Development of Imprint Materials for the Step and Flash Imprint Lithography Process

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Abstract

The Step and Flash Imprint Lithography (S-FIL™) process is a step and repeat nano-replication technique based on UV curable low viscosity liquids. Molecular Imprints, Inc. (MII) develops commercial tools that practice the S-FIL process. This talk will present the imprint materials that have been developed to specifically address the issue of process life and defects.

The S-FIL process involves field-to-field dispensing of low viscosity (<5 cps) UV cross-linkable monomer mixtures. The low viscosity liquid leads to important advantages that include:

- Insensitivity to pattern density variations
- Improved template life due to a lubricated template-wafer interface avoids "hard contact" between template and wafer
- Possibility for lubricated (in-situ) high-resolution alignment corrections prior to UV exposure

The materials that are optimal for use in the S-FIL process need to possess optimal wetting characteristics, low evaporation, no phase separation, excellent polymer mechanical properties to avoid cohesive failure in the cured material, low adhesion to the template, and high adhesion to the underlying substrate.

Over 300 formulations of acrylate based monomer mixtures were developed and studied. The imprint materials were deemed satisfactory based on the process of surviving imprinting more than 1500 imprints without the imprints developing systematic or repeating defects. For the purpose of these process studies, printing of sub-100 nm pillars and contacts is used since they represent the two extreme cases of patterning challenge: pillars are most likely to lead to cohesive failure in the material; and contacts are most likely to lead to mechanical failure of the template structures.

1. Introduction

Microlithography generically refers to processes that are used to create micron or sub-micron structures for fabricating various kinds of devices including integrated circuits, bio-chips, MEMS and optical components. Using progressively shorter exposure wavelengths along with increased complexity in photomask design has led to the reduction of the minimum feature size in photolithography. Leading edge photolithography is now operating at a wavelength of λ = 193 nm. Concurrently, λ = 157 nm followed by extreme ultraviolet lithography (EUV, λ = 13.2 nm) are being researched to succeed 193 nm optical lithography. However, with shorter wavelengths, there are long lists of new and substantial technical challenges that lead to very expensive R&D programs and extremely high tool and mask costs. The escalating cost structure of

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photolithography clearly indicates that there is a need for low-cost alternatives to photolithography. Such a technique should not only allow sub-50 nm patterning capability, it should substantially retain the overall benefits of photolithography. This need motivated us to develop a non-optical, low-cost lithography technique known as Step and Flash™ Imprint Lithography (S-FIL). This technology was first developed in the late 1990s at the University of Texas at Austin. It was later licensed to Molecular Imprints, Inc. for commercialization in 2001.

In the mid-1990s, several research groups in industry and academia started investigating “imprint lithography” methods for fabricating small features. Imprint lithography is essentially a micromolding process in which the topography of a template (mold) defines the patterns created on a substrate. Investigations by others and MII in the sub-50 nm regime [1-4] indicate that imprint lithography has almost unlimited resolution. To date, MII’s patterning resolution of about 20 nm is only limited by the electron beam resolution of the template fabrication process (see Figure 1). The S-FIL process (see Figure 2) uses ultra-low viscosity UV curable liquids that are used to fill the template. This lithography process that operates at very low pressures (~ 0.25 psi), which leads to much longer template life and much lower process defects. The use of a transparent fused silica template enables the photocuring process to occur and also allows for optical alignment of the wafer and template. The process also uses “drop-on-demand” fluid delivery that can be tailored to fabricate device geometries that have arbitrary pattern densities. As a result, S-FIL is a particularly suitable imprint technique for fulfilling the stringent requirements of volume fabrication of nano-scale devices.

Multiple materials are involved in the imprinting process. The full material sets have been developed to specifically address the issue of process life and defects. Besides the individual requirements of each material layer, the interfacial interactions of release layer, imprinting material, and transfer layer (shown as the planarization layer in Figure 2) have been carefully examined and optimized.

2. Experimental

Step and Flash Imprint Lithography is a bi-layer approach using a low viscosity, UV-curable imprint solution deposited on an underlying organic planarization layer. The quartz template is rigid and transparent, allowing for UV curing of the imprint solution. Figure 2 shows the process in cross-section. With S-FIL, an organic planarization layer is spin-coated onto the substrate. Then a low viscosity, UV photo-polymerizable imprint solution is dispensed onto the wafer to form an etch barrier in the area to be imprinted (step 2). A surface-treated, transparent template bearing patterned relief structures is aligned over the coated substrate. The template is lowered onto the substrate, thereby displacing the solution, filling the imprint field, and trapping the photo-polymerizable imprint solution in the template relief (step 3). Irradiation with UV light through the backside of the template cures the solution (step 4). The template is then separated from the substrate leaving an organo-silicon relief image on the surface of the coated substrate that is a replica of the template pattern (step 5). The wafer is then stepped and the process is repeated on the next field.

Once the wafer is fully imprinted using S-FIL, the pattern transfer is achieved using a bi-layer etch process. A halogen etch is used to clear the undisplaced, cured imprint solution so that the underlying planarization layer is fully exposed in the recessed regions of the pattern. A subsequent oxygen reactive ion etch into the planarization layer amplifies the aspect ratio of the imprinted image.

Imprint material optimization process includes selecting low vapor pressure component, controlling the viscosity of fluid mixture to be 5 cPs or less at room temperature, improving mechanical properties of the cured imprint material to achieve desirable cohesive strength, conducting wetting characteristics study of fluid on both transfer layer and template surfaces, achieving low adhesion to the template and high adhesion to the underlying substrate, and imprinting the material to check imprinting process life.

3. Results and Discussion

3.1 Original material characterization

The original imprint material was developed at the University of Texas at Austin. Low viscosity and small drop sizes are needed to achieve low pressure imprinting (< 1 psi), in-line fluid alignment, fast feature filling, pattern density insensitivity, and thin residual layers. Smaller liquid droplets tend to have faster evaporation rates due to higher surface to volume ratio. The evaporation rate of the original material was measured by sessile drop imaging technique. The evaporation curve is shown in Figure 3. The most volatile component in the original material is tert-butyl acrylate which is added at 37 part per hundred by weight. The curve suggests most of the tert-butyl acrylate is evaporated while the majority of other components are retained after 40 seconds. This inhomogeneous evaporation results in composition changes during the imprinting process and impacts the mechanical properties of the cured material adversely.

This composition change causes crosslinker concentration variation. The impact of crosslink density on curing speed was studied via real time FTIR technique. Figure 4 plots the disappearance of monomer as a function of UV exposure time. Increasing crosslink density will improve reaction rate, but too much crosslinker tends toward lower ultimate reaction conversion.

3.2 New improved materials

After addressing the inhomogeneous evaporation issue and incorporating several selective acrylic components, mechanical properties of new materials have been improved significantly. Figure 5 plots the elongation percentage verse tensile stress. Tensile modulus, elongation at break, and break stress have been improved from 80 MPa, 1-2%, 1-2 MPa for the original material to 400 MPa, 30%, 16 MPa for the new material. For the non-Si containing material, a primary and flexibilizer components are used along with crosslinker and UV initiator. The overall viscosity is maintained to be less than 5 cPs at room temperature. For the silicon containing material, the new silicon acrylic component is used in replacement of (3-acryloxypropyltristrimethylsiloxy)silane. Six new silicon containing acrylates and diacrylates have been synthesized. The Si containing material has to meet all the requirements of the non-Si material; in additional, it has to contain 10% or more Si by weight. New components were selected to balance the requirements of high Si content and good mechanical properties. The overall viscosity of Si containing material is also maintained to be less than 5 cPs at room temperature.

Following the successful improvement of mechanical properties, release performance of the template surface was studied next. The first generation tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane based SAM release layer lasts approximately one hundred imprints. To improve on this performance a new generation release layer has been developed; it can be regenerated multiple times. A four-point bending fixture [5] was adopted for the adhesion testing of release layer and other substrates. Two glass slides were laid in a cross direction pattern. Imprint material was cured in-between the slides. Four-point bending compression force was applied to separate the slides. The maximum force/load was taken as the adhesion value. The schematics are shown in Figure 6. Table 1 shows the adhesion values of imprint materials to both template and transfer layer surfaces. The new material has slightly better release performance than the original, while maintaining the high adhesion to the underneath transfer layer. The selective adhesion ratios, defined as imprint material-transfer layer/imprint material-template, are greater than 5 in both cases. Therefore, the new material achieves the desirable characteristics of both strong mechanical properties and high selective adhesion ratio. The imprint process life improvement is shown in Figure 7. Top SEM image relates to an early imprint (about 50th) of the original material in an imprinting run. The main cause of the early failure is attributed to the inhomogeneous evaporation. The performance of the new material is shown with the bottom SEM images of 50 nm lines. The same template and release layer were used through out this imprinting run. There is no visible feature degradation at the 440th imprints. Further process optimization allows MII to push the process life beyond 1557 imprints with the same template and release layer. 40 nm line SEM images are displayed in Figure 8.

To examine the uniformity of Si distribution through the bulk of imprinting material, XPS depth profile analysis was carried out (Figure 9). The depth profile started at the surface of the residual layer of Si containing material, and gradually moved into the non-Si containing underneath transfer layer. The Si

content is plotted in atom percentage, and the graph shows that Si is uniformly distributed through the bulk of the residual layer. The weight percentage of Si is 10% or higher.

Conclusions

The cohesive strengths of the solid imprint materials have been improved significantly. The new generation release layer can be regenerated multiple times, and has much better durability than the first generation tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane based SAM release layer. The new improved materials maintain good selective adhesion characteristics. Multiple materials are involved in the imprinting process. The full material sets have been developed to specifically address the issue of process life and defects. Combined with the transfer layer, the new materials can be tailored for wetting and adhesion optimization with minimum interfacial intermixing.

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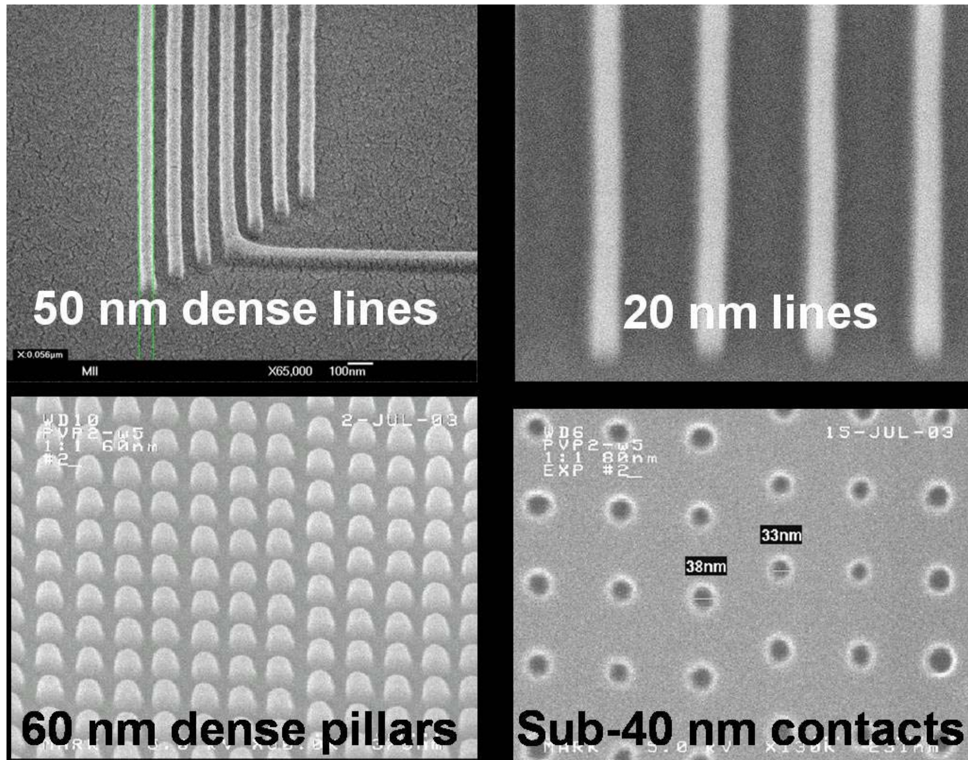


Figure 1: The S-FIL process resolution is at least 20 nm,
and appears to be only limited by the template fabrication process

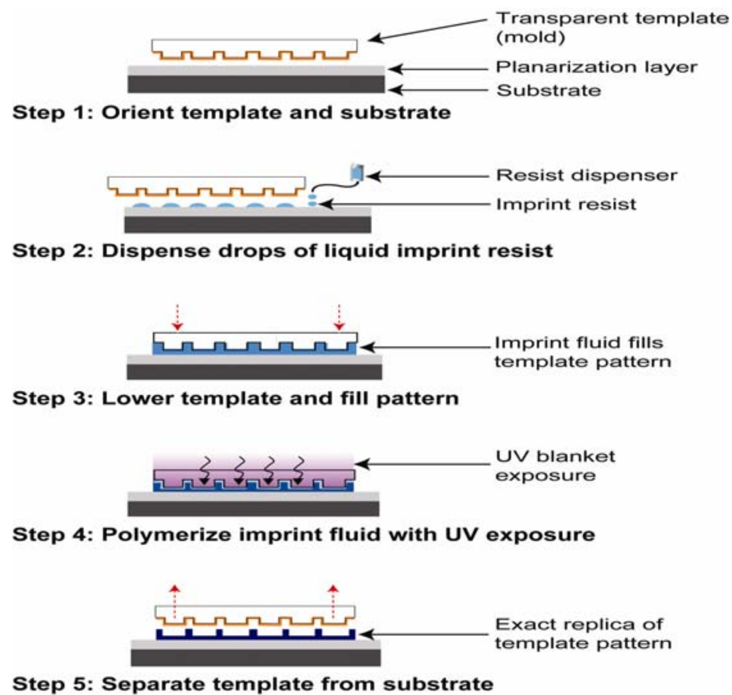


Figure 2: The S-FIL process steps

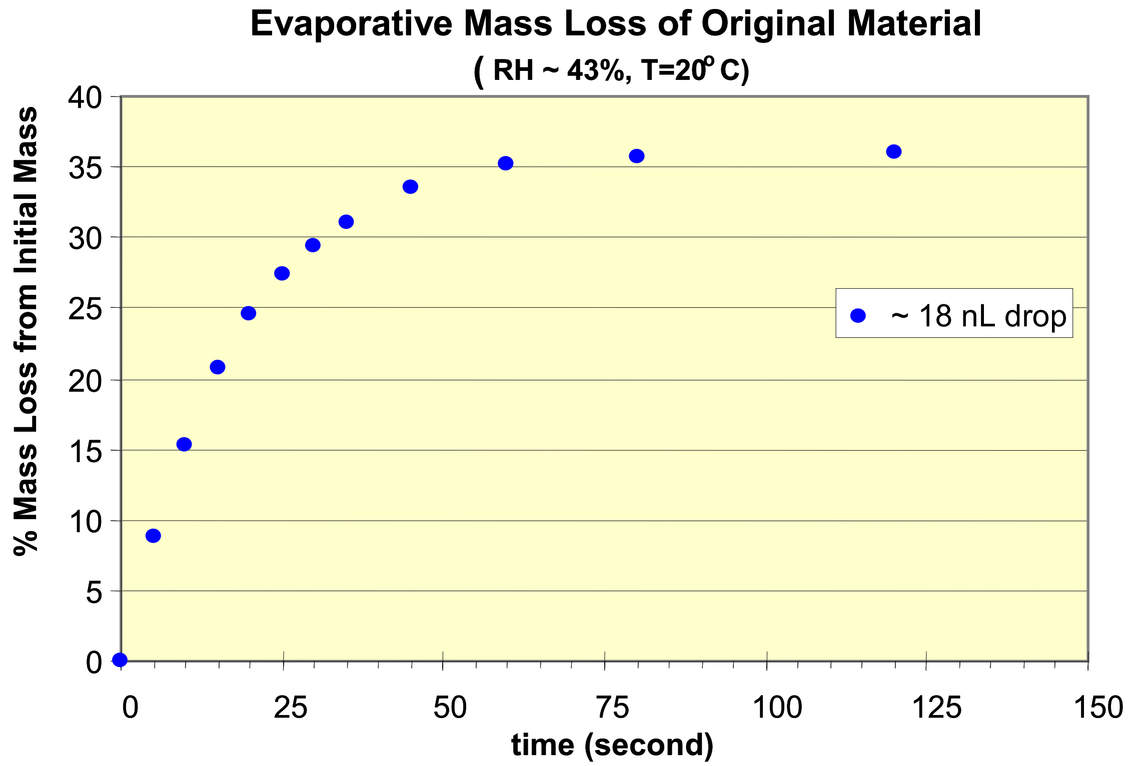


Figure 3: Evaporation Curve of the Original Imprinting Fluid

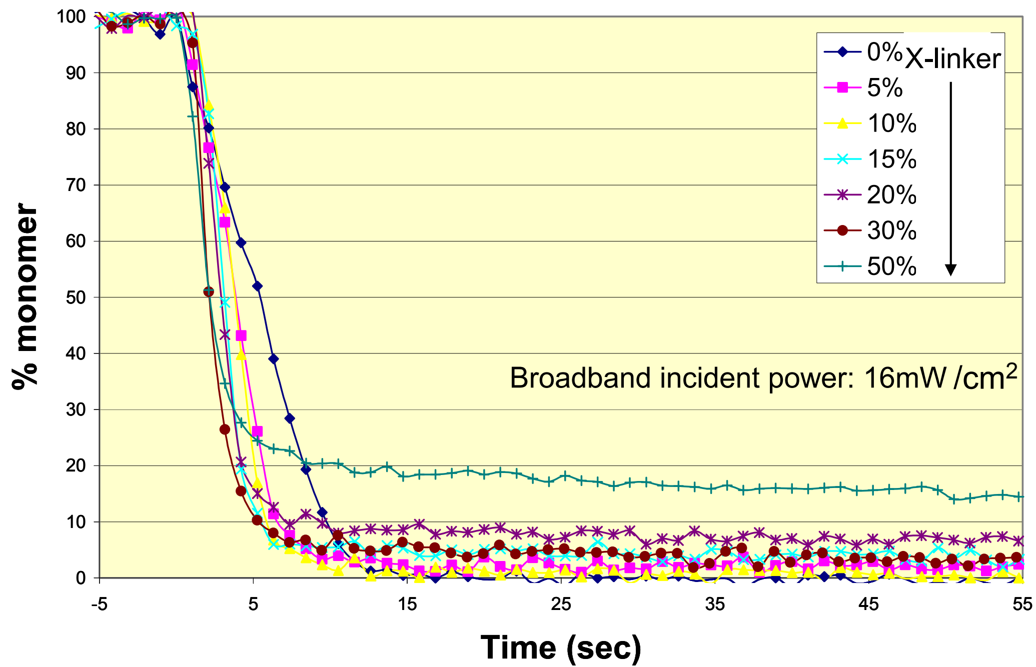


Figure 4: Impact of Crosslink Density on Curing Speed

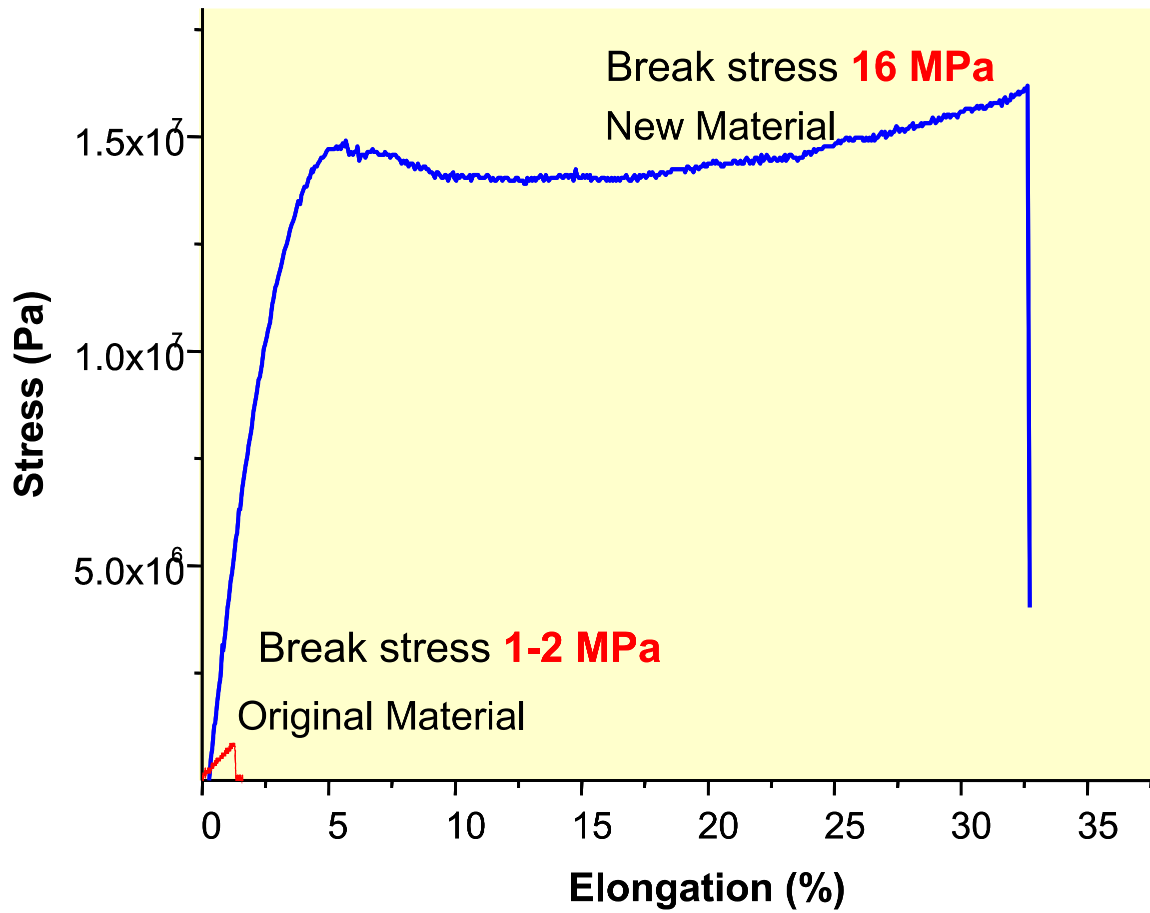


Figure 5: Stress Strain Curves of Cured Imprint Materials

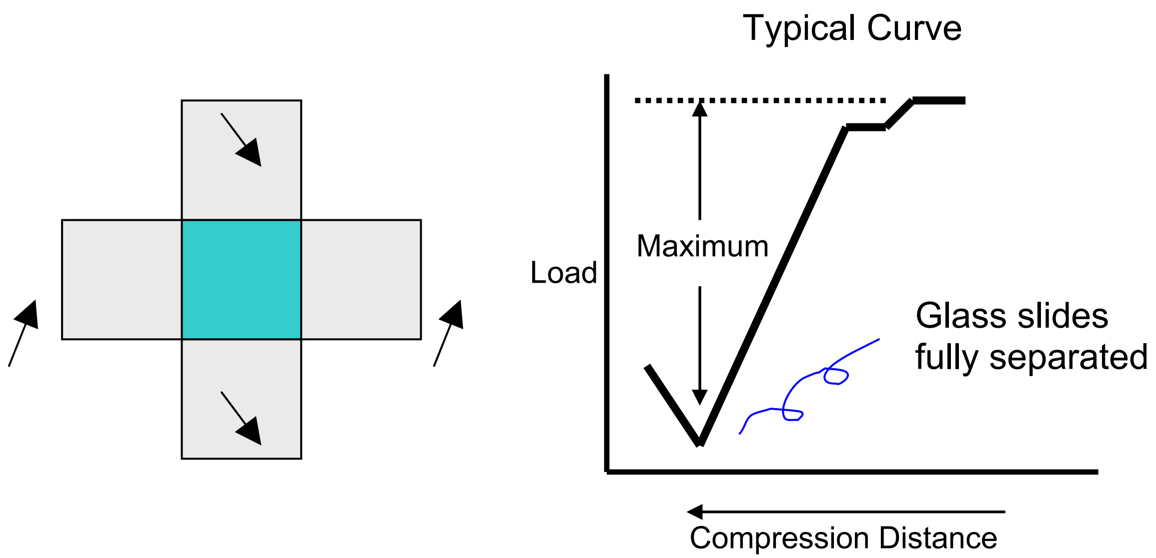
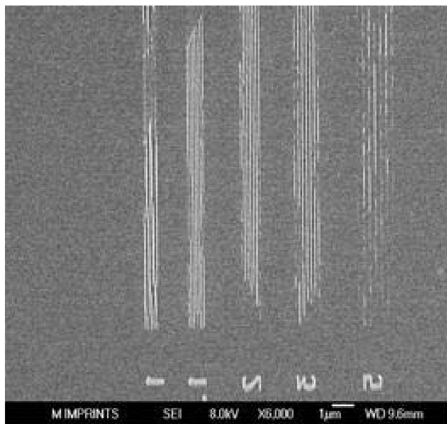


Figure 6: Four-point Bending Test for Adhesion Measurement

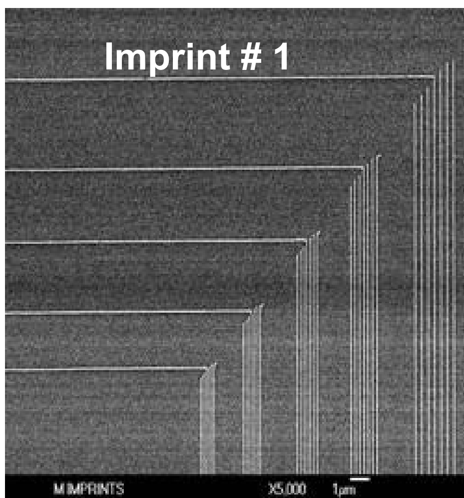
	Template / Solid Imprint	Transfer Layer / Solid Imprint	Selective Adhesion Ratio
Original Material	**1.1 lbf**	**7.7 lbf**	**> 5**
New Material	**0.95 lbf**	**8.2 lbf**	**> 5**

Table 1: Adhesions to Multiple Surfaces



Original Material
50 nm lines
Inhomogeneous evaporation

New Material
50 nm lines
Same template and release layer



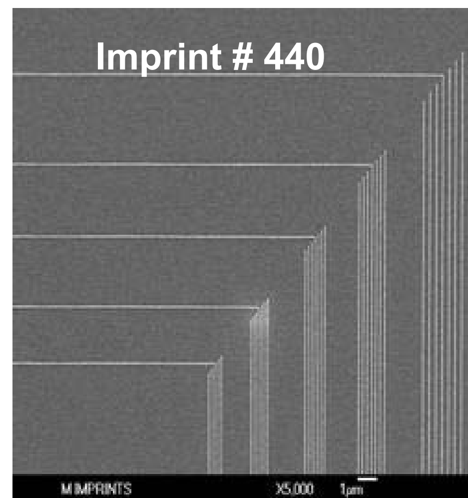
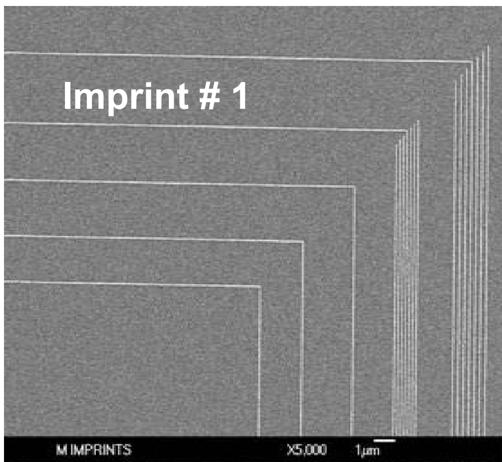
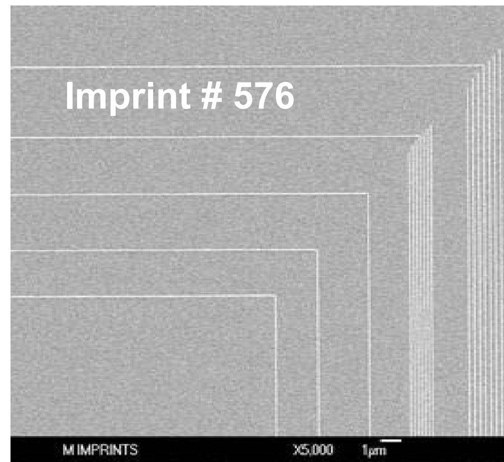
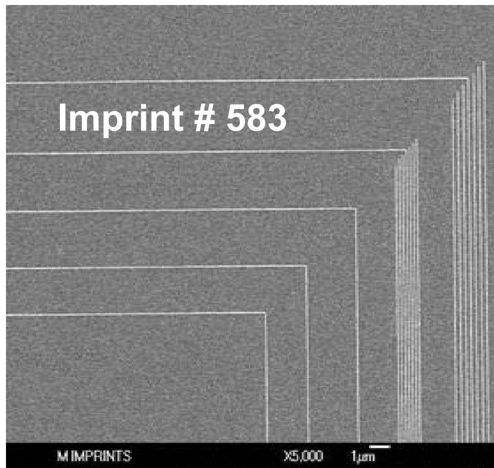


Figure 7: Process Life Improvements





40 nm lines



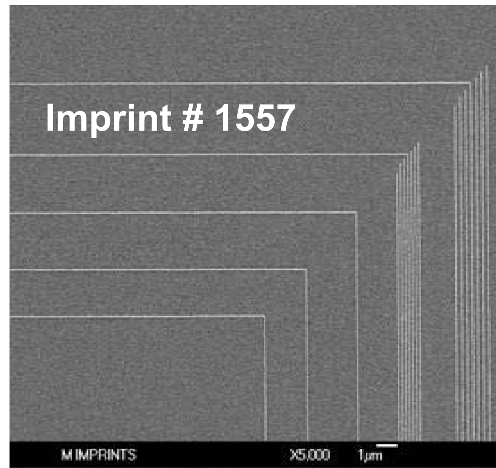


Figure 8: Further Process Optimization

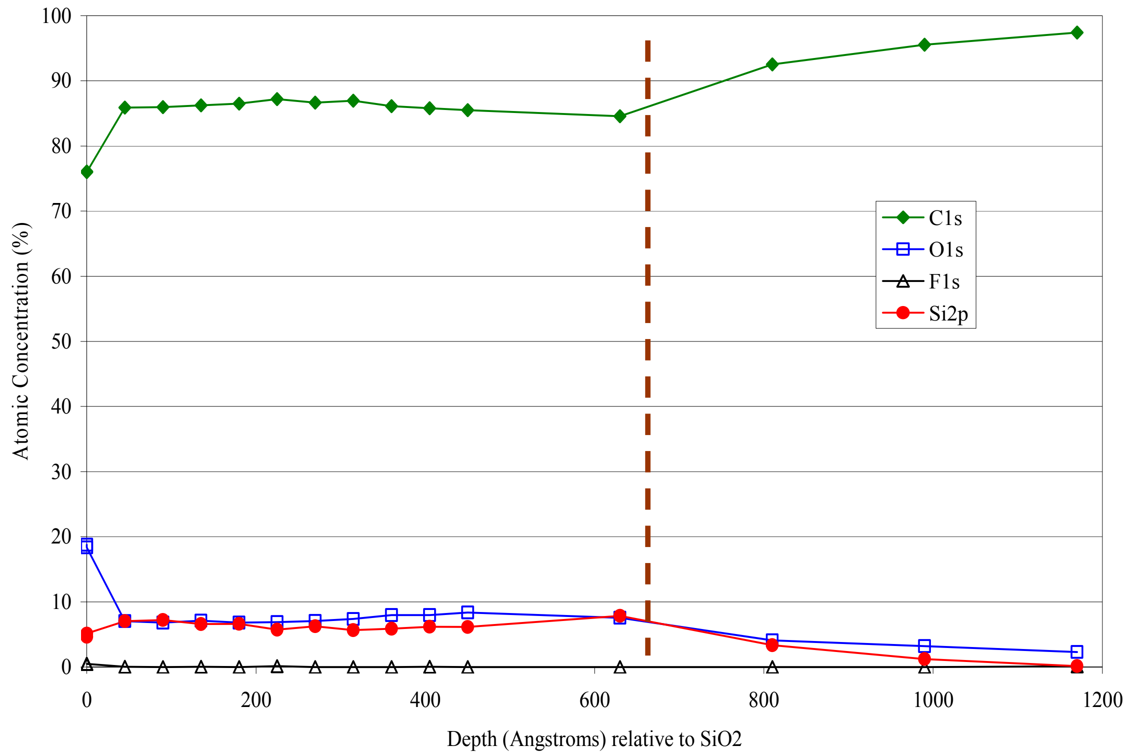


Figure 9: XPS Depth Profile of Si Containing Material