High-Resolution Functional Epoxysilsesquioxane-Based Patterning Layers for Large-Area Nanoimprinting

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ABSTRACT Epoxysilsesquioxane (SSQ)-based materials have been developed as patterning layers for large-area and high-resolution nanoimprinting. The SSQ polymers, poly(methyl-*co*-3-glycidoxypropyl) silsesquioxanes ($T^{Me}T^{Ep}$), poly(phenyl-*co*-3-glycidoxypropyl) silsesquioxanes ($T^{Ph}T^{Ep}$), and poly(phenyl-*co*-3-glycidoxypropyl-*co*-perfluorooctyl) silsesquioxanes ($T^{Ph}T^{Ep}T^{Fluo}$), were precisely designed and synthesized by incorporating the necessary functional groups onto the SSQ backbone. The materials possess a variety of characteristics desirable for NIL, such as great coatability, high modulus, good mold release, and excellent dry etch resistance. In particular, the presence of epoxy functional groups allows the resists to be solidified within seconds under UV exposure at room temperature, and the presence of the fluoroalkyl groups in the SSQ resins greatly facilitate mold release after the imprint process. In addition, the absence of metal in the resins makes the materials highly compatible with applications involving Si CMOS integrated circuits fabrication.

KEYWORDS: nanoimprint lithography · patterning · roll-to-roll · flexible substrate

Nanopatterning is a vital part of nanotechnology for fabricating nanoscale devices, components, and systems with high precision.[1] Among the emerging technologies, nanoimprint lithography (NIL) is regarded as one of the most promising techniques, which provides cost-effective solution to high-throughput nanopatterning.[2,3] With the capability to pattern sub-10 nm structures yet entail relatively straightforward equipment and processing, it has been successfully used in fabrication of electrical and optical devices, such as organic optoelectronics,[3,4] photonics,[4−8] magnetic devices,[9,10] as well as in biological applications.[11−14] ITRS has listed it as one of the contender technologies for future generation Si chip manufacturing.[15] Recent works from companies such as Toshiba have further established the viability of its application in the semiconductor industry.

A key player for the successful implementation of NIL in real industrial settings is the development of advanced materials suitable as the nanoimprint resist. Thermoplastic polymers have been widely used as resist layers for NIL. However, the viscosity of these polymers is very high even when heated at a temperature above their glass transition temperatures (T_g). As a result, the imprinting process typically requires high pressure and long imprinting times, which considerably affects the throughput. Furthermore, such high imprinting temperatures often induce undesirable thermal stresses into the replicated nanostructures, damaging the expensive and fragile SiO_2 mold. To achieve the high throughput required for high-volume industrial nanofabrication, an imprinting process with no thermal cycles is preferred. For this reason, photocurable materials, which can be imprinted at room temperature, have been developed for nanopatterning technologies.[16−18]

One of the well-known imprinting resists is an acrylate-based small molecular material used in step and flash imprint lithography (SFIL). However, there are a number of issues associated with this resist, such as high dimensional shrinkage (∼15%), insufficient modulus upon curing, high toxicity due to its high volatility, outgassing problem for process integration, and poor coating ability due to its low viscosity.[17] Therefore, such resists can only be applied to a substrate by droplet dispensing. In addition, the acrylate functional monomer is very sensitive to oxygen inhibition, making the process prone to defect generation.

Thiol−ene-[18] and vinyl−ene-based[17] resists were introduced to overcome the limitations of free radical polymerizations. Vinyl−ene materials showed high tensile strength and low viscosity; however, the separation from the mold, which is one of the most important characteristics of a resist for nanoimprinting, is still challenging.[17]
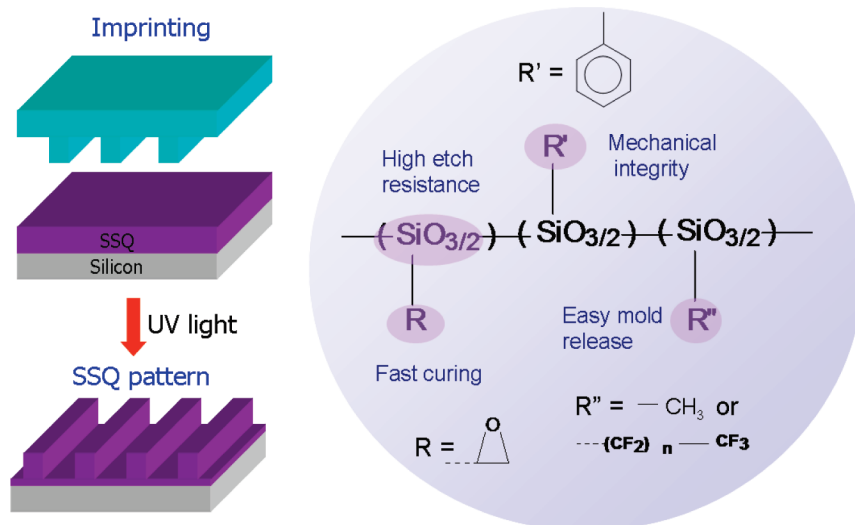
Figure 1. (Left) Schematics of the NIL process. (Right) Design and architecture of SSQ-based photocurable nanoimprint resists containing various functional groups.

On the other hand, the developed thiol−ene resists lack the appropriate chemical elements to withstand the harsh reactive ion etching processes required for pattern transfer of nanostructures into semiconductor materials.[18] In this context, we have previously developed a UV-curable formulation based on cationic cross-linking of epoxysilicone or epoxydimethylsiloxanes (PDMS) that overcomes some of the aforementioned shortcomings,[19] allowing the fabrication of both micro- and nanoscale structures at room temperature and at a pressure less than 0.1 MPa using a conventional contact-exposure tool. A brief comparison of various resist systems is provided in the Experimental Section.

A patterning layer that not only presents excellent imprinting capabilities but also shows a high versatility in its chemical design for a range of functionalities and applications is highly desired in a number of fields from biotechnology to semiconductor manufacturing. Furthermore, the development of resist materials that not only function as sacrificial layers but also remain in the device as an integral component has attracted great interest in recent times. Among several types of polymeric materials, silsesquioxane (SSQ) resins, with a three-dimensional organic−inorganic network structure that combines many desirable properties of conventional organic and inorganic components, provide an exemplary core system as versatile and functional patterning layers.[20−27] In fact, due to their unique properties, such as high thermal stability, optical clarity, high density, high modulus (in the order of GPa), and a low dielectric constant (*e.g.*, less than about 3), silsesquioxanes have been widely used in applications such as low dielectric (low-*k*) interlayer materials, photonic waveguide and device materials, protective and insulating coating, to name an important few.[20−27]

Therefore, silsesquioxane polymers have been developed as imprinting materials which can also be incorporated as functional patterns. A high-modulus methylsilsesquioxane resist was previously engineered for low dielectric constant interlayers.[28] However, this material cross-links through a thermal process that requires several hours, thus greatly reduces process throughput. Photocurable polyhedral oligomeric silsesquioxanes (POSS) have also been used as patterning layers for step and flash imprint lithography. Although such materials present good fidelity for patterning submicrometer structures, they still face some challenges; for example, a methacrylate-based POSS required an inert atmosphere for its processing due to oxygen inhibition.[29] In the same manner, a POSS synthesized with a high content of epoxide groups shows high adhesion to the mold, which can prevent the replication of small nanostructures.[30] Other promising materials are currently being investigated as patterning layers for NIL and their applications by many research groups, as well.[31−37]

We report the design and synthesis of photocurable silsesquioxane (SSQ) resins and their applications as functional patterning layers for high-resolution and large-area NIL applications. As shown in Figure 1, a unique SSQ molecule was constructed by incorporating a number of desired functional groups onto the same SSQ backbone: the low surface energy groups, such as methyl and perfluoro groups, impart the resin with good mold release properties; the high-energy groups, such as silanol groups and epoxy groups, permit the imprinted patterns to adhere to the substrate rather than to the mold; the incorporation of photocurable epoxy groups allows the nanoimprinting process to be completed within seconds at ambient temperature; the presence of the phenyl groups enhances the material toughness and patternability.[38] In addition to possessing the desired properties of epoxysilicone resists developed previously, such as low shrinkage, no oxygen inhibition, no outgassing, this novel SSQ resist offers high modulus, great release properties, great
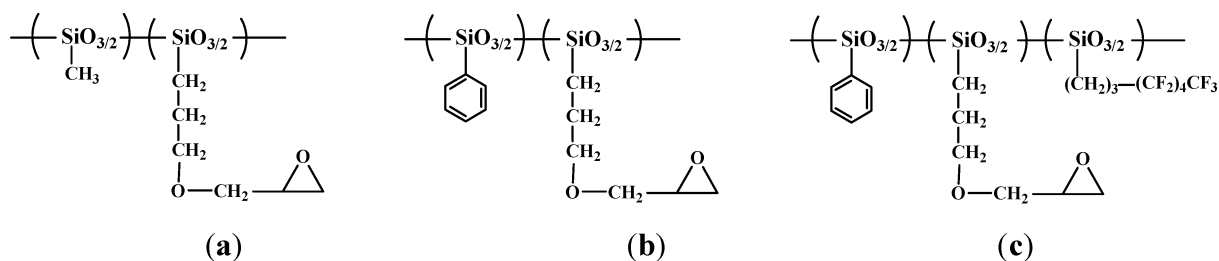
Figure 2. Three types of epoxy-containing silsesquioxanes: (a) $T^{Me}T^{Ep}$, (b) $T^{Ph}T^{Ep}$, (c) $T^{Ph}T^{Ep}T^{Fluo}$.
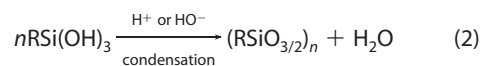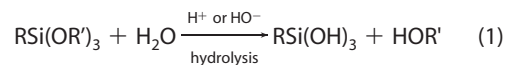
coat-ability, and high etch resistance due to higher silicon content. Finally, the evaporation and outgassing of these SSQ materials is not an issue due to its moderate molecular weight so potentially large areas can be imprinted with small variations in structure properties under a step and repeat process. The combination of these special features makes the photocurable silsesquioxane an ideal and versatile material for NIL to fabricate micro/nanostructures with high efficiency, precision, and fidelity.

RESULTS AND DISCUSSION

In the presence of a catalytic amount of base, a number of silsesquioxane resins with different chemical functionalities were synthesized through a hydrolytic condensation of the corresponding trialkoxysilanes. As shown in Figure 2, three main types of epoxy-containing silsesquioxanes have been made: $T^{Me}_{x}T^{Ep}_{1-x}$, $T^{Ph}_{x}T^{Ep}_{1-x}$, and $T^{Ph}_{x}T^{Ep}_{y}T^{Fluo}_{1-x-y}$, wherein x is the molar percent of the corresponding unit (the symbols M and T represent a monofunctional and trifunctional siloxane unit, respectively).[39] For each type of resin, the relative molar ratio of the structure unit is varied so a structure/property relationship of the resins for nanoimprinting can be established. Accordingly, the composition of the resin is listed based on the mole percent of the corresponding alkoxysilanes used in the synthesis, which is represented by the subscripts in the above notation. Their molecular weights were determined by gel permeation chromatograms (GPC) and are in the range of 3000 to 10 000 g/mol, with a rather narrow molecular distribution of 1.5 to 4.0, indicating the relative uniformity of the material (Table 1). Most of the resins present as a viscous liquid at room temperature, except sample 8, and all of them are soluble in typical organic solvents, such as PGMEA, xylene, and 2-heptanone, and can be made as a solution of varied concentration according to the coating thickness requirements. Due to its appropriate molecular weight, high-quality thin films of the resin can be formed on the top of substrates by spin-coating.

The SSQ resins have been characterized by NMR spectroscopy. Figure 3 shows ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the $T^{Me}_{0.2}T^{Ep}_{0.8}$ resin as representative spectra, in which the presence of both methyl group and 3-glycidoxypropyl groups is clearly revealed. The T(Me) group is spotted at 0.15 ppm in the ^{1}H NMR, 0.00 ppm

in the ^{13}C NMR, and −62 to −72 ppm in the ^{29}Si NMR. In particular, ^{13}C NMR analysis shows that the epoxy ring of the resin remains intact during the base-catalyzed hydrolytic process, whereas epoxy ring opening is very common with acid catalysts; the two carbons of the epoxy ring are observed at 48 ppm (f peak) and 55 ppm (e peak), respectively. The formation of silsesquioxane resins from the hydrolysis of trialkoxysilanes typically involves two steps: (a) the hydrolysis of trialkoxysilanes to form the hydrolytes (eq 1); (b) the condensation of the hydrolytes to silsesquioxane (eq 2).

$$RSi(OR')_3 + H_2O \xrightarrow[\text{hydrolysis}]{H^+ \text{ or } HO^-} RSi(OH)_3 + HOR' \quad (1)$$

$$nRSi(OH)_3 \xrightarrow[\text{condensation}]{H^+ \text{ or } HO^-} (RSiO_{3/2})_n + H_2O \quad (2)$$

In general, the hydrolysis of alkoxysilanes proceeds more efficiently under acidic conditions, whereas the condensation/polymerization step occurs more readily under basic conditions. As a result, the silsesquioxane resins made by base-catalyzed hydrolysis of trialkoxysilanes typically have much lower silanol concentration than that by acid-catalyzed processes. It is well-known that the storage stability is one of the critical issues for SSQ resins, and SSQ resins with high silanol content are typically very unstable and form insoluble gels prematurely, which severely limits its adaptability in

TABLE 1. Physical Properties of Photocurable Epoxysilsesquioxane: Molecular Weight, Polydispersity (PDI), Viscosity, and Physical Appearance at Room Temperature

| example | composition[b] | GPC result[a] | | vicosity (Pa · S) | physical appearance at 23 °C |
		M_w	PDI		
1	$T^{Me}_{0.2}T^{Ep}_{0.8}$	3755	1.97	1.7	viscous liquid
2	$T^{Me}_{0.3}T^{Ep}_{0.7}$	4454	2.17	1.3	viscous liquid
3	$T^{Me}_{0.4}T^{Ep}_{0.6}$	4936	2.25	17	viscous liquid
4	$T^{Me}_{0.5}T^{Ep}_{0.5}$	4721	2.16	20	viscous liquid
5	$T^{Ph}_{0.2}T^{Ep}_{0.8}$	1749	1.81	43	viscous liquid
6	$T^{Ph}_{0.4}T^{Ep}_{0.6}$	2269	1.78	35	viscous liquid
7	$T^{Ph}_{0.5}T^{Ep}_{0.5}$	5149	2.32	31	viscous liquid
8	$T^{Ph}_{0.8}T^{Ep}_{0.2}$	8881	3.23	solid sample	white powder
9	$T^{Ph}_{0.4}T^{Ep}_{0.5}T^{Fluo}_{0.1}$	2459	1.51	25	viscous liquid

[a]GPC data *vs* polystyrene standard. [b]Ep = 3-glycidoxypropyl group; Fluo= 1H,1H,2H,2H-perfluorooctyl group.
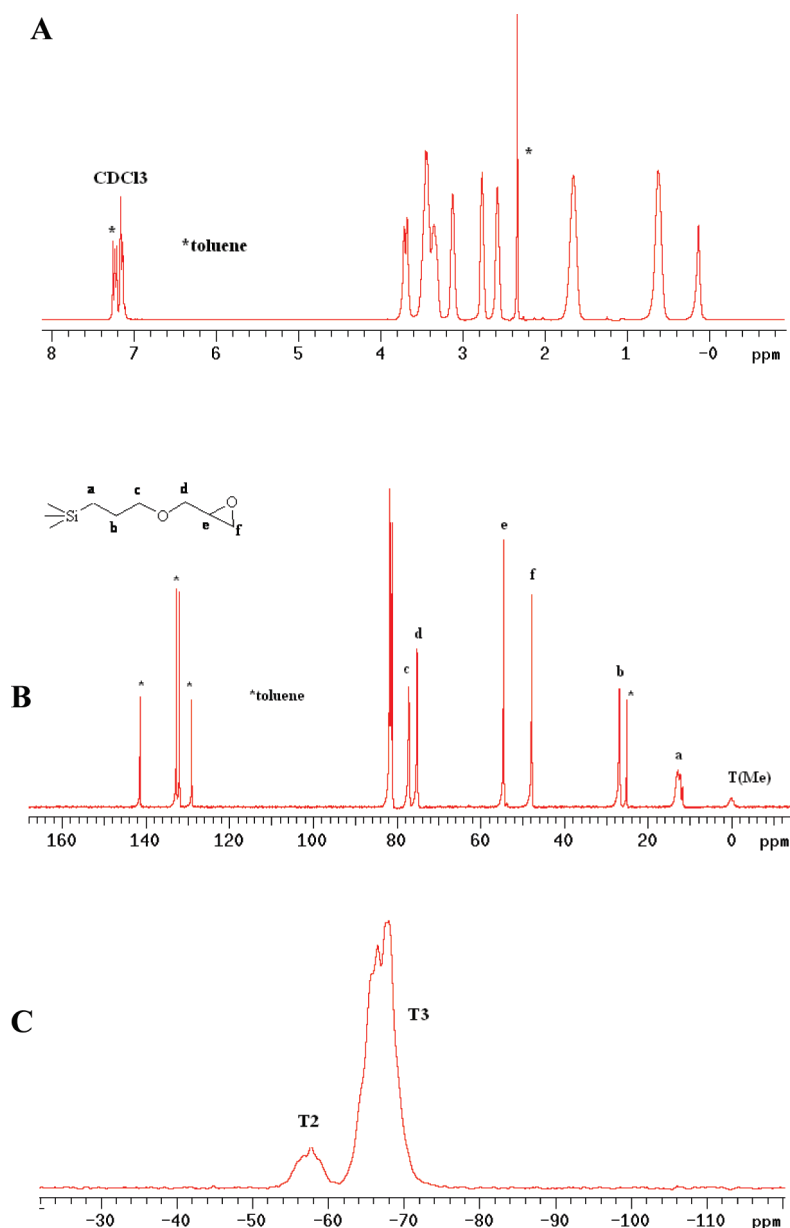
Figure 3. (A) ^1H, (B) ^{13}C, and (C) ^{29}Si NMR spectra of $T^{Me}_{0.2}T^{Ep}_{0.8}$.

many areas of applications. The low-silanol-containing resins made in this work, on the other hand, show a great shelf life even as a neat resin. In the meantime, the amount of silanol present in the resin is high enough to impart it with adequate adhesion affinity to the substrate. Figure 3C shows the ^{29}Si NMR spectrum of $T^{Me}_{0.2}T^{Ep}_{0.8}$ resin. The epoxy functional silicon atom (T^{Ep}) of the resin is observed as a broad peak from -62 to -72 ppm, overlapped with the T^{Me} resonance. The broadness of the ^{29}Si NMR peaks implies that the resin may have a relative higher molecular weight and presents as a possible mixture of random, ladder, cage, and partial cage structures.[40] In contrast to about 40−70 mol % silanol presented in SSQ resins made using acids as the catalyst, the resin made here contains around 10 mol % of silanol based on the integration of the peak at 52−62 ppm (T^2 or T(OH)/T(OR′) peak).

To make the patterning layer for NIL, a silsesquioxane resin was dissolved into an organic solvent, such as PGMEA, and followed by the addition of a photoacid generator (PAG). The concentration of the solution is adjustable by adding more solvent so that a film thickness from micrometers to nanometers could be readily obtained by spin coating.

Ideally, any shrinking caused by the UV light exposure during the curing process should be minimal to ensure an accurate replication of the nanoscale features. The degree of shrinking measured for the SSQ resins is typically low, especially in the case of epoxy-based silsesquioxanes (e.g., less than about 6%). The lower levels of shrinking in the epoxy-based SSQ resins may be attributed to the conversion of the rigid oxirane ring into a more flexible open-chain configuration in the cured material.
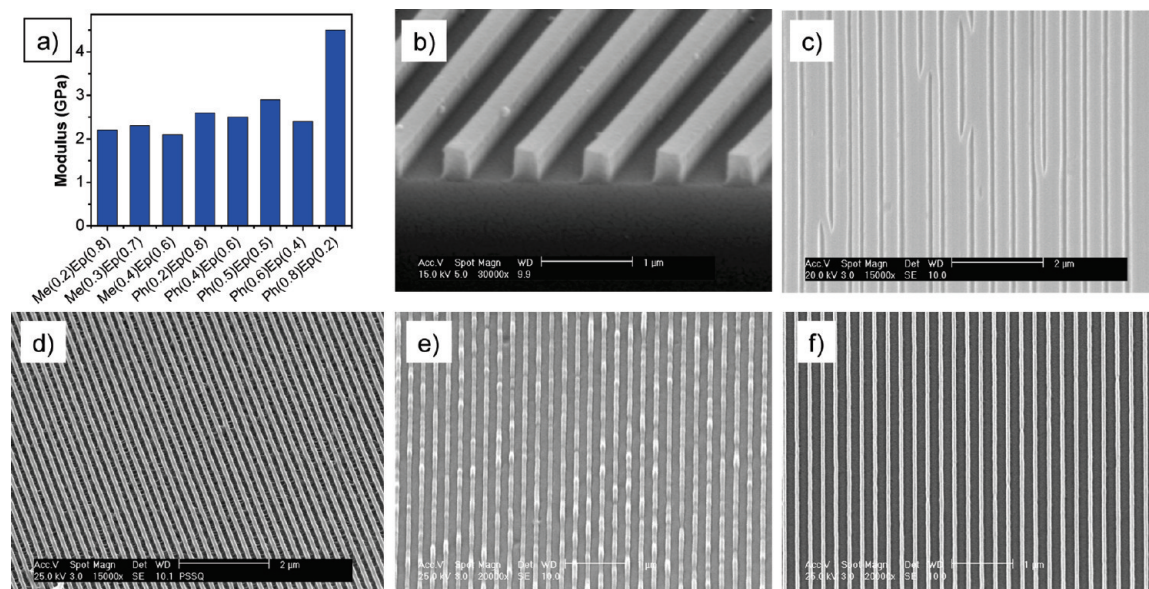
Figure 4. Nanoimprint structures with epoxy-SSQ resin: (a) modulus of the UV-cured SSQ resins measured by nanoindentation; (b) 700 nm grating pattern imprinted in $T^{Ph}_{0.2}T^{Ep}_{0.8}$; 220 nm period pattern replicated with (c) $T^{Me}_{0.50}T^{Ep}_{0.50}$ and (d) $T^{Ph}_{0.50}T^{Ep}_{0.50}$; 60 nm line width patterns replicated using SSQs with (e) high ($T^{Ph}_{0.20}T^{Ep}_{0.80}$) and (f) low ($T^{Ph}_{0.50}T^{Ep}_{0.50}$) ratio of epoxy groups.

It is known that in NIL a material with a high modulus is needed to avoid the collapsing of free-standing replicated nanostructures during the demolding step.[41] The high modulus of the epoxy-SSQ resins allowed a high fidelity nanoimprinting. The modulus of the cured materials was measured using a nanoindentation technique. A value larger than 0.1 GPa is preferred to achieve a good pattern definition and obtain lines with sharp edges.[18] As shown in Figure 4a, these epoxysilsesquioxane resins possess high modulus (greater than 0.5 GPa) after cure. Noticeably, one of the resins, $T^{Ph}_{0.8}T^{Ep}_{0.2}$, shows a modulus as high as 4.5 GPa. Such high modulus can effectively prevent the collapsing of imprinted narrow and high aspect ratio structures after mold releasing.

A major advantage of the silsesquioxane system developed in this work is the possibility of an easy modification of their chemical structures *via* chemical synthesis to produce the desired imprinting material. In general, the imprinted nanoscale structures are subject to high mechanical stresses in the demolding step, which often leads to the breakage or the deformation of the replicated structures if the materials do not have the appropriate mechanical strength. SSQ's composition thereby can be tuned to obtain a material with outstanding mechanical properties to withstand the otherwise detrimental stress present during the mold releasing step. It was found that the methyl-SSQ resins ($T^{Me}T^{Ep}$) display appropriate properties for submicrometer size replication. However, for nanosize structures with very small spacing (220 nm period and 80 nm line), the imprinted structures tend to deform, causing neighboring lines to collapse, as shown in Figure 4c. On the other hand, much improved results were obtained with the SSQs containing phenyl substituent ($T^{Ph}T^{Ep}$) (Figure 4d), which is known for being effective in enhancing the mechanical properties of SSQ resins.[38]

The concentration of epoxy functionality incorporated into the SSQ resin was optimized in order to achieve the desired mechanical properties. If the amount of epoxy groups in the resin is too high, the material tends to be too brittle for nanoimprinting upon UV curing. For instance, the structures imprinted in $T^{Ph}_{0.20}T^{Ep}_{0.80}$ (high content of epoxy groups) were broken during the releasing step, generating a high density of defects, as displayed in Figure 4e. Reducing the number of epoxy cross-linking sites by increasing the amount of phenyls in the resins can significantly reduce the breakage of the imprinted structures (Figure 4f). In general, it was found that phenyl-SSQ resins containing 40−60 mol % of epoxy groups give the best resist for NIL. The imprinted samples have been examined by SEM, and the patterns close to the middle and edge of the substrate give similar results. In addition, due to the appropriate modulus of the SSQ materials, the demolding process does not affect the quality of the patterns obtained. However, the demolding process is easier when using a flexible stamp than when employing a hard silicon oxide mold.

A great challenge facing nanoimprinting is the strong adhesion of the resist to the mold, especially for dense nanoscale features that contribute to a large interfacial area between the mold and the imprinted resist. To address this issue, perfluoroalkyl substituents, which are well-known for providing low surface energy due to the presence of CF_3 groups, were incorporated into the SSQ resists, as shown in Figure 2c, to ensure an easy mold release required for high yield and high-
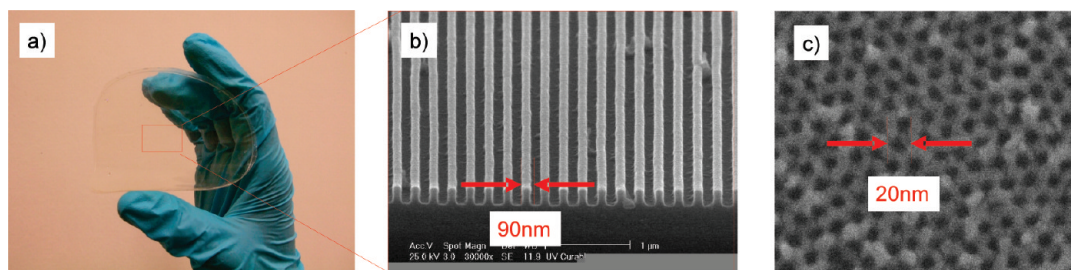
Figure 5. (a) Fluorinated SSQ patterned on top of a flexible PET substrate using a 4 in. diameter SiO$_2$ hard master; (b) SEM micrograph of the imprinted SSQ grating with 90 nm line width from the 4 in. PET sample; (c) 20 nm size dense pore structures patterned on a fluorinated SSQ.

resolution nanopatterning. On the other hand, the low surface energy resist also has a poor adhesion to the substrate, leading to possible delamination of the imprinted resist from the substrate during the releasing step. This problem can be resolved by using a "coupling" underlayer between the perfluorinated resist and the substrate, as we demonstrated previously.[42] The coupling underlayer also contains epoxy groups, which react under UV irradiation with the other epoxy moieties present in the fluorinated resist material, improving the resist−substrate adhesion. The fluorinated SSQ resist was found to be a desired material for nanopatterning, that is, replicating large areas of high-density nanopatterns such as the 110 nm half-pitch gratings covering an entire 4 in. diameter substrate shown in Figure 5a,b, as well as the 20 nm structures shown in Figure 5c, which was imprinted by using a mold fabricated by using the self-assembled block copolymer template.[43] As the SSQ resist can be easily patterned on top of a flexible substrate with no difficulties encountered during the demolding, the patterning area is only limited by the availability of the mold and the dimension of the curing light sources. Recently, we have also shown that SSQ is suitable for continuous roll-to-roll nanoimprinting.

Importantly, when a flexible mold or substrate is used, the flexibility of the mold (or substrate) itself allows an easy peeling from the mold. On the other hand, a rigid mold and rigid substrate system present more challenge in the demolding process. In this regard, the current low surface energy material can be used as a flexible and easily replicable mold to replace the original Si mold, which is often difficult or expensive to fabricate.[42]

In addition, in the case where the mold is contaminated with the SSQ material, tetrabutyl ammonium fluoride (0.1 N solution in THF) can be used to clean the SSQ residues from the mold. This solution swells the SSQ thin film stuck on the mold so it can be easily removed. Furthermore, some approaches to develop a reversible cross-linking SSQ resist system[44] that is easy to clean if adhered to the mold during mold release are currently under investigation.

In addition, this SSQ material not only shows outstanding imprinting capabilities but also serves as a good etch mask for pattern transfer into substrate. As an example, the imprinted SSQ patterns (Figure 6, left) were etched with CHF$_3$ to remove the residual layer (Figure 6, middle). This was followed by HBr plasma etching to transfer the pattern into a silicon substrate using the imprinted SSQ as a mask (Figure 6, right). A selectivity of more than 2:1 was easily achieved with the HBr chemistry. In addition, the high silicon content of the SSQ materials provides a greatly improved etch resistance to O$_2$ plasma. This feature is very attractive to a double-layer resist approach for nanopatterning: coat the SSQ resist on top of another thicker polymer layer and perform NIL on the SSQ, and then use the imprinted SSQ pattern as a mask to etch into the thicker polymer layer to produce higher aspect ratio patterns. The double-layer resist approach is also useful for processes such as lift-off, where undercut features can be produced in the underlayer during oxygen plasma etching using the SSQ as a mask, which can greatly facilitate the lift-off process.

CONCLUSIONS

In summary, novel photocurable silsesquioxane materials with excellent imprinting capabilities were
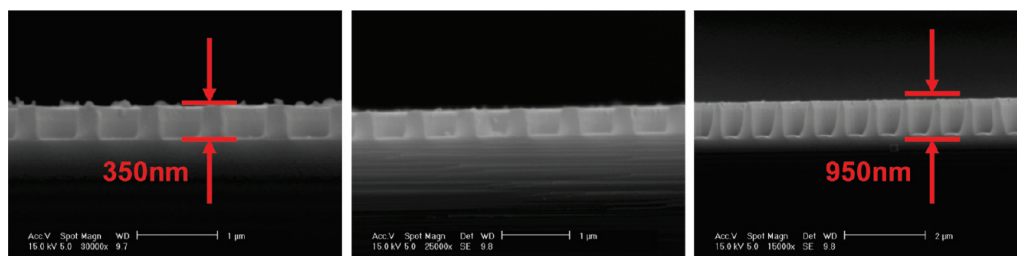

Figure 6. (Left) A 700 nm period, 350 nm height original SSQ pattern, (middle) SSQ pattern after residual layer was removed with CHF$_3$, and (right) 950 nm tall silicon structures etched with HBr.

designed and synthesized. The materials possess a variety of characteristics desirable for NIL, such as great coatability, high modulus, good mold release, and excellent dry etch resistance. In particular, the presence of epoxy functional groups allows the liquid resists to be solidified within seconds under UV exposure at room temperature to replicate structures as small as 20 nm using low-pressure nano-imprinting tools, and the presence of the fluoro-alkyl groups in the SSQ resins greatly facilitates a facile mold release after the imprint process; the high silicon content of the SSQ material provides high resistance to plasma dry etching. In addition, the absence of metal in the resins makes the materials highly compatible with applications involving Si CMOS integrated circuits fabrication.

EXPERIMENTAL SECTION

Materials and Methods. Phenyltrimethoxysilane, methyltrimethoxysilane, 3-glycidoxypropyl trimethoxysilane, and (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octyl)trimethoxysilane (CAS# 51851-37-7) were purchased either from Aldrich or Gelest. The resin synthesis was conducted under nitrogen.

Physical and Analytical Measurements. NMR spectra were recorded on a Varian XL-400 spectrometer. Chemical shifts for ^1H, ^{13}C, and ^{29}Si spectra were referenced to internal solvent resonance and are reported relative to tetramethylsilane. The GPC chromatographic equipment consists of a Waters 600 pump, a Waters 717 autosampler, and a Waters 410 differential refractometer. Molecular weight averages were determined relative to a calibration curve (third order) created using polystyrene standards covering the molecular weight range of 580 to 2,300,000.

Representative Examples for Making Epoxysilsesquioxane Resists. *Synthesis of Poly(phenyl-co-3-glycidoxypropyl)silsesquioxanes ($T^{Ph}_{0.2}T^{Ep}_{0.8}$).* To a 1 L three-necked flask equipped with a mechanical stir shaft, a Dean−Stark trap with a condenser, were added 0.2 mol of phenyltrimethoxysilane, 0.8 mol of 3-glycidoxypropyl trimethoxysilane, 200 g of toluene, 4 mol of water, and 0.001 mol of CsOH under nitrogen. The mixture was refluxed for 2 h while stirring, whereby part of the solvent was gradually removed from the Dean−Stark trap. After the solution temperature increased to about 105 °C, it was cooled and diluted with toluene. The dilute solution was then neutralized with the addition of acetic acid and washed with deionized water. Next, volatiles were removed using a rotary evaporator to yield a colorless viscous liquid.

Synthesis of Poly(phenyl-co-3-glycidoxypropyl-co-perfluorooctyl)silsesquioxanes ($T^{Ph}_{0.4}T^{Ep}_{0.5}T^{Fluo}_{0.1}$). To a 1 L three-necked flask equipped with a mechanical stir shaft, a Dean−Stark trap with a condenser, were added 0.4 mol of phenyltrimethoxysilane, 0.5 mol of 3-glycidoxypropyl trimethoxysilane, 0.1 mol of 1H,1H,2H,2H-perfluorooctyltriethoxysilane, 300 g of toluene, 4 mol of water, and 0.001 mol of CsOH under nitrogen. The mixture was refluxed for 2 h while stirring, whereby solvent was gradually removed. After the solution temperature increased to about 105 °C, it was cooled and diluted with toluene. The dilute solution was then neutralized with the addition of acetic acid and washed with deionized water. Next, volatiles were removed using a rotary evaporator to yield a colorless viscous liquid.

Nanoimprint Process. Original silicon oxide master molds were vapor-coated with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (from Gelest) in order to achieve easy mold release after the imprinting and curing processes. Ethylene tetrafluoroethylene (ETFE)[3,45] and fluoro-SSQ stamps[42] were fabricated using the original silicon oxide master mold.

The nanoimprint resist formulation was made by dissolving one of the sesquioxane resins in propylene glycol monomethyl ether acetate (PGMA) and followed by the addition of a photoacid generator (PAG) (about than 1 wt % of the SSQ resin). The photoacid generator (PAG) used in the resist was purchased from Craig Adhesive and Coating Co., Newark, NJ, under the product name of UV9390C, and it contains 30−60 wt % of bis(4-dodecylphenyl)iodonium hexafluoroantimonate as the active ingredient. The concentration of the solution is adjustable by adding more solvent so that a film thickness from micrometers to nanometers could be readily obtained by spinning coating.

The SSQ resin solution was spun on a hard silicon substrate or cast on a PET film; the substrates were previously surface treated with O_2 plasma and silane silquest 187 coated by vapor

TABLE 2. Comparison of SSQ's Properties with Other Common Resist Materials[16−18,47,48]

resist system	viscosity (Pa · S)	modulus (GPa)	% shrinkage	finest feature imprinted
SSQ	>1.0 (moderate)	1−5	6%	~20 nm
acrylates	0.0030 (low)	0.0044	10%	~20 nm
vinyl−ene	0.0019 (low)	0.91	unknown	~40 nm
thiol−ene	expected low	1.8	unknown	~55 nm

deposition. The imprinting process was performed under UV light exposure within a few seconds at room temperature by using either an ETFE or a fluoro-SSQ stamp. A Nanonex imprinting tool with vacuum capability with wavelength for UV curing at 365 nm or a light curing system ELC-430 from Electro-Lite Corporation was used for the imprinting. The imprinting pressure was typically less than 40 psi due to the low viscosity of the liquid resist.

Reactive Ion Etching (RIE). The CHF_3 dry etching of the silsesquioxane materials was performed in a Plasmatherm 790, while HBR etching was done in a LAM 9400 tool. The etching rates of these materials were determined by measuring the film thickness change using a Dektak surface profilometer. The gas flow rate during etching was 20 sccm CHF_3. The source power was 150 W for CHF_3, the gas flow rate was 20 sccm CHF_3, and the pressure was 20 mTorr. For the HBr, the source power was 70 W, gas flow rate was 100 sccm, and the chamber pressure was 12 mTorr.

Determining the Evaporation of SSQ Resists. The weight variation of a 10 mg sample of SSQ was determined using an analytical balance to study experimentally its evaporation. It was found that SSQ does not present evaporation. The 10 mg of SSQ did not show any evaporation after 1200 s. In contrast, an 8 mg drop of *tert*-butyl acrylate and a 10 mg drop of ethylene glycol divinyl ether (EGDVE) (vinyl ether) evaporated in 487 and 802 s, respectively.[46] The lack of evaporation in the SSQ material is due to its moderate molecular weight (5159 g/mol) as opposed to the low molecular weight of volatile acrylates and divinyl ether molecules.

SSQ's and the resist materials' properties are shown in Table 2.

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