

# Advances in 2D and 3D Patterning for Nanotechnology

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## Abstract:

The controlled creation of nanometer scale structures in 2 and 3 dimensions is of increasing interest in many applications ranging from biotechnology to nanotechnology. This paper will discuss new approaches for the construction of small-scale structures using methods based on advanced chemically amplified lithography. New tools derived from 2 photon processes for the formation of complex images and the development of patterned structures will be described. Finally in the production of 3 dimensional patterns, the possible role of self-assembly coupled to lithography will be examined. Photodefinable block copolymers with erodable microstructures have been successfully used to form mesoporous materials.

## Introduction:

Lithography and the processes associated with it are the backbone of the nanotechnology revolution. Several developments are occurring simultaneously: a drive to reduce minimum feature size for advances in microelectronics, the use of lithographically patterned structures to prepare devices for photonics, biotechnology and other forms of nanotechnology and finally the drive to create 3-dimensional structures for device and new materials creation.

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The fabrication of increasingly smaller feature sizes for integrated circuits requires advanced lithographic techniques with high resolution [1-3]. In the recent past, researchers invented the concept of chemical amplification in lithography [3]. This process uses the generation of acid by a UV sensitive small molecule, a photoacid generator (PAG), followed by deprotection of the photopolymer. The resulting change in polarity from a non-polar, base insoluble polymer to a deprotected, base soluble polymer provides a remarkable solubility change that permits their use as high resolution resists that are now capable of producing submicron features. This approach has been used in the work reported here.

Resolution enhancement techniques, using optical proximity correction or phase-shift masks, have demonstrated that fabrication of sub-wavelength feature sizes at 248 nm and 193 nm are possible [3]. However, a fundamental solution for enhanced resolution would be to develop lithographic techniques using shorter exposure wavelengths to avoid complexities involved in resolution enhancement methods. Therefore, with recent improvements in laser technology and optical materials, lithography at 157 nm using an F<sub>2</sub> excimer laser light source has emerged as the current choice for post-193 nm technology in the fabrication of devices with feature sizes less than 100 nm [4].

In an effort to develop single-layer resists for 157 nm lithography, we have exploited a variety of fluorocarbon containing polymers mainly focusing on non-norbornene backbones [4-7]. In the course of screening conventional acrylic and styrenic resist backbones as potential materials for 157 nm applications, it was found that the transparency of even conventional resist platforms can be significantly enhanced at 157 nm by judicious modification of highly absorbing groups such as aromatic or carbonyl [7], and similar results were also confirmed by others [8]. In the first section of this paper, we report our strategy to develop single-layer resists highly transparent at 157 nm using modified conventional resist backbones such as acrylic and styrenic backbones.

Three-dimensional microfabrication has a wide range of possible applications for micromachining structures such as light-waveguides, microfluidic devices, MEMS and data storage. Two-photon lithography not only allows the fabrication of structures that cannot be constructed by conventional single-photon lithography but also exhibits greater spatial resolution than other three-dimensional microfabrication techniques as they are currently practiced [9,10]. Two-photon lithography is based on the concept that under sufficient illumination intensity, electronic transitions that would normally require absorption of one UV photon for excitation can be accomplished by simultaneous absorption of two IR photons. When this high intensity IR light enters a photoactive material, the excitation reaction is confined to a focal point at a precise depth in a substrate. This occurs because, firstly, the photoactive material is transparent to IR light. Very little absorption occurs in the out of focus area to attenuate the light intensity. Secondly, the quadratic dependence of two-photon absorption on the incident intensity ensures confinement of the absorption to very small volumes.

The idea of applying two-photon excitation to microfabrication was initially demonstrated by Webb and coworkers on a conventional lithographic photoresist system [11]. Efforts have also been devoted to the development of high efficiency two-photon dyes and sensitizers [12,13]. Initial fabrication of three-dimensional microstructures has been accomplished by polymerization of liquid resin systems [12-14], but volume shrinkage and warping of solid images formed in these processes has been identified as a weakness of these methods. Little research has been carried out to identify a more suitable system for three-dimensional microfabrication. In the second section of this brief report we describe the creation of micron scale microfabricated 3D structures using 2-photon activated chemically amplified resists.

The synthesis of even smaller scale 3D structures is a target of modern materials science because of the important applications of these materials such as selective filtration membranes or catalyst supports. Ideally, the material self-assembles and through variations in composition allows selection of specific pore geometries and

sizes in the 10 – 100 nm range, preferably with a monodisperse pore size distribution. The microstructures observed in block copolymers therefore provide an attractive route for formation of nanoporous materials, provided that one of the blocks is easily removed after assembly of the mesophase.

Block copolymer lithography is a developing field to pattern controlled nanometer-sized objects such as quantum dots. Several kinds of organic block copolymers [15] and organic-organometallic block copolymers [16,17] have been utilized to form thin films containing periodic arrays of nanodomains suitable for nanolithography. To make the idea more versatile, we have designed a block polymer system that combines photolithographic and nanolithographic techniques to make micron-sized patterns having nanometer sized pores in them. In contrast, 157 nm photolithography is expected to be able to resolve up to 40 nm features. Even electron beam lithography can be used to produce features as small as 30 nm. Despite such progress, the use of photopatternable block copolymers can achieve features that are currently impossible with existing photolithographic techniques such as DUV lithography.

In the final section, this paper describes a unique photopatternable block copolymer based on poly( $\alpha$ -methylstyrene-*b*-4-hydroxystyrene) (PMS-*b*-HS). PHS is a negative-tone photoresist when a crosslinker (CL) and a photoacid generator (PAG) are used in combination. UV irradiation produces a strong acid as a result of the photochemistry of the PAG, and the acid catalyzes crosslinking between PHS and the CLs, rendering the exposed regions insoluble. Since the Tg of PHS itself is ~180 °C, crosslinked-PHS can be used as a continuous matrix. Through controlled depolymerization of  $\alpha$ -methylstyrene nano-sized holes in micron-sized patterns can be prepared by photolithography.

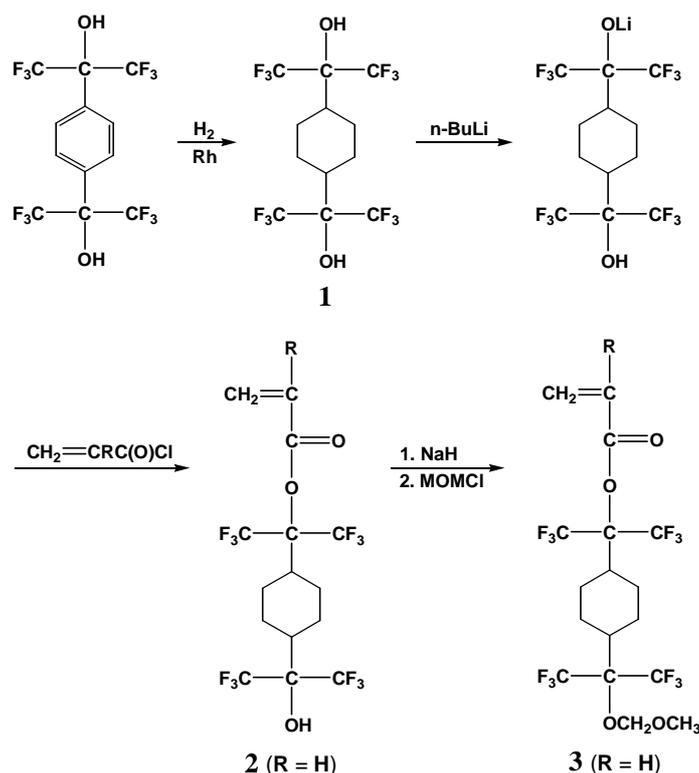
## **Experimental:**

### ***157 nm Resist Materials:***

**Synthesis of 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane (1), see Scheme 1.**

1,4-Bis(2-hydroxyhexafluoroisopropyl)benzene (24.6 g, 0.06 mol), dissolved in 70 mL of 2-propanol, was placed in a Parr reactor and to this was added 3 g of a supported rhodium catalyst (5 wt% on carbon powder) [18]. Hydrogenation reactions were typically run overnight under ~600 psi of hydrogen at 130 °C. Upon completion, the heterogeneous solution was filtered to remove the catalyst and the 2-propanol solution was concentrated. The product was purified by fractional distillation at 58–60 °C (0.02 mmHg) to give 23.1 g of 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane as a clear oil (93% yield).

**Synthesis of 2-[4-(2-hydroxyhexafluoro-isopropyl) cyclohexane] hexafluoro isopropyl acrylate (2).** To a solution of **1** (30.0 g, 0.07 mol) in 100 mL of dry THF, was added 45 mL of 1.6 M n-butyllithium (0.07 mol) under nitrogen over a period of 30 min. After 2 h, the resulting solution was treated during 30 min by the dropwise addition of acryloyl chloride (6.5 g, 0.07 mol) dissolved in 100 mL of dry THF. The resulting solution was stirred overnight at room temperature and hydrolyzed by the addition of 100 mL of distilled water. The aqueous phase was extracted with ethyl ether, and the combined organic phase was dried over MgSO<sub>4</sub>. The crude product was purified by column chromatography and recrystallization to yield 15.9 g (49% yield): mp 85–86.4 °C.



Scheme 1. Synthesis of Monomers **2** and **3**

**Polymerization.** Radical polymerization of HFIPA-functionalized monomers was carried out using 2,2'-azobisisobutyronitrile (AIBN) in THF at 70 °C. The calculated amounts of monomers, solvent, and initiator were charged into the polymerization tubes, which were then immersed in a Dewar flask containing liquid nitrogen. After three cycles of freeze-thaw treatment under N<sub>2</sub>, the tubes were sealed and placed in an oil bath at 70 °C for 24 h. Polymers were recovered by precipitation into distilled water twice and dried in vacuum at 50 °C.

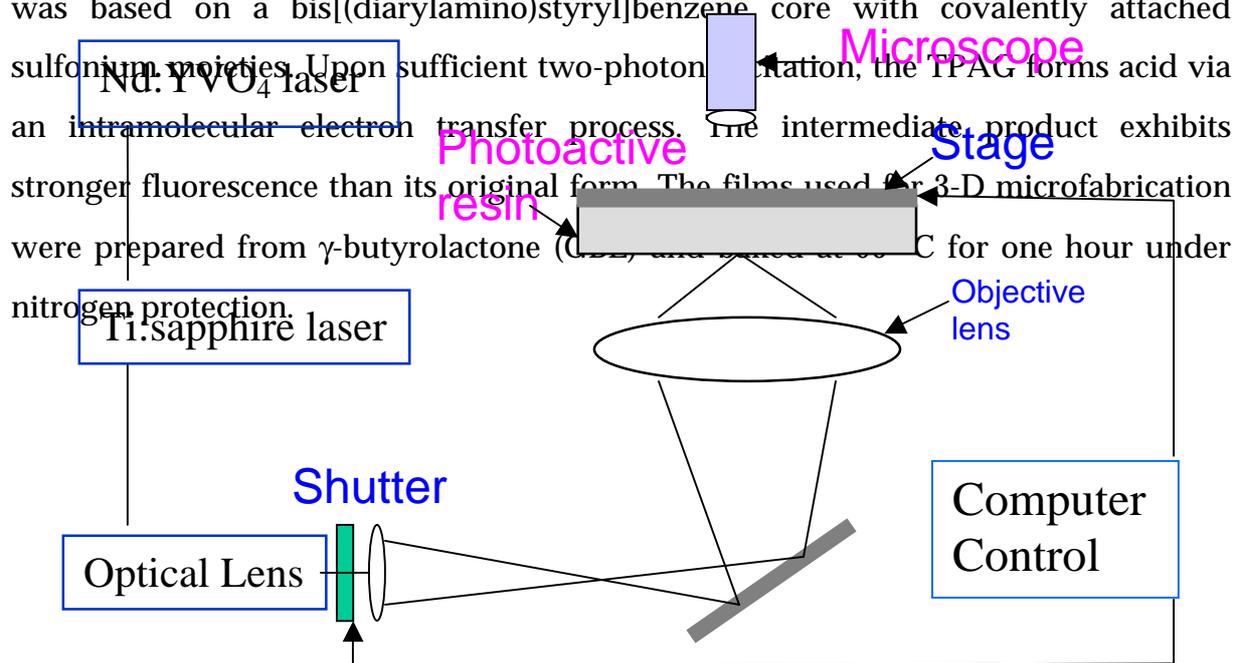
**Instrumentation.** IR spectra of samples were measured with a Mattson Infinity Gold series FTIR as thin films coated on silicon wafer. <sup>1</sup>H and <sup>19</sup>F NMR spectra were measured in CDCl<sub>3</sub>. Spectra were recorded on a Varian Inova-400 spectrometer. <sup>1</sup>H NMR spectra were measured at 400 MHz. Proton decoupled <sup>19</sup>F NMR spectra were recorded at 376 MHz. <sup>1</sup>H chemical shift (δ) was referenced to a selected resonance of residual protons in the solvent employed. Optical spectra of the polymer films were recorded on a VU-301 vacuum ultraviolet variable angle spectroscopic ellipsometer (VUV-VASE) instrument (J. A. Woollam Co.) at International SEMATECH. Samples

for VUV-VASE measurements were prepared by spin-coating resists on a silicon wafer, primed with hexamethyldisilazane (HMDS) gas, followed by soft-bake at 115 °C for 120 sec.

**Lithographic Processing.** Exposure at 248 nm was carried out using a Nikon 248 nm stepper (NA = 0.42,  $\sigma = 0.5$ ) equipped with a KrF excimer laser (Cymer CX-2LS). Copolymers were dissolved in propylene glycol methyl ether acetate, and to the solution was added a photoactive compound. The resist solution was filtered through a 0.2  $\mu$ m membrane filter and spin-coated onto silicon wafers that are either primed with HMDS gas or treated with antireflective coatings. Post-apply bake (PAB) and post-exposure bake (PEB) was carried out at 90~130 °C,. The film thickness was measured on a Tenkor P-10 Surface Profiler and developed patterns were imaged with a Leo 982 (Zeiss) scanning electron microscope (SEM). Imaging experiments at 157 nm were carried out at International SEMATECH using an Exitech 157 nm Microstepper (NA = 0.6,  $\sigma = 0.7$ ).

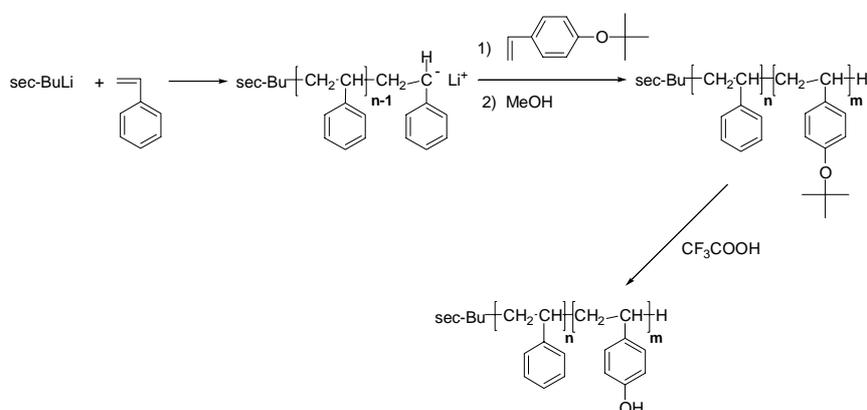
**2-Photon Lithography:**

Three-dimensional fabrication was carried out using thick polymeric films (~50  $\mu$ m). A resin system was created by blending 4wt-% of the two-photon acid generator into the above-synthesized copolymers. The two-photon acid generator (TPAG) used here was based on a bis[(diarylamino)styryl]benzene core with covalently attached sulfonium moieties. Upon sufficient two-photon excitation, the TPAG forms acid via an intramolecular electron transfer process. The intermediate product exhibits stronger fluorescence than its original form. The films used for 3-D microfabrication were prepared from  $\gamma$ -butyrolactone (GBL), and baked at 80 °C for one hour under nitrogen protection.



**Exposure and Development:** Exposures were performed using a two-photon microscope (see Fig. 1) incorporating a mode-locked Ti: sapphire laser pumped by a frequency doubled Nd:YVO<sub>4</sub> laser (Spectra-Physics Millennia). The Ti:Sapphire repetition rate is 82 MHz and the pulse width on the exciting laser is typically  $80 \pm 10$  fs. At the sample, group-velocity dispersion may cause the pulses to broaden to as much as 150 fs. The PAG was excited at 745nm. The samples were mounted upside down on a computer-controlled stage. The incident beam was focused through an oil-immersion objective with a numerical aperture of 1.4. By scanning the laser beam's focal point through the film, 2- and 3-dimensional patterns can be defined. The exposure dose is the combination of laser power and stage's linear scan speed. After exposure, the film was post-baked at various temperatures and developed in 0.26N tetramethylammonium hydroxide (TMAH) aqueous solution directly monitored under optical microscope except for sensitivity comparison experiments where the development time was fixed at 1min.

***Lithographic Processing Of Block Copolymers of Poly( $\alpha$ -methylstyrene-*b*-4-tert-butoxystyrene) (PMS-*b*-tBuS):***



Scheme 2.

**Poly( $\alpha$ -methylstyrene-*b*-4-tert-butoxystyrene) (PMS-*b*-tBuS) Block Copolymer**

Monomers,  $\alpha$ -methylstyrene and 4-tert-butoxystyrene, were distilled from  $\text{CaH}_2$  and dibutylmagnesium successively under high vacuum prior to use. PMS-*b*-tBuS was synthesized by sequential anionic polymerization in THF at  $-78^\circ\text{C}$ , with *sec*-butyllithium as the initiator. The PMS block was polymerized first for 3.5 hrs and an aliquot of poly( $\alpha$ -methylstyryllithium) was isolated and terminated with degassed

methanol. The PtBuS was then introduced into the reactor and the reaction was terminated with degassed methanol after 12 hrs.

### **Poly( $\alpha$ -methylstyrene-*b*-4-hydroxystyrene) (PMS-*b*-HS) Block Copolymer**

The reaction used for the synthesis of PMS-HS block copolymer is shown in Scheme 2. The PMS-*b*-tBuS block copolymer was converted to PMS-*b*-HS by reaction with trifluoroacetic acid. The block copolymer was first dissolved in dichloromethane, and 10 molar excess trifluoroacetic acid was added. The mixture was reacted at r.t. under an atmosphere of nitrogen for 24 hrs. The polymer was precipitated into hexane and underwent dissolve-precipitate cycle from THF solution to methanol/water (1:1 v/v) mixture twice and dried in vacuum oven for 2 days.

### **Results and Discussion:**

Protected phenols and carboxylic acids are employed as indispensable structural units in the design of conventional resists [1,19]. Deprotection of these protected acidic functions by photochemically generated acid creates large dissolution selectivity between exposed and unexposed areas in an alkaline developer. This renders possible the delineation of mask patterns on the silicon wafer surface. Kunz et al. reported that conventional resists containing such acidic functions must be less than 60 nm thick to achieve an optical density of 0.4, which is required to produce a vertical resist wall profile, at 157 nm [20]. Since this is due to the strong absorbance of aromatic and carbonyl groups at this wavelength, the incorporation of transparent acidic functions within a polymer backbone has been an overriding concern in the resist design for 157 nm lithography.

It has been reported that fluorine-containing polymers are highly transparent at 157 nm and fluorocarbinols, with  $pK_a$  values comparable to those of phenols, can be used as acidic functional groups in the design of chemically amplified and aqueous base developable resists [21,22]. Przybilla et al. [21] introduced hexafluoroisopropyl alcohol (HFIPA) as an alternative acidic group in the design of polystyrene-based resists and dissolution inhibitors for a 248 nm applications, and further extension to 193 nm resist design was made by Ito et al. [22] during the preparation of

poly(norbornene sulfone)-based resists. In both cases, HFIPA was incorporated using hexafluoroacetone, and this acidic alcohol was protected by a *tert*-butoxycarbonyl group. Although the poor dry etch resistance of poly(norbornene sulfone)-based resists limits their practical use for lithography, it is notable that, when HFIPA-substituted norbornene is used in the alternating copolymerization with sulfur dioxide, the resulting copolymer exhibits high transparency at 157 nm with an absorbance of  $\sim 3 \text{ m}^{-1}$  [23]. Since this unusual transparency arises from the presence of HFIPA, norbornene HFIPA-substituted norbornene monomers have been actively investigated as transparent building blocks in the design of novel resists for 157 nm lithography [23-26].

**Tailoring Transparency of Polyacrylates at 157 nm.** Our strategy to prepare highly transparent resist platforms at 157 nm involves the incorporation of the highly fluorinated building block, 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane (**1**), that has two HFIPA functional groups, into various acrylic monomers as shown in Scheme 1. This scheme allows the straightforward synthesis of various HFIPA-containing acrylic monomers where R is H, CH<sub>3</sub>, F, or CF<sub>3</sub> using a corresponding acid chloride. The highly fluorinated building block, **1**, was prepared by simple hydrogenation of 1,4-bis(2-hydroxyhexafluoroisopropyl)benzene using a supported rhodium catalyst (5 wt% on carbon powder) [18]. Using Scheme 1,  $\sim 50\%$  yield was obtained on the basis of **1**, and the separated product by column chromatography included 52.2 mol% of **2** (R = H), 15.5 mol% of diacrylate, and 32.3 mol% of **1**. The protection reaction of the HFIPA group in monomer **2** was carried out using methoxymethyl chloride to yield monomer **3** (R = H) with an acid labile methoxy methyl group.

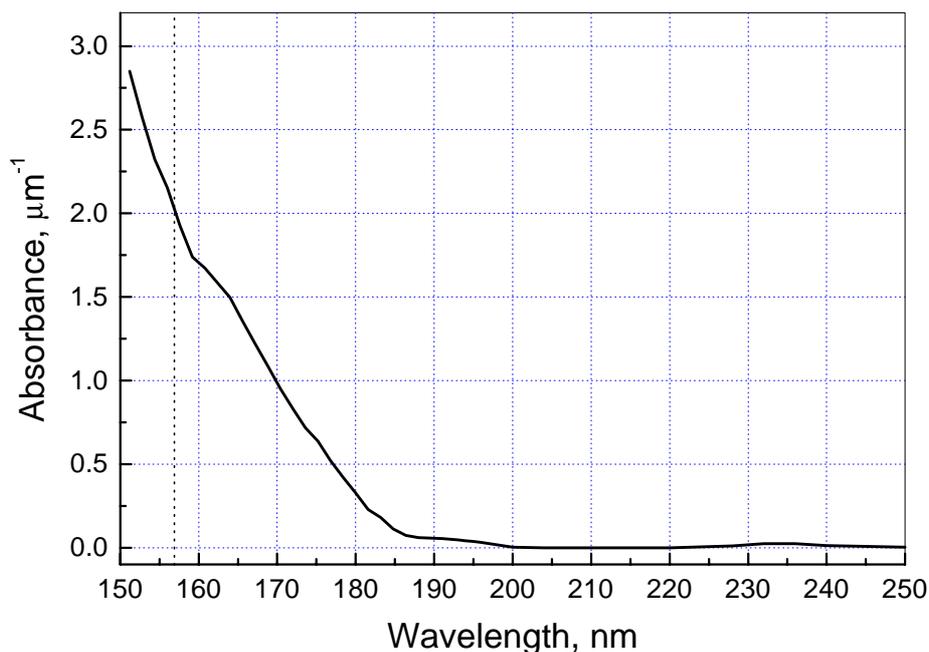


Figure 2. VUV/VASE Results from Poly(2).

In order to examine the effect of a fluoroalkyl group on the absorbance of the acrylic backbone, monomer **2** was polymerized by simple radical polymerization and the absorbance of the resulting poly(**2**) was measured using VUV-VASE. As shown in Figure 2, poly(**2**) exhibited unusually high transparency at 157 nm and the absorbance at this wavelength was found to be  $1.93 \text{ m}^{-1}$ . Although this is the lowest absorbance value reported for polyacrylates, further decrease in absorbance can be easily achieved by replacing the  $\alpha$ -hydrogen in poly(**2**) with an  $\alpha$ -fluorine or an  $\alpha$ -trifluoromethyl group. Since Willson et al. reported that poly(methyl  $\alpha$ -trifluoromethylacrylate) exhibits an absorbance of  $\sim 2.7 \text{ m}^{-1}$  at 157 nm [24], it is expected that further tailoring the transparency of poly(**2**) is available by incorporation of an  $\alpha$ -trifluoromethyl group.

The unusual transparency of poly(**2**) may be accounted for in terms of the electronic structure of the carboxyl group as well as the volume effect of the trifluoromethyl group. The effect on the electronic structure of the carboxyl group of geminal trifluoromethyl groups, incorporated in the  $\beta$ -position to the acrylate ester oxygen,

can be readily seen from  $^{13}\text{C}$  NMR spectroscopy. While the chemical shifts of carboxyl carbons in poly(alkyl (meth)acrylate)s are observed at  $\sim 175$  ppm, the carboxyl carbon in poly(**2**) exhibits an upfield shift by  $\sim 5$  ppm and the chemical shift is observed at  $\sim 170$  ppm. This indicates that the geminal  $-\text{CF}_3$  group in the  $\beta$ -position to the acrylate ester oxygen induces significant changes in the electronic structure of the carboxyl carbon in poly(**2**), rendering the carbonyl chromophore less absorbing than expected at 157 nm.

### **Chemically Amplified Acrylic Resist Functionalized with HFIPA**

Lithographic performance of poly(**2-co-3**), (monomer **3** is a protected version of monomer **2**) with 28 mol% of protected monomer **3**, was tested using a 248 nm stepper. Although the resist film exhibited clear latent images after exposure at 248 nm followed by post-exposure bake (PEB), imaging was not successful after development in 0.262 *N* tetramethylammonium hydroxide (TMAH) solution. While poly(**2**) exhibited good wetting properties on a HMDS vapor-primed silicone wafer, poly(**2-co-3**) exhibited relatively poor wettability most probably due to its non-polar nature after partial protection with a methoxy methyl group. Attempted development in 0.262 *N* TMAH solution containing various amounts of isopropyl alcohol was less than satisfactory, and the resist exhibited poor adhesion properties even with a few % of isopropyl alcohol in 0.262 *N* TMAH solution. It appears that, although HFIPA alone was successfully demonstrated by Przybilla as an acidic functional group, [21] it is necessary to incorporate a more acidic functional group in order to achieve high contrasts resulting from enhanced dissolution selectivity between exposed and unexposed areas.

In a series of experiments with poly(**2-co-THPMA**<sup>3</sup>) resists, 3 wt% PAG was employed in the formulation with three compositions and imaging experiments were carried out without changing other processing parameters. Figure 3 shows contrast curves obtained with 3 wt% PAG. Under these conditions, three systems exhibited

clearing doses much lower than with 1 wt% PAG and, poly(**2**<sub>60</sub>-*co*-THPMA<sub>40</sub>) exhibited decrease in the clearing dose by a factor of ~3 compared to the previous result with 1 wt% PAG. Although it is difficult to explain the relatively low clearing dose with poly(**2**<sub>80</sub>-*co*-THPMA<sub>20</sub>), the lower clearing dose with poly(**2**<sub>60</sub>-*co*-THPMA<sub>40</sub>) than with poly(**2**<sub>70</sub>-*co*-THPMA<sub>30</sub>) clearly indicates that the former undergoes acid-catalyzed deprotection more efficiently with 3 wt% PAG.

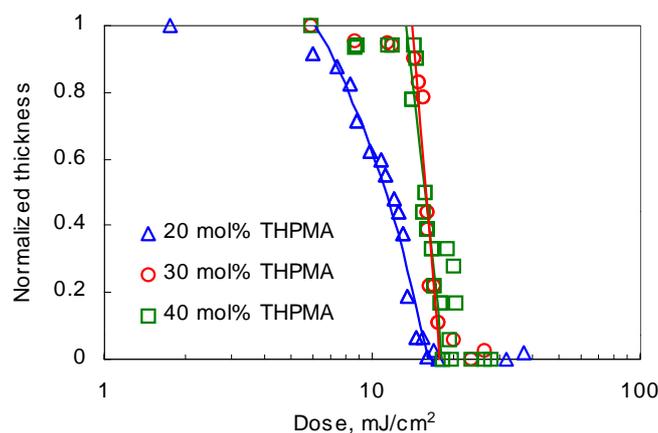


Figure 3. Contrast curves obtained with poly(**2**-*co*-THPMA)-based resists in the presence of 1 wt% PAG: PAB at 115 °C for 60 sec, PEB at 90 °C for 60 sec, development in 0.262 *N* TMAH for 60 sec.

SEM images obtained in the presence of 3 wt% PAG are shown in Figure 4 and dramatic improvement in lithographic performances was achieved in terms of resolution and photospeeds. Exposure doses less than ~9 mJ/cm<sup>2</sup> were enough to print SEM images with excellent exposure latitude. Top-rounding was significantly alleviated with poly(**2**<sub>80</sub>-*co*-THPMA<sub>20</sub>), and dense lines were resolved down to 300 nm with poly(**2**<sub>70</sub>-*co*-THPMA<sub>30</sub>) and poly(**2**<sub>60</sub>-*co*-THPMA<sub>40</sub>). Although a lower dose was required with poly(**2**<sub>60</sub>-*co*-THPMA<sub>40</sub>), similar lithographic performances were achieved with poly(**2**<sub>70</sub>-*co*-THPMA<sub>30</sub>) and poly(**2**<sub>60</sub>-*co*-THPMA<sub>40</sub>) in terms of resolution. These fluorinated, chemically amplified resists are thus extremely well suited for 157 nm lithography.

<sup>3</sup> THPMA = tetrahydropyranyl methacrylate

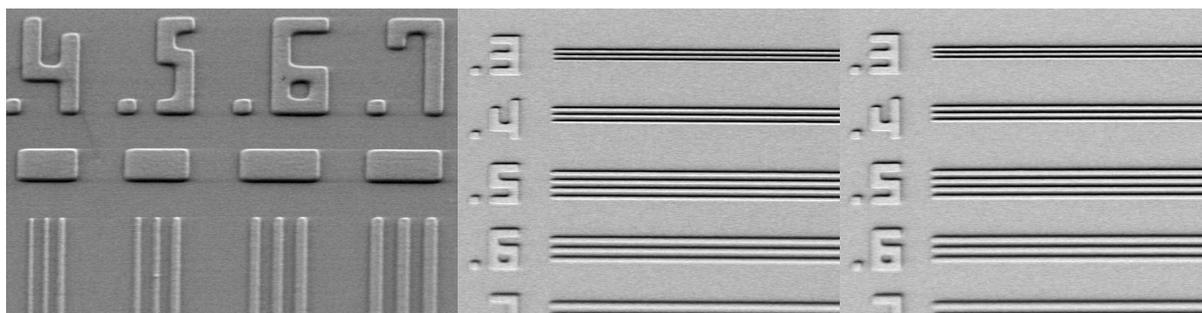
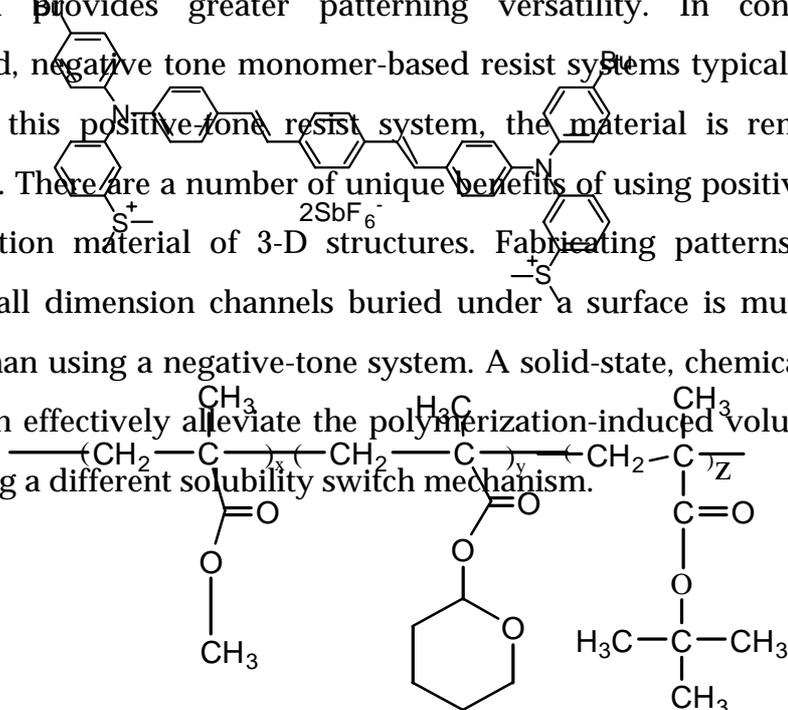


Figure 4. SEM images obtained with poly(2<sub>80</sub>-co-THPMA<sub>20</sub>) (A), poly(2<sub>70</sub>-co-THPMA<sub>30</sub>) (B), and poly(2<sub>60</sub>-co-THPMA<sub>40</sub>): other processing conditions are same as listed in Figure 3.

### 3D Lithography

In contrast to single photon UV lithography, where the photoresist serves only as a sacrificial pattern transfer layer, in 3-D lithography the photopolymer can form the final structure or act as a template for structure formation. It not only opens a door to a host of applications, but also imposes many new criteria to materials development. The resin systems should not only be two-photon sensitive but also possess other necessary properties to meet the requirements of the applications listed above. In this paper, we focus on developing a solid-state, chemically amplified positive-tone polymeric system which undergoes little or no structural distortion during processing. (A) provides greater patterning versatility. In contrast to the photocrosslinked, negative tone monomer-based resist systems typically used in 3D lithography, in this positive-tone resist system, the material is removed in the exposed regions. There are a number of unique benefits of using positive-tone resists as the construction material of 3-D structures. Fabricating patterns with empty regions and small dimension channels buried under a surface is much easier and more efficient than using a negative-tone system. A solid-state, chemically amplified resist system can effectively alleviate the polymerization-induced volume shrinkage problem by using a different solubility switch mechanism.



Scheme 3. (A): Chemical structure of the two-photon acid generator used in this work. (B):  
The generic structure of the copolymers used in this work.

Random copolymers of tetrahydropyranyl methacrylate (THPMA), methyl methacrylate (MMA) and tert-butyl methacrylate (tBMA) were designed and synthesized. The generic chemical structure is shown in Scheme 3. In the presence of acid, a deprotection reaction that generates methacrylic acid after the removal of the THP and t-butyl protecting groups converts the insoluble polymer to one that is soluble in aqueous base developer. The MMA provides strength and optical clarity while MAA provides the correct solubility properties. The ability to remove the material only at the exposed region makes it much more efficient for the creation of buried channels than the negative-tone liquid resin systems. By tailoring the polymer structure, it is also possible to fabricate the 3-D structures with selected surface properties. For example, in our material, the pendent chemical groups at the pattern surface are methacrylic acid groups that provide a variety of important options for surface functionalization. This feature is especially useful for microfluidic devices and other biological applications and makes study of both chemical and geometrical influences possible.

Based on information obtained from the investigation of the channel forming process, we were able to design and produce the optical grating structure shown in Fig. 5 which contains 12 parallel channels buried about 10 microns below the surface and connecting two reservoirs on both sides. We have also back-filled the structure with a low molar mass liquid crystal mixture to demonstrate its microfluidic and microoptical characteristics. This demonstrates that complex microfluidic structures and optical gratings, waveguides and photonic structures can be fabricated in this kind of materials system using two-photon lithography.

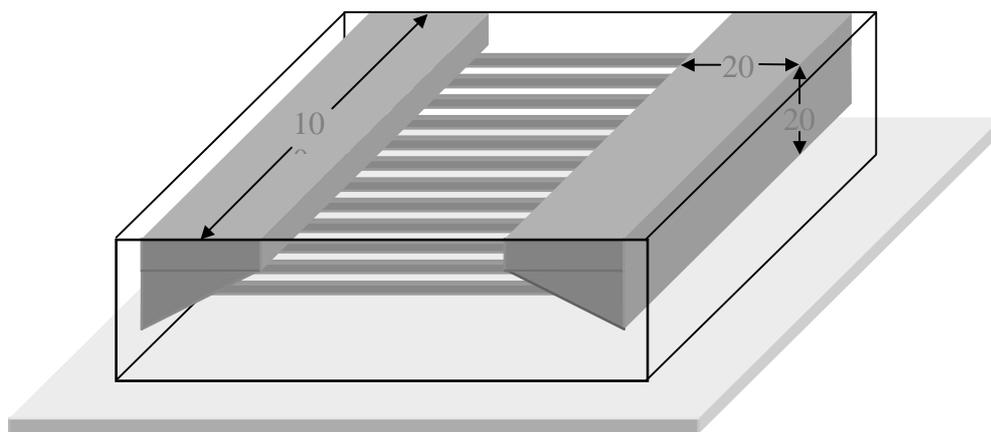


Figure 5. Schematic of 3D pattern produced using 2-photon lithography.

To our knowledge, this work is the first reported 3-D fabrication system based on a positive-tone resist. There are many issues that need careful investigation and further improvement. In 3-D microfabrication, the film has to be mechanically robust to maintain structural stability and at the same time has to maintain a degree of elasticity to prevent cracking during the baking processes. A small amount of plasticizer may provide some flexibility to the system. Mass transport is another issue in complex 3-D fabrication. The materials must be efficiently removed from the internal region while the surface features must remain undistorted. A low molecular weight polymer and the incorporation of dissolution inhibitors are possible strategies to improve diffusion during development and increase dissolution contrast. Two-photon lithography is a point-to-point scanning process that takes time to expose a structure depending on its degree of complexity. During this process, the photo-generated acid may diffuse from the exposed area and degrade the precision of the patterned interface. Adopting strategies from high-resolution lithography, the addition of some base into the formula may alleviate this effect.

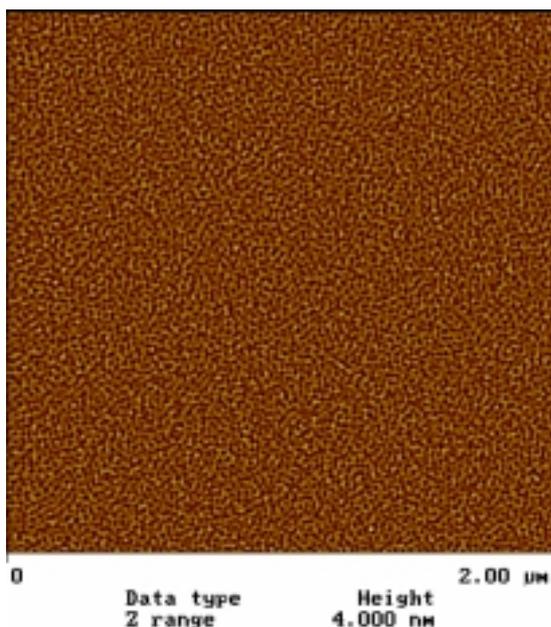
### **Investigation of Patternable Block Copolymers**

AFM measurements of block copolymer films were taken after spin coating (spin rate: 3000 rpm) a PMS-b-HS solution (solvent; propylene glycol methyl ether acetate, PGMEA) on a silicon wafer. Film thickness was measured to be 72 nm. Cylinders having a diameter of 20 nm standing up on the wafer were observed. The additives did not affect the morphology. First irradiation ( $450 \text{ mJ/cm}^2$  @250nm) and followed by heating (115 °C for 60 sec) were applied to make the matrix of PHS block rigid in order to avoid capillary collapse upon removal of the PMS block. Crosslinking occurred between the PHS block and CL via O-alkylation in the presence of acid coming from the PAG. Therefore only the continuous matrix was made rigid by the irradiation process. An AFM image obtained after the irradiation showed that the cylinders remained. Cylindrical holes were obtained after a second strong irradiation cycle ( $70 \text{ J/cm}^2$  @365 nm) under high vacuum as shown in Figure 6. PMS materials were removed from the cylindrical domains to give black spots on the AFM image. The size of the

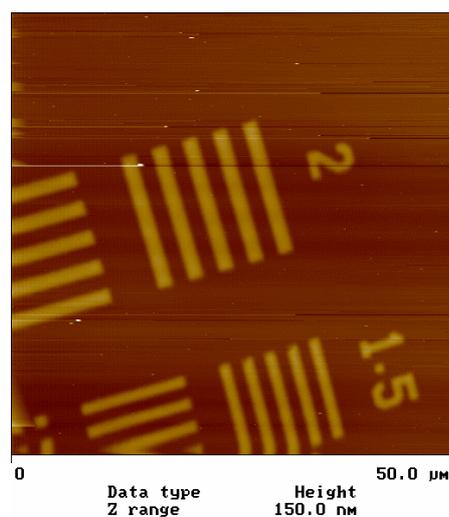
holes was measured to be 15 nm. The diffraction data suggests basically that the cylinders stand up on the wafer. Comparison using the samples before removal is now under investigation to confirm that the holes stand up on the silicon wafer surface.

### **3.2 Photoimaging of Block Copolymers**

It was found that the first weak irradiation with subsequent heat treatment made the entire matrix insoluble in an appropriate solvent (cyclohexanone / isopropanol = 50/50 in weight). Therefore the solvent can be used as a developer after weak irradiation to form negative tone photoresist patterns. Imaging on a 248 stepper (NA = 0.42 and  $\lambda = 0.5$ ) gave high resolution images with features as small as 300 nm lines. Finally the second strong irradiation by using 365 nm UV source produced holes on the patterns as shown in Figure 7. Some black parts representing holes were observed. Although the holes here obtained do not look as well formed as those shown in Figure 6 due to a top-rounding of the patterns, this can be corrected to make the holes more precise by optimization of formulation and process conditions, resulting in a rectangular profile. Surface roughness of the resists should be very important in case of such a thin film. It has been known that surface roughness of resists can be controlled by molecular weight and MW distribution of polymers. Basically low molecular weight and a sharp MW distribution gives low surface roughness. Therefore block polymers having a very sharp MW distribution can be an ideal system from the viewpoint.



**Figure 6.** AFM image obtained from a thin film of PMS-b-PHS after removal of the PMS materials.



**Figure 7.** AFM images after removal of PMS materials from patterned polymer matrix.

### Conclusions:

It was found that fluorocarinol-modified acrylic and styrenic monomers can be used in the design of chemically amplified photoresists, highly transparent at 157 nm. Improvement in transparency was also achieved by adding a transparent building block, **1**, to highly absorbing acrylates, such as PMMA. This result demonstrates that fluorocarinol-containing small molecules can be used as transparent dissolution inhibitors after protection with acid-labile groups. Preliminary results in 157 nm lithography proved that, with judicious molecular-level design, the synthesis of single-layer resists for 157 nm lithography is possible using simple chemistries.

In conclusion, we have established a general procedure for 3-D microfabrication in a chemically amplified positive resist system using two-photon lithography. A series of polymers with selected acid cleavage activities were prepared and served as a platform to evaluate the effect of two types of acid-deprotection groups and associated processing conditions. The concept of qualitative definition of develop provides a new strategy for 3-D fabrication. We also proposed an aspect ratio

parameter as one measure of materials' channel forming ability and developed the concept of normalizing the channel development to the bulk development. A three-dimensional optical grating structure was fabricated and back-filled with liquid crystals. Such a 3-D fabrication approach based using a positive system may be valuable for fabrication of microfluidic and microoptical devices. In addition, the first steps to producing 3D structures derived from photopatternable block copolymers have also been carried out.

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