

Recent Advances in Step and Flash Imprint Lithography

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The goal of the Step and Flash Imprint Lithography (SFIL) development program is to enable patterning of sub-100 nm features in a manner that has dramatic cost savings over conventional projection lithography techniques. The SFIL process is performed at room temperature and with minimal applied pressure, and we believe the use of low viscosity materials and photopolymerization chemistry will enable SFIL to achieve the throughput required for use in the microelectronics industry. Additionally, the rigid transparent imprint template used in SFIL enables a precision in overlay alignment that is difficult to achieve in other imprint schemes. This paper presents recent work that has focused on improving the resolution of the etch barrier formulation, modeling the free radical polymerization reaction to include oxygen inhibition, and improving the etching processes used to amplify the aspect ratio of the polymer features. Replacing the silylated crosslinker component in the etch barrier with ethylene glycol diacrylate has greatly reduced the viscosity of the solution without sacrificing feature resolution. Etch process development has shown that a CF_4/O_2 feed rich in CF_4 provides sufficient etch selectivity to etch the residual etch barrier layer, while O_2 rich feed provides sufficient selectivity for the transfer layer etch. With this recent work we have demonstrated polymer-on-Si semi-dense lines smaller than 50 nm made with the SFIL process. Studies of defectivity have not revealed significant defect generation, and in fact have revealed no substantial defect propagation. Oxygen diffusion into the polymerizing imprint material inhibits the free radical curing reaction to such an extent around the imprint perimeter so as to create a

narrow tacky ring at the imprint edge. Our reaction model confirms this result, and we are using this model to find ways to mitigate this effect.

1. Introduction

The resolution of optical projection lithography is ultimately limited by the fundamental physics and chemistry of the imaging process. Photolithographic resolution is known to depend on the wavelength of the light, the numerical aperture of the lens, the optical system, and the resist material.¹ A combination of improvements in optics, reduction in wavelength, and the introduction of more complex photomasks and processes has enabled printing of features smaller than 100 nm by photolithography. These improvements have come at a cost, however, and this cost has increased exponentially with time.² It is believed that cost of ownership of lithography tools will ultimately be the practical barrier to resolution improvements. The Semiconductor Industry Association International Technology Roadmap for Semiconductors² has identified alternative next generation lithography (NGL) imaging techniques based on X-ray and extreme ultraviolet (EUV) ionizing radiation, as well as techniques based on projection and direct-write electron beam lithography. Each technique has its advantages and disadvantages, but all are expensive.

Many research groups are exploring alternative forms of imprint lithography, as an inexpensive patterning method capable of sub-100 nm resolution on various substrates.³⁻⁸ Although imprint equipment requires precision X-Y stages, layer-to-layer alignment systems, and wafer handling equipment common to other lithography techniques, imprint lithography realizes significant cost savings because it does not require lasers or projection optics. Imprint lithography has several important advantages over conventional optical lithography and NGL techniques: It is non-optical by design, and the resolution appears to be limited only by the structures that can be generated in a master template. Imprint templates are typically fabricated using imaging tools such as electron beam writers that provide high resolution but lack the throughput required for mass production. By using imprint templates defined by e-beam lithography, imprint lithography makes use of this resolution capability without being limited by e-beam

throughput issues. Since the main advances required to improve resolution are expected to be in the area of the imprint template development and process chemistry, an imprint tool built for one technology generation could conceivably extend to future technology nodes.

There are many imprint lithography techniques, all based on the concept that a template or mold with a prefabricated topography is pressed into a displaceable material. This material takes the shape of the pattern defined in the template, and through some curing process, the shaped material is hardened into a solid. Imprint lithography is by nature a contact patterning process that transfers topography without scaling. There are common challenges to all of these imprint techniques, the foremost being the dependence of this technology on 1-X imprint master resolution and the potential for defect production and propagation because of the contact nature of the replication process.

2. Background

2.1 Step and Flash Imprint Lithography Process Overview

Step and Flash Imprint Lithography (SFIL) uses photopolymerization of an organosilicon solution through a rigid transparent imprint template to define the pattern topography on a substrate. The use of a low-viscosity UV curing solution allows imprinting at room temperature with minimal applied pressure. Typically the imprinting process is performed over a blanket layer of organic polymer, creating a bilayer structure. This removes the need to imprint high aspect ratio features, since the pattern aspect ratio can be subsequently amplified by dry etching. The use of a rigid transparent imprint template allows flood exposure of the photopolymer to achieve cure, and enables classical optical techniques commonly used in mask aligners, photolithography steppers, and scanners for layer-to-layer alignment.

Details of the SFIL process are shown in Figure 1. An organic polymer layer (transfer layer) is spin-coated on a substrate, typically silicon. A low viscosity, photopolymerizable, organosilicon solution (etch barrier) is then dispensed on the wafer in the area to be imprinted. A transparent template bearing patterned relief structures is aligned over the coated silicon substrate. The template is lowered onto the substrate, displacing the etch barrier that fills the imprint field and trapping the etch barrier solution in the

template relief. Irradiation with UV light through the backside of the template cures the etch barrier into a crosslinked polymer film. A fluorocarbon release layer on the template allows separation from the substrate, leaving an organosilicon relief image that is a replica of the template pattern. A halogen etch is used to break through the undisplaced etch barrier material (residual layer) exposing the underlying transfer layer. An oxygen reactive ion etch (RIE) is used to transfer the image through the transfer layer thereby amplifying the aspect ratio of the imprinted image.

The resolution of imprinted features is defined by the pattern resolution on the imprint templates. SFIL templates have been fabricated using a process that is similar to conventional phase-shift reticle processing.^{9,10} In a typical Cr process, a 6-in \times 6-in \times 1/4-in fused silica reticle blank coated with a thin Cr film is spin-coated with an electron beam resist, and baked to drive off excess casting solvent. The plate is then exposed in a high resolution direct-write e-beam tool. The resist is then developed, leaving a resist pattern that exposes selected portions of the underlying Cr film. This resist pattern is used as an etch mask to pattern the Cr with Cl-based RIE. The resist is removed after etching, leaving behind a patterned Cr layer on the silica substrate. A fluorine-based RIE transfers the image into the fused silica substrate to a depth of 100 to 200 nm, depending on design constraints. The Cr layer is typically left on the templates until after the cutting process, which is described below; this facilitates template pattern recognition, and minimizes mistakes in cutting.

Template fabrication schemes employing a transparent conducting oxide into the final template have also been investigated. The addition of a blanket conducting layer dissipates charge during SEM inspection of the final templates. One such scheme involves coating the fused silica plate with a film of indium tin oxide (ITO), which is transparent and conducting.^{9,11} The ITO film is then covered with a film of deposited SiO₂, followed by e-beam resist. The resist is patterned using an e-beam tool, and chemically developed. The patterned resist is used as an etch mask to pattern the underlying SiO₂ film. A convenient result is that the ITO serves as an etch stop for the SiO₂ etch process. The resist is finally stripped, resulting in an imprint template of patterned SiO₂ features resting on a blanket film of ITO on fused silica substrate. The SiO₂ features will define the imprinted features in the SFIL process, while the

ITO film is transparent to allow the SFIL process exposure and conducting to allow SEM inspection of the template.

Another template scheme consists of spinning a film of hydrogen silsesquioxane (HSQ) on the ITO layer. The HSQ is directly written with e-beam lithography,¹² and the unexposed regions are developed away, leaving the cured HSQ topography. In its cured state, HSQ becomes a durable oxide making it a very convenient material for direct patterning of SFIL template relief structures. One benefit of this scheme is that it eliminates the etching processes associated with other template fabrication methods.

These process flows have been used to fabricate imprint templates with resolution better than 30 nm, as shown in Figure 2. Additionally, all three processes yield templates that are amenable toward the surface treatment reaction described, ensuring clean release of the template from the substrate after imprinting.

Careful tailoring of the chemistries of the release layer, the photopolymer formulation, and the transfer layer has allowed faithful replication of any feature on the imprint template. We have patterned areas of high and low pattern density, and produced a functional micropolarizer array with 100 nm Ti lines/spaces using a metal lift-off process.¹³ SFIL has also been used to pattern directly over a non-flat substrate,¹³ including curved surfaces.¹⁴ We have patterned semi-dense and isolated lines smaller than 30 nm,^{9,10} and demonstrated the capability of layer-to-layer alignment.¹⁵ The process is simple in concept, but every step in the process presents interesting challenges in materials engineering and science. This work presents improvements in etch barrier formulation, etch barrier reaction modeling, etch process development, and defectivity analysis.

3. Recent Results

3.1 Etch Barrier Composition

The etch barrier formulation disclosed by Colburn⁴ was very useful in early SFIL process development. It was determined experimentally, however, that the stable resolution of that particular formulation may be limited to features larger than 100 nm. In order to identify a potential etch barrier

material that possessed low viscosity for dispensing and also high-resolution printing capabilities, a series of experiments was undertaken whereby the concentrations and/or type of crosslinker, high-Si monomer, and low-MW monomer were varied, as shown in Table 1. Results indicated that resolution, or “printability,” increased in all cases with increasing crosslinker concentration, but solution viscosity also increased, as shown in Table 2 and Figure 3. The viscosities of the methacrylate and mixed acrylate/methacrylate solutions that possessed reasonable printabilities were determined to be too high for dispensing in the current equipment. Only the acrylate formulation using ethylene glycol diacrylate as the crosslinker possessed both low viscosity (<2 cP) and good feature profile. A consequence of lowering the viscosity of the etch barrier solution will be an accompanying decrease in the residual layer thickness.¹⁶ Formulation A4 was therefore chosen as the current baseline etch barrier formulation.

3.2 Etch Barrier Curing Kinetics

The presence of oxygen dissolved in the etch barrier and in the ambient environment causes two undesirable effects on the curing of the acrylate etch barrier. Oxygen dissolved in the etch barrier consumes photoinitiated radicals, resulting in an inhibition period before polymerization begins. Furthermore, oxygen diffusion into the etch barrier limits the curing reaction around the perimeter of the template. This results in a partially cured, tacky residue around the perimeter of the etch barrier. Such partially cured residues can adhere to the template and generate defects in subsequent imprints.

We modeled the SFIL curing process to explore the extent of these oxygen-related inhibition effects, as well as to explore how they could be mitigated. The model is based on standard free-radical polymerization kinetics. As an initial set of reaction conditions, the model used a dissolved oxygen concentration of 1×10^{-3} mol/L,¹⁷ a 45 mW/cm² medium pressure mercury arc light source, and used the absorption characteristics of Darocur 1173 (CIBA) photoinitiator. Reaction coefficients for acrylate monomers for the model were taken from the literature.¹⁷ Using these conditions, the model predicted an inhibition period of ~300 msec and an uncured tacky region of ~10 μ m thick around the perimeter of the

cured etch barrier, as shown in Figure 4. Future work on the model will include measuring the reaction coefficients in the etch barrier and incorporation of auto-acceleration effects.

Changes to either the type or quantity of initiator used or modifications the lamp power can reduce the extent of oxygen inhibition effects. Doubling the light intensity, according to the model, results in a reduction in inhibition time to ~150 msec and a reduction in the size of the uncured ring to ~6 μm . Future publications will further explore the effects of varying these parameters.

3.3 Etch Process Development

Two key steps in printing resist features on bare substrate with SFIL are the breakthrough and transfer etches. Once low aspect ratio patterns have been printed in the etch barrier, they must then be transferred through the underlying transfer layer. The first step, commonly referred to as the “break-through” etch, anisotropically removes residual etch barrier to break through to the underlying transfer layer. The second step, the “transfer” etch, uses the patterned low aspect ratio etch barrier as an etch mask to transfer the pattern into the underlying transfer layer. These steps are shown schematically in Figure 5.

Since the etch barrier contains silicon and the transfer layer does not, the etch chemistries for the two steps must necessarily be different. The concentration of CF_4 in a feed of O_2 was varied, and the etch rates of transfer layer and etch barrier were measured, as shown in Figure 6. Gas feeds rich in CF_4 yield greater etch selectivity of etch barrier to transfer layer, providing a recipe for the break-through etch, while feeds rich in O_2 etch the transfer layer faster than the etch barrier. Imprinted samples, such as is shown in Figure 6 (left), were etched in the CF_4 -rich process (center), followed by etching in the O_2 -rich process, yielding high resolution, high aspect ratio polymer features on the Si substrate (right).

3.4 Defectivity

We have undertaken an effort to quantify defectivity as a function of repeated imprints. Early results were very encouraging, showing no catastrophic generation or propagation of defects. Figure 8 shows a micrograph of an imprint template before installation in the SFIL stepper, and then again after only two imprints. The handling of the template during installation in the current operating procedure can impart

some contamination on the template, but imprinting actually cleans away that contamination. This effect has also been seen by Harai⁷ and Bender.⁸ The final imprinted pattern consists of desired features resting on a blanket layer of the same polymer. This yields film thickness contrast between the features and the field, but no material contrast, resulting in poor contrast for inspections. Current work toward defect analysis is directed toward removing inspection barriers caused by this poor pattern contrast, as well as imprecise die placement on the UT SFIL stepper.

4. Summary

The etch barrier formulation has been dramatically improved by changing the replacing the Si-containing crosslinker used in the past with ethylene glycol diacrylate. This monomer provides the structural stability of the silylated crosslinker, but at a greatly reduced viscosity. Reaction modeling results indicate that O₂ diffusion inhibits the etch barrier polymerization in the bulk until the dissolved oxygen has been consumed. Additionally, oxygen diffusion into the etch barrier through the film perimeter locally inhibits the polymerization to such an extent as to create a tacky layer around the film perimeter. This inhibition lag time and the thickness of this tacky layer are influenced by the lamp intensity, initiator characteristics, and oxygen concentration in the ambient environment.

Etch gas feeds of O₂/CF₄ that are rich in CF₄ provide good selectivity for etching the residual etch barrier layer. This etch step exposes the organic transfer layer, which can then be etched in pure O₂. These etch processes are able to provide sub-50 nm polymer features on the Si substrates.

Defectivity analysis has revealed no catastrophic level of defect generation. Recent results indicate the need for improving the feature/field contrast, as well as the die placement from the UT stepper.

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Table 1. Etch barrier formulation matrix.

Methacrylate formulations

Formulation	SIM6487.6	SIB1402.0	Darocur 1173	MMA	Si wt %
M1	45	0	4	51	11.96
M2	45	10	4	41	13.41
M3	45	20	4	31	14.86
M4	45	35	4	16	17.04
M5	45	50	4	1	19.22

Mixed acrylate/methacrylate formulations

Formulation	SIA0210.0	SIB1402.0	Darocur 1173	n-BA	Si wt %
AM1	44	0	4	52	12.09
AM2	44	10	4	42	13.55
AM3	44	20	4	32	15
AM4	44	35	4	17	17.18
AM5	44	50	4	2	19.36

Acrylate formulations

Formulation	SIA0210.0	EGDA	Darocur 1173	t-BA	Si wt %
A1	44	0	4	52	12.09
A2	44	5	4	47	12.09
A3	44	10	4	42	12.09
A4	44	15	4	37	12.09
A5	44	20	4	32	12.09

High-Si monomers:

SIM6487.6 - methacryloxypropyltris(trimethylsiloxy)silane

SIA0210.0 - (3-acryloxypropyltristrimethylsiloxy)silane

Crosslinkers:

SIB1402.0 - 1,3-bis(3-methacryloxypropyl)tetramethyldisiloxane

EGDA - ethylene glycol diacrylate

Low-MW monomers:

MMA - methyl methacrylate

n-BA - n-butyl acrylate

t-BA - t-butyl acrylate

Table 2. Etch barrier formulation viscosities.

Formulation	Viscosity/cP
M1	1.03
M2	1.37
M3	1.86
M4	3.32
M5	6.09
AM1	1.45
AM2	1.87
AM3	2.46
AM4	4.17
AM5	6.57
A1	1.42
A2	1.52
A3	1.73
A4	1.95
A5	2.18

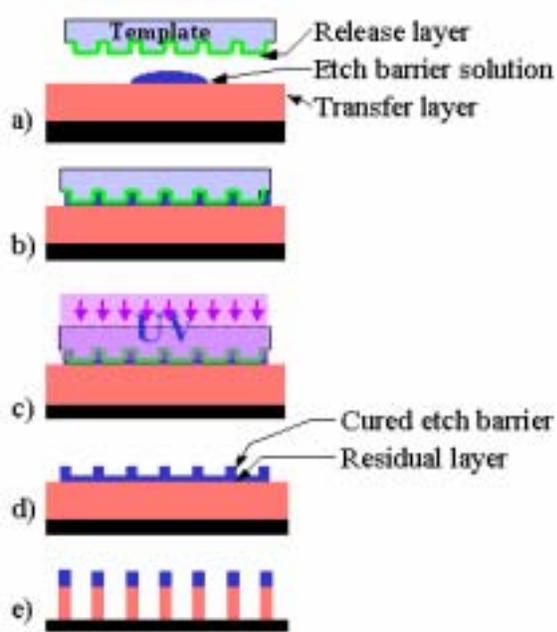


Figure 1. SFIL process flow. The process employs a template/substrate alignment scheme to bring a rigid template and substrate into parallelism (a), trapping the etch barrier (b). The gap is closed until the force that ensures a thin base layer is reached. The imprint is then illuminated through the backside of the template (c) to cure the etch barrier. The template is withdrawn (d), leaving low-aspect ratio, high resolution features in the etch barrier. The residual etch barrier (base layer) is etched away with a short halogen plasma etch, after which the pattern is transferred into the transfer layer with an anisotropic oxygen reactive ion etch (e), creating high-aspect ratio, high resolution polymer features.

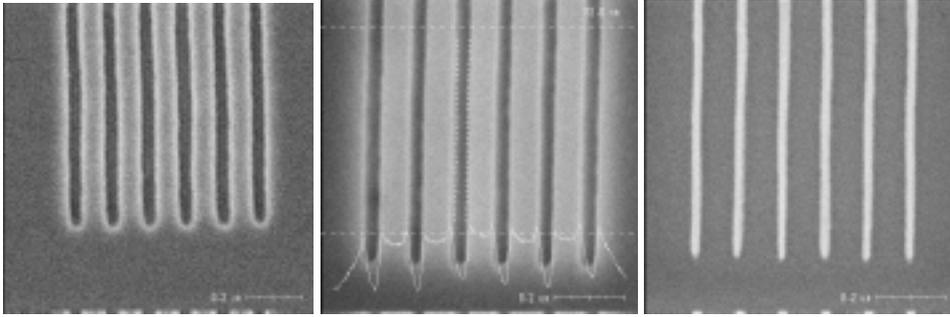


Figure 2. Template features from various template process flows. 30 nm trenches from standard thin Cr process template (left), 20 nm trenches from PECVD oxide/ITO process (center), and 20 nm lines from HSQ/ITO process (right).

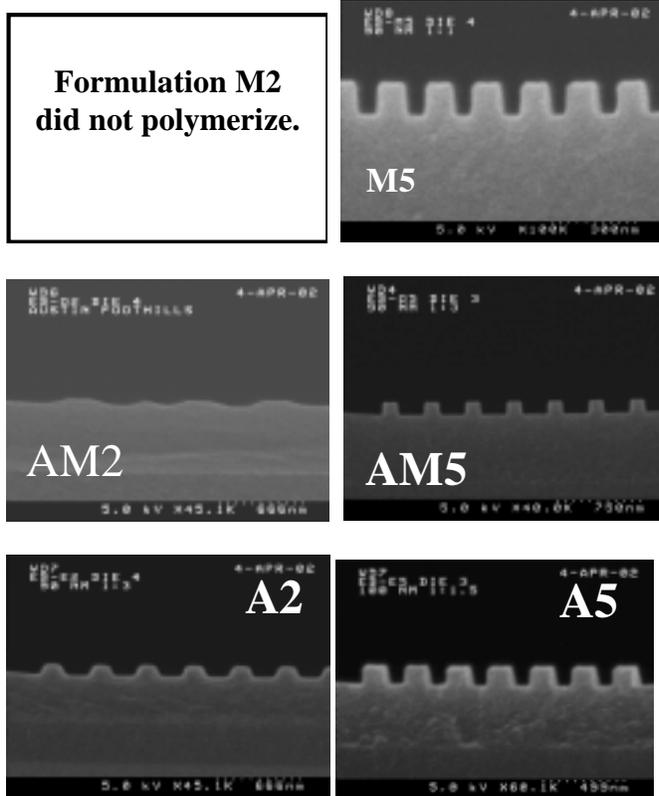


Figure 3. Dramatic profile improvements are observed in all etch barrier formulations with increasing crosslinker concentration. Formulation M2 did not print.

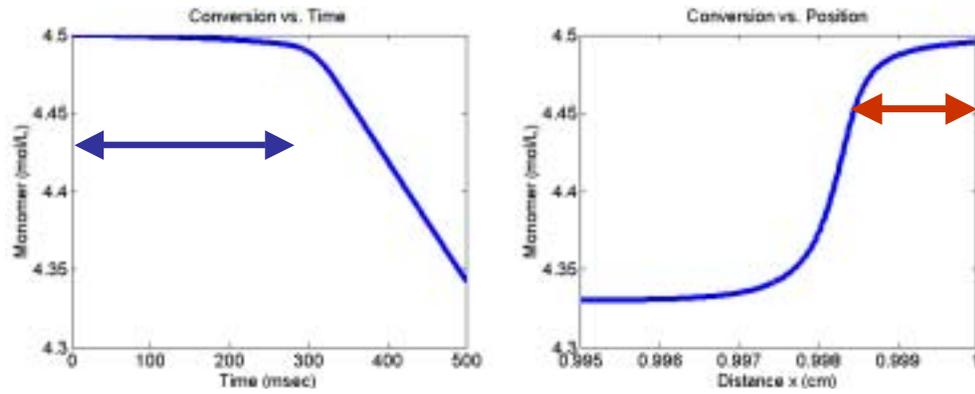


Figure 4. Typical results from reaction modeling. Oxygen concentrations in the etch barrier result in polymerization inhibition (left). As the reaction proceeds, the etch barrier material within $\sim 10 \mu\text{m}$ of the perimeter of the etch barrier remains saturated with O_2 , creating an inhibition zone, or uncured region.

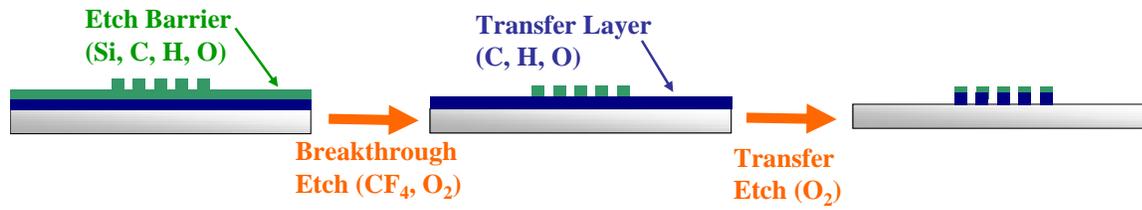


Figure 5. Etching steps required to process SFIL imprinted patterns. The CF₄ is needed in the break-through etch to attack the Si in the etch barrier.

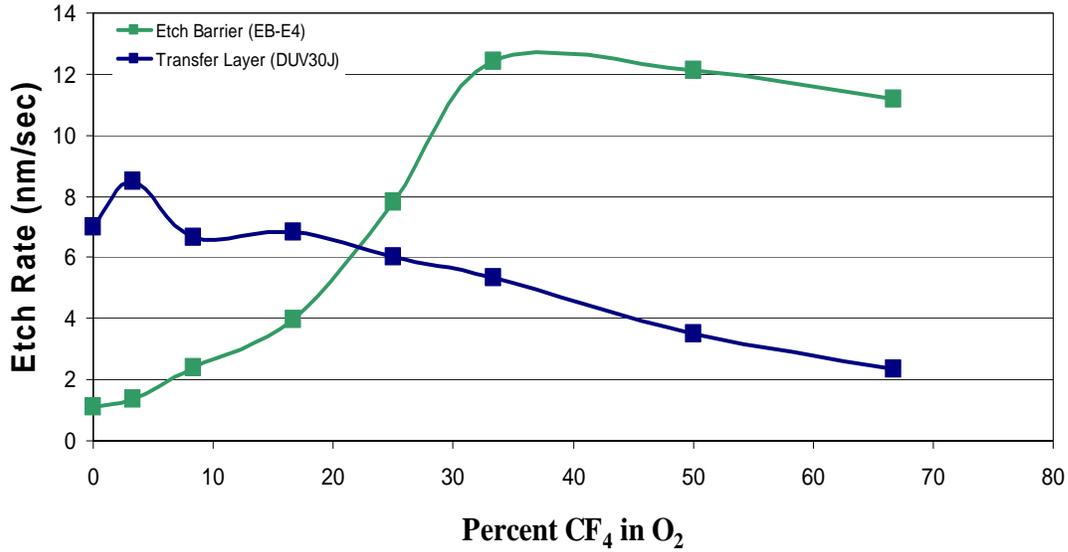


Figure 6. Etch rates of transfer layer (DUV30J, dark squares) and etch barrier (A4, lighter squares) as a function of CF₄ concentration in O₂. The high selectivity of etch barrier to transfer layer with high CF₄ loading is ideal for the break-through etch, while the selectivity of transfer layer to etch barrier in pure O₂ is ideal for the transfer etch.

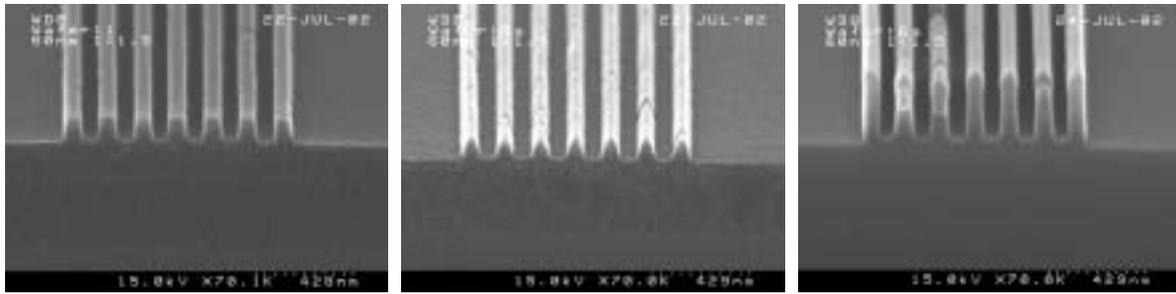


Figure 7. SEM images of 60 nm/920 nm lines/spaces after imprinting (left), break-through etch (center), and transfer layer etch (right). The final image does not appear to be completely cleared out. Even with the faceting, the CD integrity seems to be maintained.

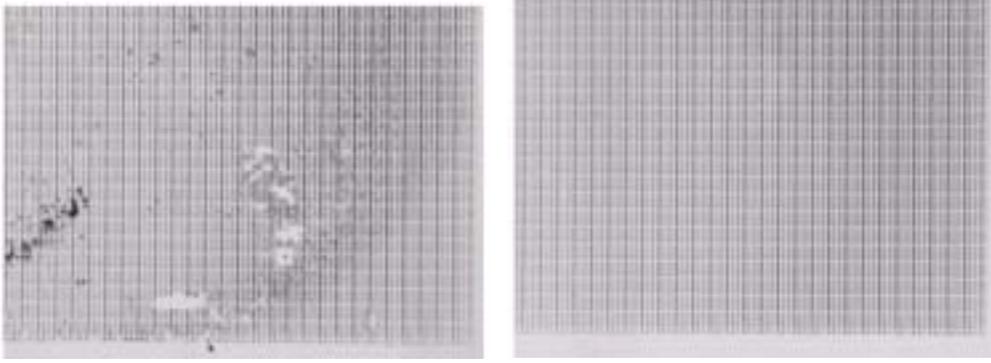


Figure 8. Images of an imprint template before (left) and after (right) two imprints. Template contamination is removed during imprinting.