

Design of Reversible Cross-Linkers for Step and Flash Imprint Lithography Imprint Resists

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Nanoimprint lithography (NIL) has emerged as a possible successor to traditional optical lithography for the 32 nm device fabrication node and beyond because of its ability to faithfully reproduce sub-30 nm features with fidelity and high throughput.¹ The nanoimprint process utilizes a patterned, 3-D mold (template) to define patterns by embossing a soft or liquid material. Once the material has completely filled the template cavities, it is vitrified, and the template is removed to produce a 3-D replica of the mold.

Step and Flash Imprint Lithography (S-FIL, a trademark of Molecular Imprints, Inc.), shown in Figure 1, is a low-temperature, low-pressure UV-NIL process targeted for applications in complementary metal oxide semiconductor fabrication.² In this process, a low-viscosity liquid monomer fills the space between the template and a substrate and is then exposed to UV irradiation, which initiates a polymerization that vitrifies the imprint fluid. Although many variations on the imprint resist formulation exist, imprint resist formulations for UV-NIL

ABSTRACT Progress in the semiconductor manufacturing industry depends upon continuous improvements in the resolution of lithographic patterning through innovative materials development and frequent retooling with expensive optics and radiation sources. Step and Flash Imprint Lithography is a low-cost, nanoimprint lithography process that generates nanopatterned polymeric films *via* the photopolymerization of low-viscosity solutions containing cross-linking monomers in a transparent template (mold). The highly cross-linked imprint materials are completely insoluble in all inert solvents, which poses a problem for reworking wafers with faulty imprints and cleaning templates contaminated with cured imprint resist. Degradable cross-linkers provide a means of stripping cross-linked polymer networks. The controlled degradation of polymers containing acetal- and tertiary ester-based cross-linkers is demonstrated herein. The viscosity and dose to cure are presented for several prepolymer formulations, along with imprint resolution and tensile modulus results for the cured polymers. Optimum conditions for de-cross-linking and stripping of the cross-linked polymers are presented, including demonstrations of their utility.

KEYWORDS: nanoimprint · lithography · S-FIL · cross-linker · reworkable · template

applications generally consist of a solution containing a free radical generator and monofunctional, cross-linking, and etch-resistant monomers. The difunctional cross-linking monomers are incorporated to provide the mechanical properties necessary for successful template separation from the

cured imprint resist without deformation of high-resolution features or cohesive failure within the polymer. The etch-resistant monomers typically contain inorganic elements such as silicon to provide resistance to oxygen reactive ion

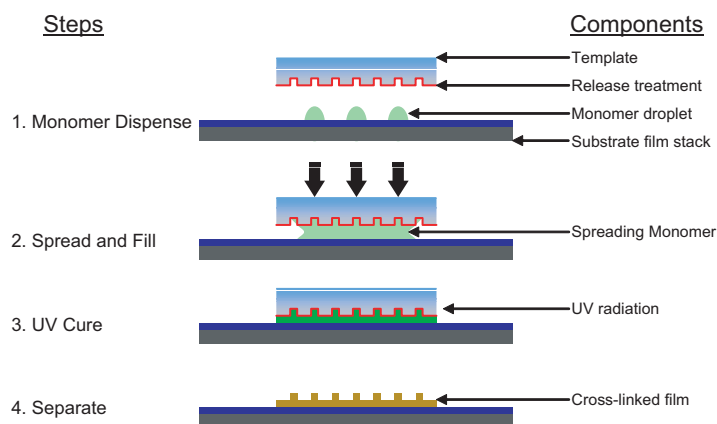


Figure 1. The UV-NIL (S-FIL) process.

TABLE 1. Example S-FIL Formulation and Component Description

name	wt %	function
cyclohexyl methacrylate	28	low-vapor-pressure linear monomer; provides high- T_g polymer
isobutyl acrylate	20	low-viscosity, reactive diluent: improves monomer flow
ethyleneglycol diacrylate	20	cross-linker; improves mechanical properties
acryloxypropyl-tris(trimethylsiloxy)silane	30	silicon-containing monomer; provides oxygen etch resistance
2-hydroxy-2-methyl-1-phenyl-1-propanone	2	photoinitiator; generates free radicals upon exposure to UV radiation

etching. When the inorganic materials are exposed to oxidative environments, a nonvolatile inorganic oxide residue is generated that acts as an etch mask.

Kim *et al.* established the material properties requirements for S-FIL imprint resist precursors and postexposure, cured polymers.³ Low-viscosity (<5 cP) monomer solutions are desirable to aid fluid spreading and template filling, which improves film uniformity, reduces film thickness, and increases process throughput. A low-vapor-pressure monomer is required to minimize evaporation between the dispense and imprint steps to maintain a consistent resist composition (Figure 1). Acrylic or vinyl ether functional groups are incorporated due to their high polymerization rate and high degree of conversion. Tough materials with tensile moduli over 100 MPa are required for faithful pattern replication at the nanometer scale. Further, the resist must contain at least 9% silicon to provide sufficient oxygen etch resistance for pattern transfer.^{4,5} No current S-FIL formulations produce easily strippable polymers due to the high degree of cross-linking (10–30%).^{6,7} The components and associated functions of a typical acrylic imprint formulation are shown in Table 1.

Solvent stripping of cross-linked imprint resist from wafers and templates is impossible with traditional solvents due to their high cross-link density. Oxidative chemistries such as oxygen plasma etching and piranha cleaning produce inorganic oxide deposits that are chemically indistinguishable from the wafer and template surfaces and cannot be selectively removed by reactive etching without eroding the substrate. Ultrasonic agitation and powerful jets of solvent can damage fragile parts of the template pattern, rendering them unusable for most S-FIL rework applications.

The fabrication of templates with large areas of high-density nanopatterns represents the greatest cost associated with a nanoimprint process in a manufacturing setting. Template patterns must be written at $1\times$ magnification with slow and expensive direct write processes such as e-beam lithography. Furthermore, there are significant costs associated with inspection and re-

pair of nanoscopic template patterns. For these reasons, it is important to maximize the number of imprints that can be obtained from each template (template lifetime). An easily dissolved imprint resist would provide a means for nondestructive contamination removal, leading to significantly improved template lifetime.

S-FIL formulations may be modified by replacing ethyleneglycol diacrylate, a nondegradable cross-linker, with a degradable (de-cross-linkable) cross-linker to enable stripping of the photopolymerized material with conventional solvents. Several de-cross-linking systems, such as Diels–Alder adducts, hydrogen-bonding monomers, degradable esters, and acetals, have been demonstrated elsewhere, but they have not been implemented in a UV-NIL process.^{8–11} Many potential degradable cross-linker designs create compatibility or solubility issues in standard imprint formulations, and the need for low viscosity and high molar concentration eliminates many of the candidates. Ogino's work demonstrates the viability of the tertiary ester structure as a thermally degradable material but requires both a high-temperature de-cross-linking step and a base-catalyzed wash to remove the anhydride cross-links formed as a byproduct of the thermal decomposition.¹⁰ The degradable acetals presented by De Clercq are photopolymerizable macromonomers with molecular weights much greater than those of components suitable for S-FIL formulations.⁹

These designs were adapted to provide the acetals and hindered esters demonstrated in this report as materials more suitable for the S-FIL process. The diacrylate-functionalized derivatives of the acid-degradable materials shown in Figure 2 exhibit good compatibility with standard S-FIL formulations. Each contains two acrylic moieties that undergo free radical polymerization to generate cross-links. The tertiary ester diacrylate (TEDA) cross-linker is unstable in the presence of strong acids and heat.¹² The acetal diacrylate (ADA) cross-linker undergoes hydrolysis in the presence of water and strong acid at room temperature.⁹

The TEDA cross-linkers decompose into 1,1-disubstituted olefins and carboxylic acid groups (Scheme 1b), which are known to form anhydride linkages at high temperatures, resulting in a re-cross-linked polymer network.¹⁰ Therefore, the de-cross-linking temperature must be optimized. The ADA cross-linker undergoes hydrolysis to produce hydroxyl groups

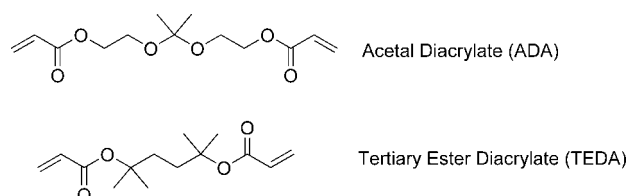
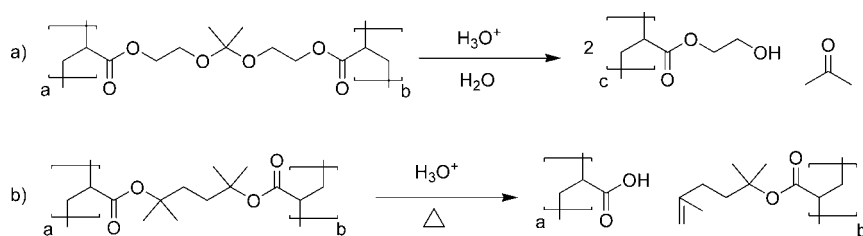


Figure 2. Acid-degradable cross-linker structures.



Scheme 1. De-cross-linking reactions of (a) poly(ADA) and (b) poly(TEDA).

(Scheme 1a) that are not expected to undergo side reactions under similar conditions. The acetal de-cross-linking may be carried out at or near room temperature.

RESULTS AND DISCUSSION

The properties listed in Table 2 show the compatibility of TEDA and ADA with S-FIL processing. Their low molecular weight and viscosity maximize cross-link density while improving template filling dynamics. Process throughput is improved by high photospeed achieved during free radical polymerization of the acrylate functional groups. These materials were implemented in existing imprint formulations and processes with minimum development work.

Experimental imprint resist formulations were prepared from the acid-degradable cross-linkers listed in Table 2 and the linear monomers shown in Table 1. These formulations were photopolymerized, and their physical properties and stripping characteristics were studied at cross-linker concentrations between 5 and 20 wt %. The concentration of isobutyl acrylate ranged from 20 to 35 wt %, to complement changes in cross-linker concentration.

A control die was imprinted on a silicon wafer using the imprint resist formulation in Table 1, an experimental formulation including the de-cross-linking chemistry was imprinted next to the control die, and then the wafer was cleaved in half. The wafer stripping process was applied on one half of the wafer to demonstrate the effectiveness of the cross-linking and de-cross-linking chemistry. The difference is dramatic, as can be seen in Figure 3.

The decomposition reaction begins when the polymer film is exposed to the acid reagent at a sufficient temperature. Once initiated, the decomposition reaction reaches completion in less than 1 min, as indicated by iterative experiments with variable acid exposure times. The decomposition reaction is assumed to proceed simultaneously throughout the bulk film rather than by a surface erosion mechanism. The bulk reac-

tion mechanism is supported by the successful stripping results observed when using a two-step process where the acid reagent is removed during the solvation step.

The de-cross-linking reaction must achieve high conversion before the polymer is rendered soluble; therefore, iterative experiments were used to determine the maximum concentration of cross-linker that produced easily strippable polymers. TEDA-containing films were successfully stripped with cross-linker concentrations less than 10 wt %. Above 10 wt %, the cross-linked films would swell, crack, and delaminate but did not become completely soluble. ADA cross-linked films gave similar results, with a maximum strippable cross-linker concentration of 15 wt %. Gelation occurs in a system at the instant, called the gel point, when a critical concentration of polymer branches exist.¹³ Insoluble polymer formulations occur at high concentrations of degradable cross-linkers due to the high degree of decomposition needed to reach the gel point, below which solvation is possible.

Cleaning templates with imprint resist contamination is difficult and expensive to demonstrate directly because of the small feature size and difficulty with cross-section examination of quartz template substrates. To demonstrate template cleaning, silicon wafers coated with a 1 μm film of silicon oxide (similar to template quartz) with contact holes as small as 130 nm in diameter and a 7:1 aspect ratio were imprinted with the strippable formulations using the automatic process described in the Experimental Methods section. Figure 4 shows deep contact holes filled with cross-

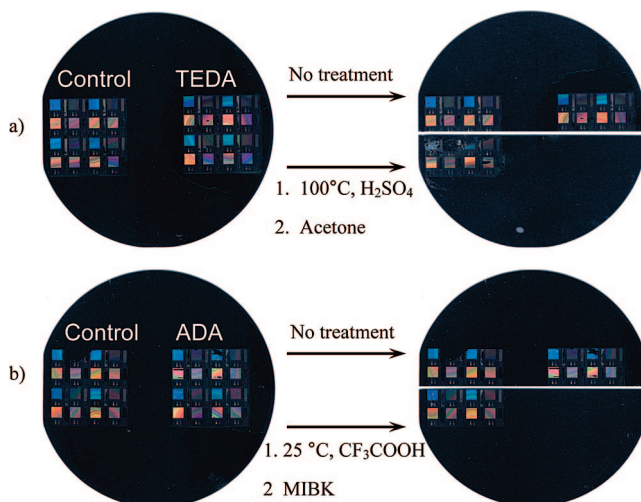


Figure 3. Wafer stripping demonstrations. Control imprints made with a standard formulation are on the left side of each wafer, and experimental formulations are printed on the right. (a) The stripping of a TEDA cross-linked imprint and (b) the stripping of an ADA cross-linked imprint.

TABLE 2. Material Properties of the Degradable Cross-Linking Monomers

name	MW (g/mol)	viscosity (cP)	dose to cure (mJ/cm ²)
TEDA	272.29	21.1	13.5 @ 52% conv.
ADA	254.32	12.3	58.3 @ 63% conv.
desired values	NA	<20	<90 @ >50% conv.

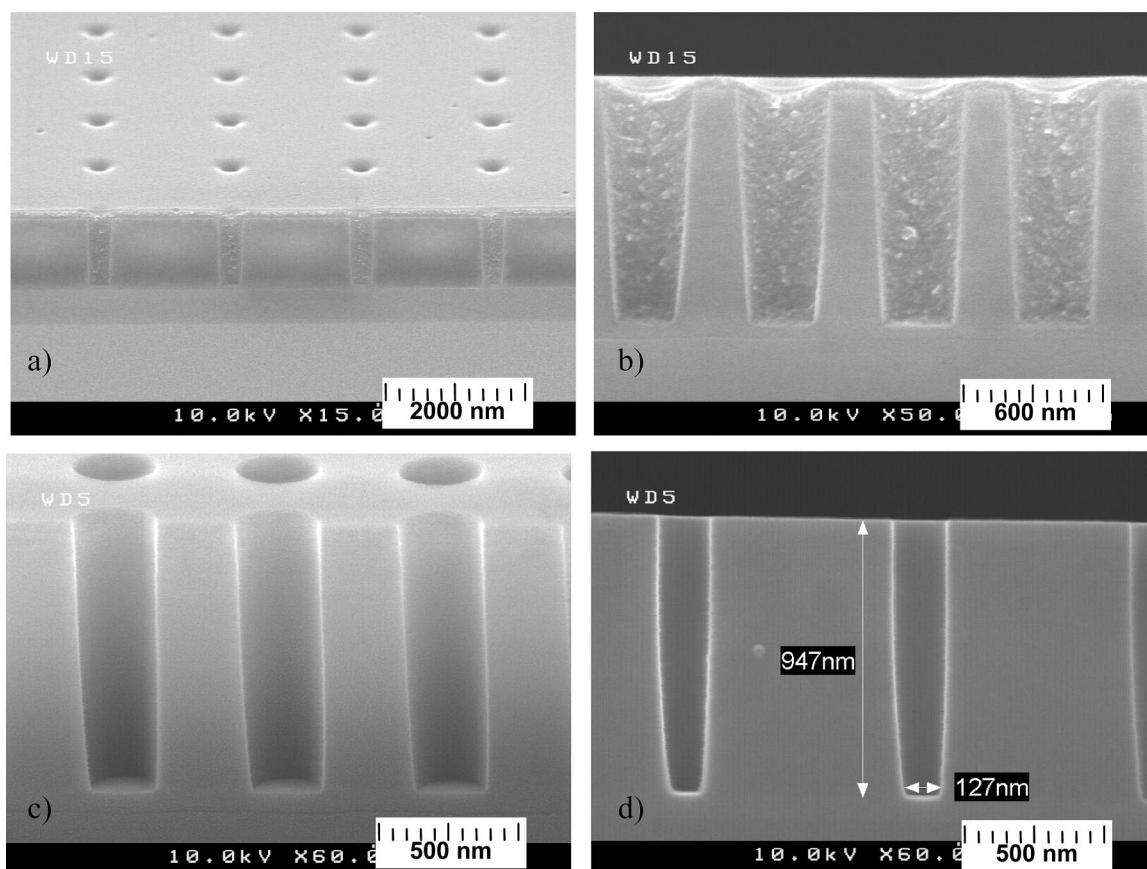


Figure 4. Simulated template cleaning results: (a,b) contact holes filled with cured, degradable imprint resist, and (c,d) clean contact holes after the stripping process.

linked polymer and fully opened contact holes after undergoing the template cleaning process. Even the highest aspect ratio patterns on the template were cleaned completely, as shown in the cross-section view. The sidewalls show absolutely no residue of imprint resist polymer. This is strong evidence that recessed template features contaminated with an inorganic-containing imprint resist can be cleaned completely by de-cross-linking and stripping.

The bulk tensile moduli of formulations containing TEDA and ADA are shown in Figure 5. TEDA shows a significantly stronger effect on the tensile modulus than

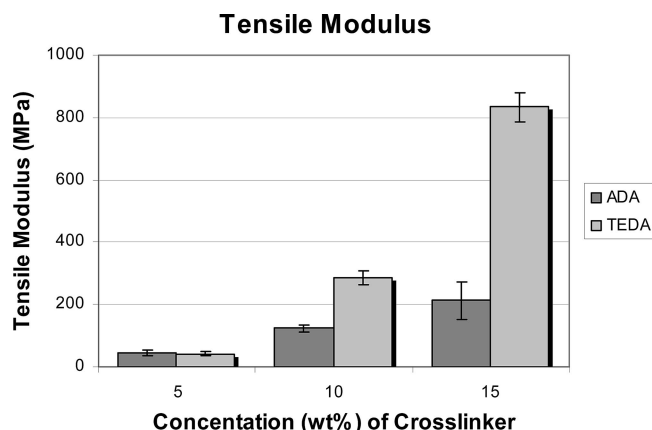


Figure 5. Tensile moduli of TEDA and ADA formulations.

ADA. The strain to yield was recorded at $0.38 \pm 0.002\%$ for TEDA and $0.21 \pm 0.003\%$ for ADA. On the basis of these mechanical properties, TEDA cross-linked films are expected to show higher ultimate resolution than ADA cross-linked analogs.

Accurate replication of high-resolution template patterns is a key function of the imprint resist formulation. Scanning electron micrographs (SEMs) of imprinted experimental formulations were examined for imprint quality. The morphology of an imprinted feature is dependent on mold properties such as corner sharpness and feature sidewall angle, as well as material properties such as curing shrinkage and elastic modulus. Because it is difficult to directly inspect a template surface, the experimental imprint SEM images were compared to imprints of the standard formulation. The SEM images of $1 \mu\text{m}$ posts in Figure 6 indicate that TEDA reproduces high-fidelity patterns. The control and TEDA imprints show similar corner rounding and sidewall angles, which indicates that these are properties of the template. The image made from the 15% ADA-containing formulation in Figure 6c shows slightly bent and deformed posts. Plastic deformation of ADA cross-linked features occurs due to its lower strain to yield point relative to that of the 10% TEDA-containing formulation. This problem becomes less sig-

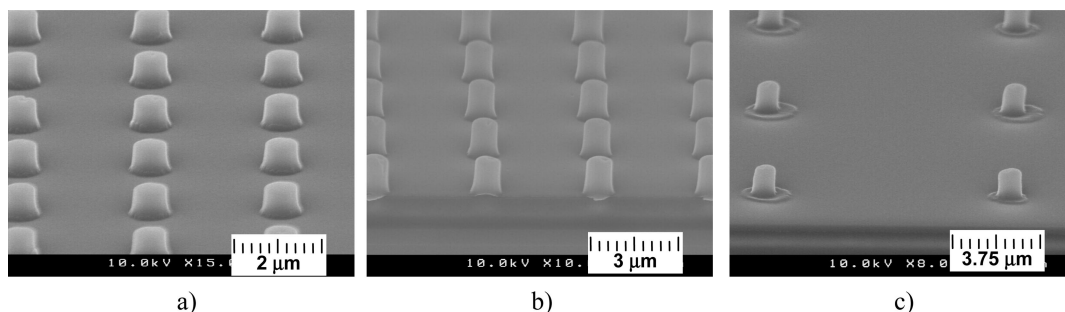


Figure 6. Tilt SEM images of 1 μm diameter posts, printed with (a) control formulation (Table 1), (b) 10% TEDA experimental formulation, and (c) 15% ADA experimental formulation showing tilted and bent posts.

nificant for patterning larger, more mechanically robust feature geometries with low aspect ratios.

CONCLUSIONS

Incorporation of degradable cross-linkers can provide strippable and reworkable imprint resist formulations. The properties of TEDA and ADA are compatible with UV-NIL and S-FIL imprint resist requirements. Cured imprint formulations with 10 wt % TEDA and 15

wt % ADA were successfully de-cross-linked, stripped from wafers, and cleaned from high-aspect-ratio contact holes. The formulation containing 15 wt % ADA showed only minor pattern defects under SEM inspection, and the formulation with 10 wt % TEDA showed excellent imprint fidelity. High-resolution imprint lithography has been successfully coupled with a convenient template and wafer reworking process.

EXPERIMENTAL METHODS

General Materials. All solvents and reagents were obtained from Aldrich or Fisher Scientific and were used without further purification except where noted. The syntheses of TEDA and ADA were adapted from the literature.^{10,14}

Measurement of Dose To Cure. Thin films of neat TEDA were examined by reflectance-mode, FT-IR spectroscopy by pressing a drop of the liquid monomer between an aluminum-coated silicon wafer and a sodium chloride window. The dose to cure was measured by real-time FT-IR spectroscopy, utilizing the acrylate double bond to monitor monomer conversion.⁶ Dose to cure energies were obtained from the fractional conversion during polymerization as a function of time.

Imprinting. The S-FIL process shown in Figure 1 was used to prepare samples for de-cross-linking and stripping demonstrations. An Imprio 55 automated imprint tool, manufactured by Molecular Imprints Inc., was used to prepare thin-film samples (50–200nm) and high-resolution patterns (<1 μm).^{15,16} Some samples were produced using a manual imprint process by pressing a drop of monomer between a quartz plate and a silicon wafer. Wafers were treated with an adhesion promoter, AP410, obtained from Silicon Resources Inc., and templates were treated with a 0.2 wt % solution of (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane in toluene to aid in adhesive release from the template.¹⁷ The formulation was cured through a quartz plate with a 300 mW/cm² i-line source for 4 min. Templates used for making high-resolution post structures were prepared using the standard chromium on quartz process.¹⁸

Stripping. The de-cross-linking and stripping process for TEDA was accomplished by immersing in concentrated sulfuric acid at 100 °C for 1 min. The acid-treated films were then readily soluble in acetone or similar organic solvents. Stripping ADA cross-linked films was accomplished by immersion in a solution of 10 wt % trifluoroacetic acid and 4-methyl-2-pentanone at room temperature. Complete dissolution of all films was achieved in less than 5 min.

Measurement of Mechanical Properties. The mechanical properties of cured films were measured using an Instron 4858 Micro Tester operating in tensile extension mode. Samples were prepared by photopolymerizing the experimental imprint formulations between glass microscope slides and quartz plates using 150 μm

spacers to control the film thickness. Film samples were separated from the glass and quartz substrates and measured for thickness and width before tensile testing until failure.

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