.222 mol) bis-(hydroxymethyl)-dimethyl silane, 4.72 g (0.0148 mol) mercuric acetate, and 3 g (0.0296 mol) triethyl amine. The reaction mixture was heated to 50 °C and stirred for 72 h, after which time it was cooled to room temperature, poured into a 2 L separatory funnel containing 400 mL of brine, and the aqueous phase was extracted with diethyl ether (150 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and the solvent was re-

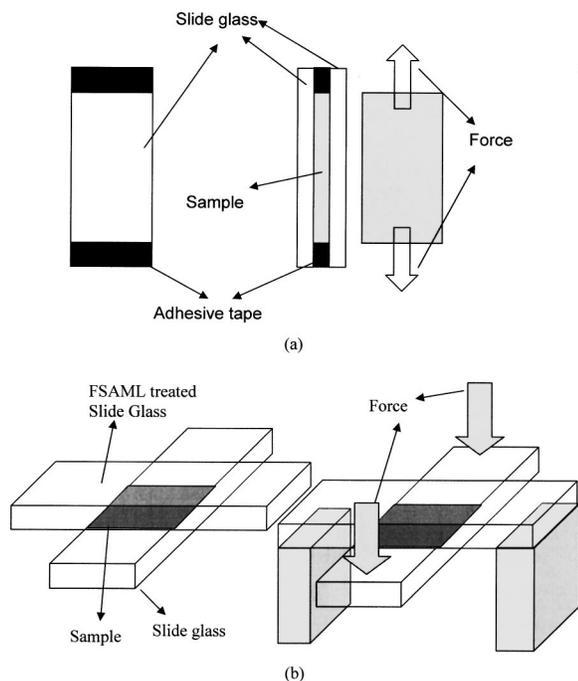


FIG. 3. Sample preparation and testing method: (a) tensile strength measurement, and (b) separation force measurement.

moved by rotary evaporation. Vacuum distillation (48–52 °C, 20 mmHg) afforded 24.96 g (65%) of a colorless liquid that was 99% pure by GC.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.15 (s, 6H), 3.39 (s, 4H), 3.95 (*d*, 2H), 4.20 (*d*, 2H), and 6.53 (*m*, 2H).

1,1,3,3-tetramethyl-1,3-bis(vinyloxymethyl) disiloxane (24.62 g; 68%) was synthesized using the same method.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.14 (s, 12H), 3.23 (s, 4H), 3.94 (*d*, 2H), 4.21 (*d*, 2H), and 6.53 (*m*, 2H).

### C. Viscosity and curing rate measurement of vinyl ethers

Viscosities were measured using a Cannon-Fenske capillary viscometer using The American Societies for Testing and Materials (ASTM) method D 446. Viscosity is very sensitive to temperature, so measurements were made with the viscometer immersed in a water bath to minimize temperature fluctuations. The curing rate was measured by real-time Fourier transform infrared (FTIR)<sup>3</sup> using a Nicolet Magna-IR 550 FTIR spectrometer with an external, liquid-nitrogen-cooled MCT detector from Axiom Analytical. UV irradiation was provided by a “Novacure” UV lamp from EXFO. The experimental setup consisted of the monomer sandwiched between an aluminum coated silicon wafer and a NaCl salt cell. IR illumination was at normal incidence to the cell and used the aluminum coating to reflect the signal back to the detector. UV irradiation was provided at an angle of 30° to the normal. The variations in peak height of the C=C bond at 1615  $\text{cm}^{-1}$  (vinyl ethers) and 1640  $\text{cm}^{-1}$  (acrylates) over time were used to monitor the reaction.<sup>10</sup>

TABLE I. Chemicals used in this study.

Chemical Name	Chemical Structure	Silicon Content	Viscosity (cps@ 25°C)	Viscosity (acrylate equivalent)
1,1,3,3-tetramethyl-1,3-bis(vinyloxymethyl) disiloxane (BVMSO)		22.8 %	1.4	
Dimethyl-bis(vinyloxymethyl) silane (BVMS)		16.3 %	1.0	
Ethylene Glycol Divinyl ether (EGDVE)		0 %	0.75	3.7
t-Pentyl vinyl ether (t-PVE)		0 %	0.48	
Cyclohexyl vinyl ether (CHVE)		0 %	1.1	3.0
4,4-bis-(t-butylphenyl) iodonium tris(trifluoromethanesulfonyl) methide (PAG)		0%		

### D. Tensile strength and separation force of vinyl ethers

The tensile strengths of vinyl ether and acrylate formulations were collected using an MTS Sintech 1/D using test method ASTM D882. Figure 3(a) shows the sample preparation method and test configuration. The etch barrier formulation was introduced into the preset gap between the slide glasses with the aid of capillary forces. The sandwich samples were cured using a JBA LS65 UV lamp using a 4.4  $\text{J}/\text{cm}^2$  broadband dose to cure the thick samples. After curing, the sample was separated from the slide glasses using a razor blade, and was measured.

The sample preparation for separation force is illustrated in Fig. 3(b).<sup>11</sup> The etch barrier formulation was dispensed onto a slide glass, and another slide glass, which is coated with a fluorinated self-assembled monolayer, was used to sandwich the liquid.<sup>12</sup> This cross-shaped sample was cured using the same UV lamp as with a dose of 2.2  $\text{J}/\text{cm}^2$ . The sample was then loaded in a modified four-point bending setup, and then the lower slide glass was progressively pushed downward to separate the slides.<sup>11</sup> The maximum load, which is referred to as the separation force, was measured using the MTS Sintech 1/D.

### E. Imprint and SEM

Bottom antireflection coating coated silicon wafers were provided by International Sematech, and templates were pre-

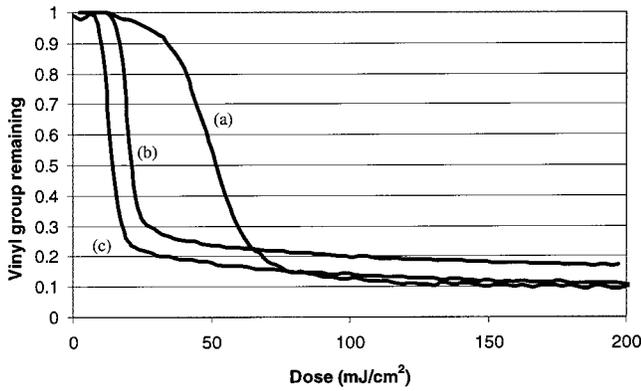


FIG. 4. Extent of cure of etch barrier formulations as a function of exposure dose (UV lamp intensity: 2.5 mW/cm<sup>2</sup>): (a) current etch barrier (acrylate), (b) vinyl ether etch barrier formulation (BVMS/EGDVE/PAG = 80/18/2 wt %), and (c) vinyl ether etch barrier formulation (BVMS/*t*-PVE/PAG = 80/18/2 wt %).

pared at the Motorola laboratory. Imprinting was performed using the University of Texas stepper.<sup>13</sup> Scanning electron microscopy (SEM) images were acquired using a Hitachi 4500 SEM.

III. RESULTS AND DISCUSSION

Vinyl ether monomers are, typically, lower in viscosity than equivalent acrylate structures. For example, in Table I, the viscosity of ethylene glycol divinyl ether is 0.75 cPs, while that of ethylene glycol diacrylate is 3.7 cPs. 1,1,3,3-tetramethyl-1,3-bis(vinyloxymethyl) disiloxane (BVMSO) and dimethyl-bis(vinyloxymethyl)silane (BVMS) synthesized above both meet the requirements for SFIL since both contain more than 12 wt% silicon, with which the oxygen plasma etch rate of the etch barrier is ten times slower than that of the organic transfer layer.<sup>14</sup> The viscosities of these vinyl ether monomers are close to that of water. If they are mixed with nonsilicon containing vinyl ethers, such as

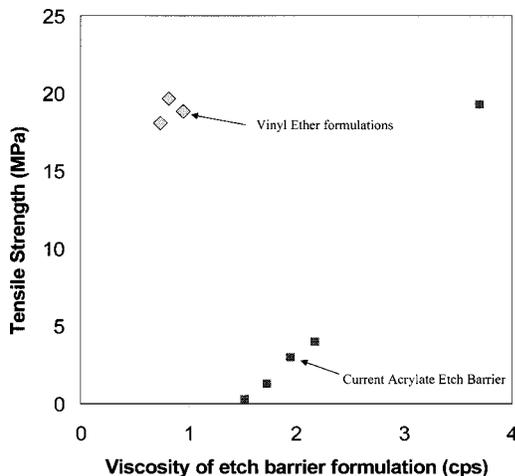
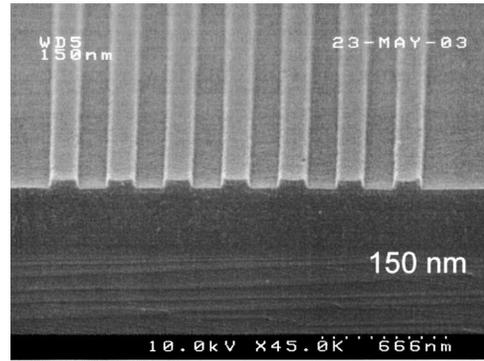
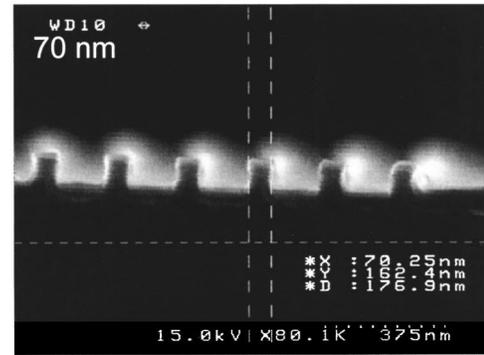


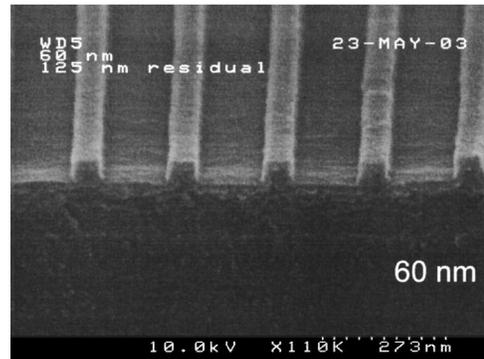
FIG. 5. Tensile strength of cured acrylate based etch barrier formulation compared with the viscosity.



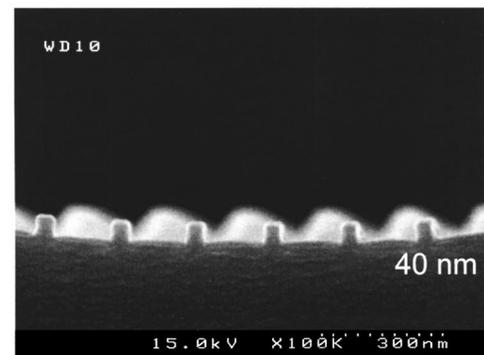
(a)



(b)



(c)



(d)

FIG. 6. Imprint images of vinyl ether based etch barrier formulations: (a) vinyl ether etch barrier formulation (BVMSO/EGDVE/PAG = 60/38/2 wt %), (b) vinyl ether etch barrier formulation (BVMS/EGDVE/PAG = 80/18/2 wt %), (c) vinyl ether etch barrier formulation (BVMSO/EGDVE/PAG = 60/38/2 wt %), and (d) vinyl ether etch barrier formulation (BVMS/*t*-PVE/PAG = 80/18/2 wt %).

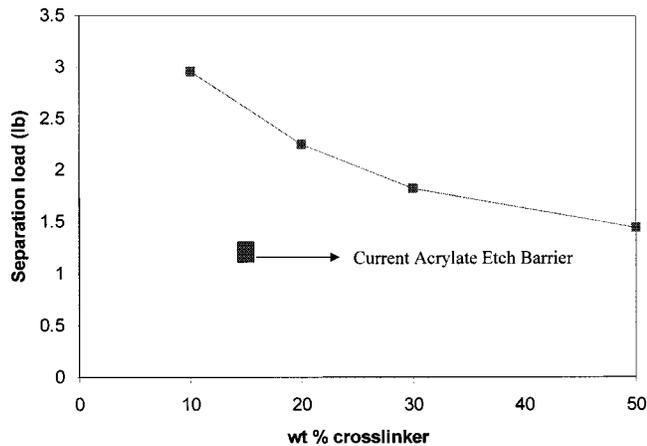


FIG. 7. Separation force of poly *t*-pentyl vinyl ether-co-ethyleneglycol vinyl ether as a function of the cross linker.

*t*-pentyl vinyl ether and ethyleneglycol divinyl ether, the etch barrier formulation viscosity is lower than 1 cps.

Figure 4 illustrates the extent of cure of vinyl ethers as a function of dose in comparison with an acrylate etch barrier formulation. It can be seen that for a given dose, the extent of cure of the vinyl ether formulations is greater than that of the acrylate system. Only 25 mJ/cm<sup>2</sup> is required to completely cure the vinyl ethers.

Because tensile force is applied to the cured etch barrier during the separation process, the tensile strength is related to the feature integrity after the separation process. If the tensile strength is much lower than separation force, the feature can be broken during the separation process. The tensile strength of acrylates increased with the increase of viscosity, as shown in Fig. 5. Therefore, it is not easy to make the etch acrylate barrier formulation with low viscosity and high tensile strength. To meet the requirement of low viscosity in acrylate formulation, the tensile modulus of the current acrylate etch barrier formulation is about 3 MPa. However, the viscosities of vinyl ether formulations are about 1 cps, and their tensile strength is five times larger than that of the current acrylate etch barrier formulation. Figure 6 shows the imprint images using vinyl ether etch barrier formulations. Due to the good mechanical properties of the vinyl ether etch barrier formulation, 40 nm features can be patterned.

Although vinyl ether based etch barrier formulations have low viscosities, rapid polymerization, and high tensile strength, the vinyl ether system has one observed drawback as an etch barrier formulation in SFIL. The separation force of vinyl ethers appears from experiments to be approximately twice that of acrylates using similar surfaces. High separation forces are intuitively undesirable and might contribute to feature fidelity degradation. Although the separa-

tion force of vinyl ether formulations is twice higher than that of acrylate formulations, as shown in Fig. 7, the tensile strength of the vinyl ether formulation is five times larger than that of acrylates, as shown in Fig. 5. Therefore, the feature integrity of vinyl ether formulations can be better than that of acrylate formulations.

#### IV. CONCLUSIONS

The vinyl ether-based etch barrier formulations possessed lower viscosities and faster polymerizations than the present acrylate formulations used by SFIL in this group. In addition, the tensile strength of cured vinyl ether etch barrier formulations is higher than that of acrylate systems of similar viscosity. Using vinyl ether-based etch barrier formulations, 50 nm features have been readily printed. The separation force of cured vinyl ethers from the template is higher than that of the cured acrylate etch barrier formulation and future work will focus on reducing these separation forces to more acceptable levels.

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