Step and Flash Imprint Lithography for sub-100nm Patterning

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Abstract

Step and **F**lash **I**mprint **L**ithography (**SFIL**) is an alternative to photolithography that efficiently generates high aspect-ratio, sub-micron patterns in resist materials. Other imprint lithography techniques based on physical deformation of a polymer to generate surface relief structures have produced features in PMMA as small as 10nm [1], but it is very difficult to imprint large depressed features or to imprint a thick films of resist with high aspect-ratio features by these techniques. SFIL overcomes these difficulties by exploiting the selectivity and anisotropy of reactive ion etch (RIE). First, a thick organic "transfer" layer (0.3μm to1.1μm) is spin coated to planarize the wafer surface. A low viscosity, liquid organosilicon photopolymer precursor is then applied to the substrate and a quartz template applied at 2psi. Once the master is in contact with the organosilicon solution, a crosslinking photopolymerization is initiated via backside illumination with broadband UV light. When the layer is cured the template is removed. This process relies on being able to imprint the photopolymer while leaving the minimal residual material in the depressed areas. Any excess material is etched away using a $CHF_3/He/O_2$ RIE. The exposed transfer layer is then etched with O_2 RIE. The silicon incorporated in the photopolymer allows amplification of the low aspect ratio relief structure in the silylated resist into a high aspect ratio feature in the transfer layer. The aspect ratio is limited only by the mechanical stability of the transfer layer material and the O_2 RIE selectivity and anisotropy. This method has produced 60nm features with 6:1 aspect ratios. This lithography process was also used to fabricate alternating arrays of 100nm Ti lines on a 200nm pitch that function as efficient micropolarizers. Several types of optical devices including gratings, polarizers, and *sub*-wavelength structures can be easily patterned by SFIL.

Keywords: imprint lithography, optoelectronic, polarizer, gratings

Introduction

Several imprint lithography techniques are being investigated as low cost, high throughput alternatives to conventional photolithography for high-resolution patterning [2-4]. Use of "classical" imprint lithography in manufacturing requires several considerations: i) pressures greater than 10MPa are typically required to generate the relief structures, ii) temperatures greater than the T_g of the polymer film must be used, iii) aspect ratios have been limited to ~3:1 except for certain low density patterns [5,6]. **S**tep and **F**lash **I**mprint **L**ithography (**SFIL**) benefits from its unique use of photochemistry, the low temperature, and pressure required to carry out the process. The high aspect ratio images that can be generated by this process are a consequence of the high etch contrast between the organosilicon and organic films in anisotropic, O_2 reactive ion etching.

Process Description

The SFIL process has been described previously [2]. In brief review, a substrate is coated with an organic planarization layer and brought into the proximity of a transparent, low surface energy template with a low aspect-ratio topography. A UV-sensitive organosilicon solution is deposited between the template and coated substrate. The template is then brought into contact with the substrate using minimal pressure. The template is then illuminated through its backside thereby crosslinking the organosilicon solution at room temperature. The template is separated leaving behind an organosilicon replica of the template relief on the planarization layer. This pattern is then etched

with a short halogen break-through, followed by an oxygen RIE to form a high-resolution, high aspect-ratio feature in the planarization layer.

The SFIL development program has proceeded down two parallel paths. An SFIL Stepper was developed to allow for production of multiple imprints on a single wafer. This machine is required to study the complexities of imprinting at minimal pressure with a rigid quartz template. At the same time, a collaboration with Agilent Technologies was established to develop an etch transfer process based on the Agilent imprint technique. The two versions of the SFIL process are shown below in Figure 1.

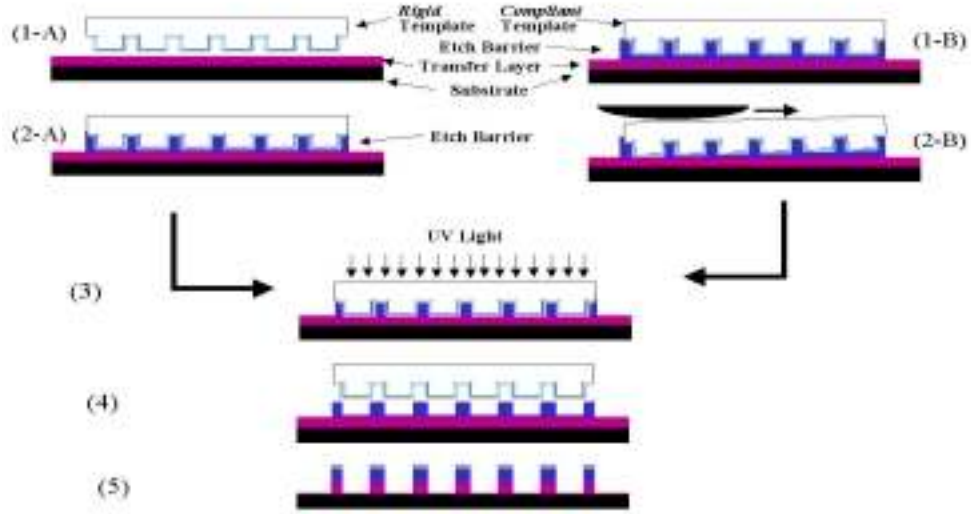


Figure 1. Step and Flash Imprint Lithography Process using a rigid template with the SFIL stepper(A) and using a compliant template with Agilent imprint equipment (B).

Experimental Description

A study was carried out to determine the weight percent of silicon that must be incorporated into the etch barrier formulation in order to achieve an acceptable etch rate ratio between the etch barrier and the transfer layer. Formulations with varying silicon content were prepared by mixing cyclohexyl acrylate (Aldrich) and (3-acryloxypropyl)-tris(trimethylsiloxy)silane (Gelest) with a constant 5wt% of 1,3-bis(3-methacryloxypropyl) tetramethyldisiloxane (Gelest). The mixtures ranged from 95wt.% cyclohexyl acrylate to 95wt.% (3-acryloxypropyl)-tris(trimethylsiloxy)silane. A 1:1 mixture of bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819, Ciba) and 1-benzoyl-1-hydroxycycloxhexane (Irgacure 184, Ciba) were added to the above solution at 3wt.% to initiate free radical polymerization upon UV illumination. For ~30wt.% silicon samples, acryloxypropylmethsiloxane-dimethylsiloxane copolymer (UMS-182,Gelest, Inc) was used. The UV free radical initiator was a 1:1 mixture of Irgacure 184 and Irgacure 819 added at 3wt.% of the UMS-182 and diluted in cyclohexanone.

Two model organic films were used during the RIE studies: polystyrene and poly(methyl methacrylate) (PMMA). Polystyrene with a molecular weight of 50,000 was diluted 1:10 by weight in Toluene then spin coated at 4000 revolutions per minute (RPM) for 60 seconds and baked at 90°C for 90 seconds. PMMA with a molecular weight of 496,000 was diluted 1:10 in chlorobenzene was spin coated at 4000 to 6000 RPM for 60 seconds depending on desired thickness then hard baked at 200°C for 4 minutes under vacuum.

An MRC parallel plate, capacitively coupled reactive ion etcher with 6″ grounded electrode, 6″ driven lower electrode, and a 2" electrode gap was used. The substrate rested on a ¼″ thick 6″ diameter quartz plate. The etch rates were measured using *in-situ* HeNe interferometry and validated by both pre-etch and post-etch two-angle ellipsometry and profilometry measurements.

The etch conditions for oxygen RIE were 40 standard cubic centimeter per minute (sccm) O_2, and 200 V at 20 mTorr. This etch was approximately 80% anisotropic providing the degree of undercut necessary for subsequent metal lift-off. The halogen etch conditions were 56 sccm CHF_3, 12.5 sccm He and 450V at 6mTorr. For the high resolution

etch transfer process, the undercut was reduced by lowering the O_2 etch pressure to 6mTorr. The high resolution halogen etch conditions were 56 sccm CHF_3, 12.5 sccm He, 1.0 sccm O_2, and 450V at 6mTorr.

At Agilent, master templates were prepared on a Si or GaAs substrate using in PMMA resist with a JEOL electron beam lithography tool. These templates were used to generate daughter templates by replicating the relief in J-91 (Summer) polycarbonate. The daughter templates were then coated with ~10nm of a fluorinated film deposited in a C_3F_8 plasma deposition chamber at 500 mTorr and 100W. The water contact angle was greater than 90° after deposition.

A droplet of etch barrier, detailed previously, was placed on the wafer prior to bringing the template into proximity of the substrate [2]. The solution wicks the template as it was brought into contact with the planarization layer. The etch barrier was cured while under approximately 2 psi compression. Pressure could not be applied during exposure at Agilent. Consequently, the etch barrier formulation used was primarily 95wt.% UMS182:5wt.% free radical generator. This mixture was diluted in cyclohexanone, spin coated for 60 seconds at 4000+ RPM onto the substrate to generate a liquid film 100nm to 500nm thick. This film was then imprinted according to the process shown in Figure 1 (1.1-B through 1-5).

Results and Discussion

Ideally, in SFIL, the etch barrier is completely displaced, but in practice, some undisplaced etch barrier, called the base layer, always remains after imprinting. Four kinds of base layer thickness variations are shown in Figure 2. An analysis of the displacement predicts that a 1cP fluid, such as the etch barrier used in SFIL, will be displaced to a thickness of 100nm with as little as 2 PSI in a matter of seconds [3]. Using the SFIL method described in Figure 1(1.1-B through 1.5), the base layer thickness was measured to be less than 55nm after cure. Figure 3a shows an SEM of such a base layer. The base layer for this sample ranges from <10nm to 80nm thickness measured across a 1"x1" patterned region based on two angle ellipsometry (shown in Figure 3b). This is quite extraordinary considering that the templates utilized ~1% patterned area meaning that 99% of the solution had to be displaced. These thin base layers allow for the etch process to amplify the low aspect ratio relief into high aspect ratio features, but the oxygen etch transfer process also required development.

An etch study designed to measure the effect of silicon content on etch rate was conducted in which the composition of the etch barrier formulations were varied from almost entirely organic to 30wt.% silicon. The etch rate was measured in both halogen and oxygen RIE using *in-situ* HeNe interferometry and initial and final thicknesses were collaborated by both two angle ellipsometry and profilometry. Figure 4 shows that the etch barrier must contain greater than 11wt.% silicon to achieve the ~15:1 O_2 etch selectivity required for the transfer etch. The etch barrier solutions therefore contain a minimum of 15wt.% silicon. It was found that lowering the pressure from 20mT to 6mT during the O_2 etch further improved the selectivity to 80:1 as well as reduce undercut.

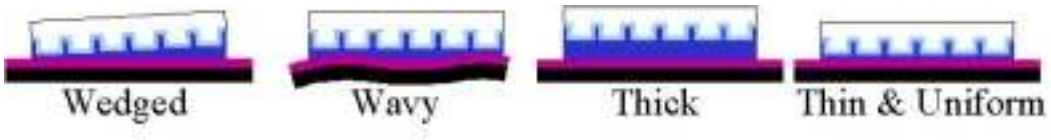
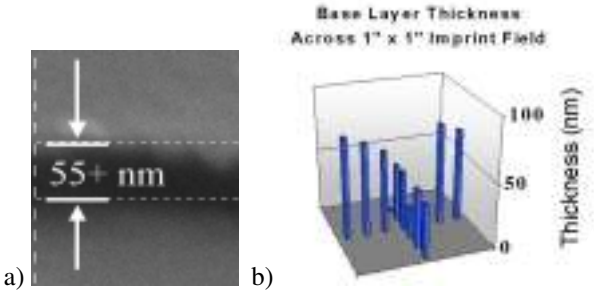


Figure 2. Several types of base layers are shown. Only the thin uniform base layer allows for successful etch transfer over the entire imprint field.



a) b)

Figure 3. a) SEM of 55+nm base layer using polycarbonate template. b) Base layer across a 1" x 1" patterned region measured with ellipsometry.

The RIE process consisted of a 20-second halogen "break-through" etch that removed the thin base layer and the O_2 "amplification" etch used to generate the high aspect ratio. The 20-second $CHF_3/He/O_2$ break-through etch removes ~20nm of etch barrier. After which the anisotropic O_2 transfer etch amplified the low aspect ratio relief structure in the imprinted silicon photopolymer into a high aspect ratio feature in the transfer layer.

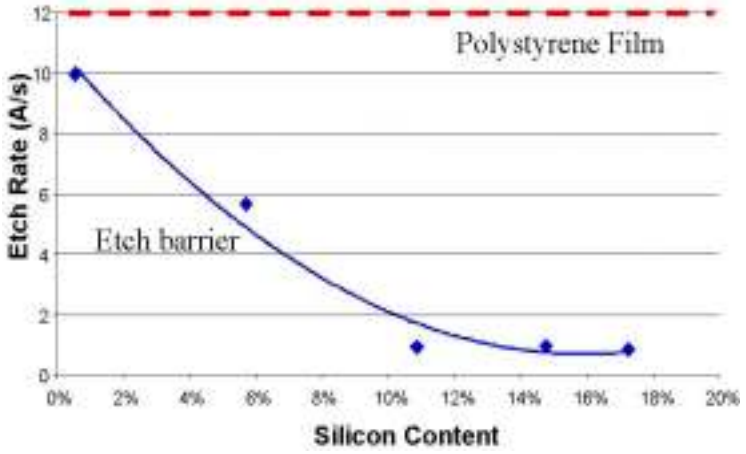


Figure 4. Etch rate of etch barrier (solid line) compared to a polystyrene film (dashed line) during O_2 etch. The etch was conducted with 40 sccm O_2 at 20mTorr and applied voltage of 250V (33W).

A high resolution template was created using a single pass e-beam exposure in 100nm of PMMA. The result was a master with ~60nm features that was etched ~50nm deep. A daughter template was replicated from this master on polycarbonate. Wafers were coated with 300 nm of hard baked PMMA and patterned with these 60nm features. A short 20 second halogen break-through etch and a O_2 transfer etch generated 60nm features with 6:1 aspect ratio and the slight under cut demanded for lift-off metalization. On a separate sample, Ti was deposited on 100nm structures at a rate of 2.5nm/s in a metal evaporator. The Ti metal lines remained after acetone lift-off in an ultrasonic bath. Figure 5b shows 100nm metal lines patterned by this technique with a 100nm line and space (L/S) template. The height of the metal lines is 50nm.

a) b)

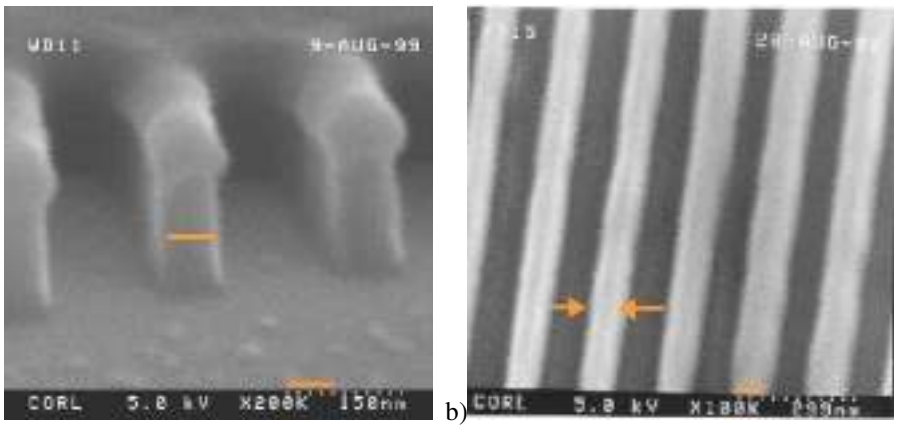


Figure 5. a) 60nm features etched through 350nm. b)100nm Ti metal lines created using metal lift-off and SFIL.

A high resolution template with an array of alternating regions of horizontal and vertical 100nm L/S was replicated, etch transferred, and used to perform metal lift off as before. The result is the alternating array of micropolarizers shown in the optical micrograph of Figure 6. These alternating arrays pass a single polarization of light. Figure 6a was taken with polarized light show the desired alternating light and dark regions.

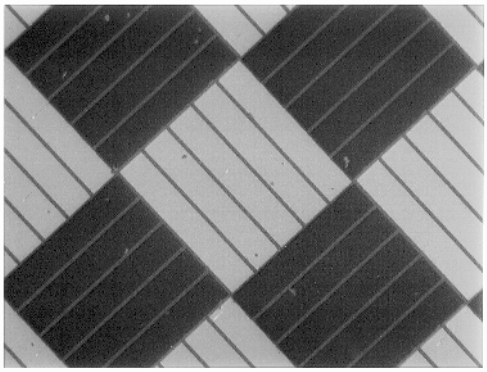
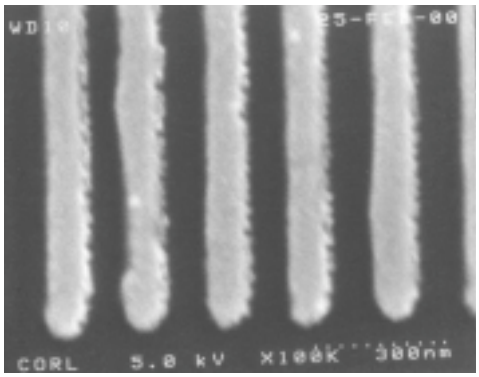
a)  b) 

Figure 6. a) Optical micrograph of a micropolarizer array illuminated with polarized light. b) SEM of the micropolarizer metal lines

Conclusions

Step and Flash Imprint Lithography is capable of high resolution patterning at room temperature with minimal applied pressure. The low viscosity photopolymer formulation used in this process is readily displaced resulting in base layers less than 55nm thick with under 2psi of contact pressure. Step and Flash Imprint Lithography has been successfully applied to the patterning of 60nm lines with 6:1 aspect ratio. Using metal lift-off, we have successfully patterned 100nm metal L/S arrays and demonstrated their utility as a micropolarizer array.

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