

Ultrasmall Structure Fabrication *via* a Facile Size Modification of Nanoimprinted Functional Silsesquioxane Features

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Nanostructure fabrication is made possible in part due to the advancement in nanolithography techniques.^{1,2} However, the precise control of ultrasmall structures on the order of 10 nm remains a challenge because of physical and technological limitations of current lithographic technologies.^{3–5} Nanoimprint lithography (NIL) was developed as an alternative and low cost technique for high throughput nanopatterning with demonstrated resolution down to 2 nm.^{6–8} However, it is still very challenging to fabricate large area NIL master molds with dimensions smaller than 30 nm for general applications. In addition, different applications require vastly distinct feature sizes, from tens of nanometers^{9,10} to micrometers,¹¹ and often demand adjustment of patterned structure sizes to optimize the device performance. Certain specialized micro/nanofabrication processes are often necessary to modify the dimensions of the patterned structures,^{9,12} which are often inaccessible to researchers working in the general fields. A technique named SPLE (self-perfection by liquefaction) was developed to control the dimensions of patterned structures. This process greatly improves lateral edge roughness but structure size is difficult to control accurately due to its reliance on polymer reflow.^{13,14} In another example, a process involving shadow evaporation was used to shrink grating gap sizes down to 10 nm, however it requires several steps of time-consuming vacuum depositions to achieve the final results.¹⁵

A promising solution to fabricate nanoscale structures with high precision is the combination of top-down and bottom-up approaches.^{16–20} In fact, metallic structures

ABSTRACT We propose a simple and robust scheme for a precise and controlled fabrication of ultrasmall structures through the direct size modification (either reduction or increment) of functional nanoimprinted silsesquioxane (SSQ) patterns. The size modification of nanopatterned SSQ polymer features was achieved according to two different independent approaches. In the first approach, feature size was reduced by a simple heat-induced mass loss mechanism; in the second approach structure size increment was achieved by building multiple polymeric layers on top of imprinted patterns. The fabricated arrays follow the shape contour of the patterned structures so the original imprinted profile is preserved. The engineered capabilities were applied to produce high resolution stamps for nanoimprinting. These approaches free the need for sophisticated nanofabrication techniques and expensive facilities required for nanopatterning.

KEYWORDS: nanoimprinting · silsesquioxane · functional pattern · nanofabrication

as small as 30 nm were obtained using a layer-by-layer deposition approach.²¹ Though the technique can provide 2 nm precision due to the molecular size, the process is laborious and time-consuming if a significant modification of the line width are desired because several molecular layer coating cycles as well as metal vapor deposition and lift off steps are required.²² Similar approaches of growing molecular layers have been reported but unfortunately also require long processing times.^{23–25} Finally, a useful approach to reduce pitch dimensions is a process named SAFIER (shrink assist film for enhanced resolution).²⁶ Structures as small as 20 nm are generated with simple chemical coating steps on prepatterned structures, while lateral edge roughness is reduced; this process also keeps the sidewalls vertical after a few shrinking steps. Unfortunately, the top of the coated structures becomes rounded as the number of coating steps increases.

To overcome these limitations, we propose effective ways to directly modify

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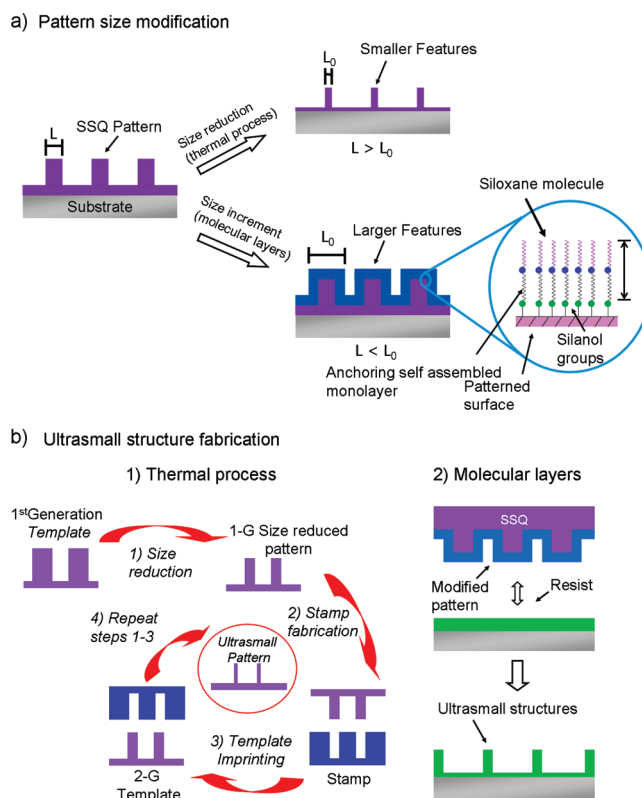


Figure 1. (a) Scheme showing the developed pattern size modification approaches: (1) structure miniaturization with a thermal process and (2) a feature enlargement by growing molecular layers, (b) process flow depicting ultrasmall structure fabrication with SSQ patterns after initial size modification by using (1) the thermal process and (2) the molecular layers approach.

nanoimprinted polymeric silsesquioxane structures by simple chemical and physical processes (Figure 1) for a precise and controlled fabrication of ultrasmall structures (<10 nm). Two independent and straightforward methods were developed to reduce, or increase, the dimensions of functional nanopatterned structures accurately. In particular as shown in Figure 1a, feature size was reduced by a simple heat-induced mass loss mechanism, and structure size increment was attained by growing polymeric layers on top of imprinted patterns. Both methods can produce significant changes in feature size by controlling the process conditions and molecular structures. Furthermore, sharp features required for many applications, for example, subsequent nanoimprinting, can be maintained following both methods because the original pattern contour remains unmodified. The process flow to fabricate ultrasmall features using the SSQ patterns following (1) a thermal process and (2) a polymeric layer growth approach after initial size modification is depicted in Figure 1b.

In addition, by fluorinating the patterned surface, the dimensionally modified patterns can be used directly as a flexible and transparent nanoimprint mold for high resolution NIL.

Therefore, the proposed pattern size modification methods can be used in close combination with nanoimprint technology to fabricate ultrasmall structures or

can also be used directly for making nanoimprint molds. It is important to emphasize that the aim of these techniques is to modify the dimensions of the imprinted features but does not change, for example, the pitch of a periodic pattern; techniques for pitch modification have been previously demonstrated.²⁷

The material selected as the imprinted layer is a silsesquioxane (SSQ) polymer, which can be easily patterned under simple UV exposure at room temperature. This material was chosen because imprinted SSQ possess the appropriate chemical design and physical properties to act as an active functional layer for the subsequent processing steps aimed to fabricate ultrasmall structures. SSQ resins as organic–inorganic hybrid materials possess many desirable properties for micro-/nanopatterning, such as high thermal stability, high density, and high modulus (in the order of GPa). In comparison with poly(dimethylsiloxane) (PDMS) based materials, it offers much higher modulus, and lower solvent swelling. In addition SSQ properties are easily tunable by molecular design to suit the NIL application²⁸ and can be used directly as a mold by incorporating fluoro-functionality directly into the molecular structure.²⁹

RESULTS AND DISCUSSION

Thermal Size Reduction Process. Size reduction by thermal treatment is achieved by heating an UV-imprinted

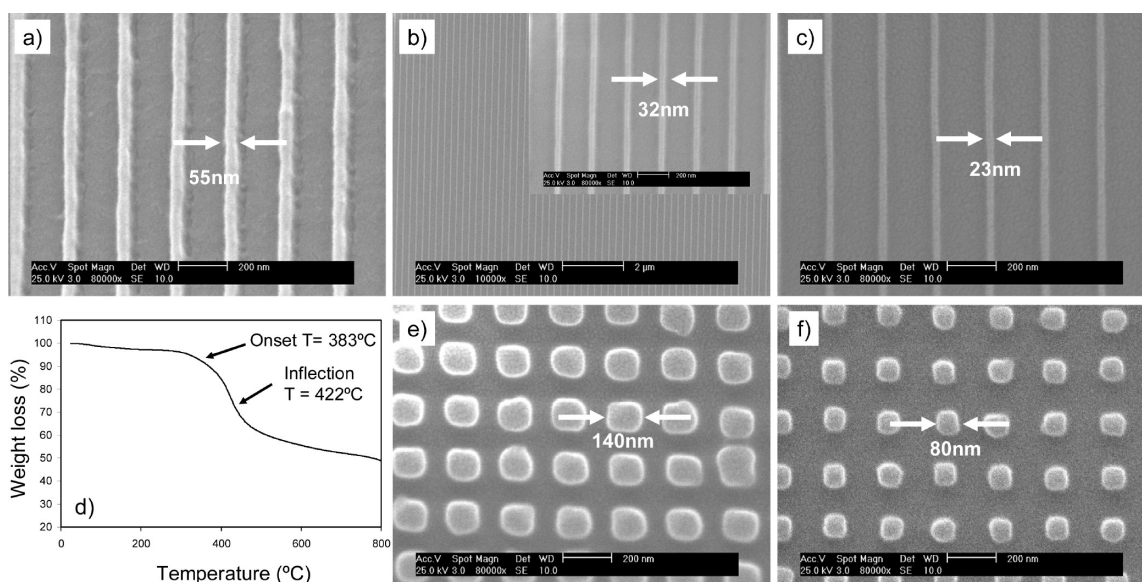


Figure 2. (a) Control grating sample of 220 nm period and 55 nm line width, (b) 1-G pattern heated to 350 °C (line width is 32 nm), (c) 1-G pattern heated to 700 °C (line width is 23 nm), (d) TGA of the epoxy-SSQ (SSQ-A), (e) control nanopillars sample of 140 nm size, (f) 1-G nanopillar sample heated to 700 °C (pillar size is 80 nm).

epoxy-SSQ (SSQ-A)-pattern, hereby referred as the first generation (1-G) template, to the required temperature simply using a hot plate or in a furnace. This simple process generates a SSQ pattern with feature dimensions smaller than initially replicated, but maintains the similar aspect ratio. It can be repeated as depicted in Figure 1b to produce progressively smaller features.

The size reduction approach is temperature dependent, as presented in Figure 2. When a grating pattern was heated to 350 °C, its line width decreased from 55 nm (Figure 2a) to 32 nm (Figure 2b). A further size reduction was observed when the sample was heated to 700 °C, whereby 23 nm line width structures were obtained (Figure 2c).

The thermally induced size reduction process takes advantage of thermal decomposition of the organic groups in the hybrid SSQ materials (Figure 2d) since these groups normally undergo either degradation or oxidation at temperatures above 200 °C. In addition, residual silanol groups from the SSQ resins will condense with one another at such temperatures to form a Si–O–Si linkage with concomitant release of water, shrinking the nanostructures as proposed previously.³⁰ The hypothesis was verified by the increase in siloxane bonds (–Si–O–Si–) and the decrease of corresponding silanol (–OH) bonds by FTIR (Experimental Section).³¹ The thermal induced densification process appears to be quite smooth under these conditions, without generating much material stress or any significant size of pores originated by the release of small organic molecules in the film. This is important as mechanical integrity of the modified SSQ structures is not impacted. The net result of these processes is the dimensional reduction of the imprinted structures. Indeed it is found that the thickness of SSQ thin films as measured

by ellipsometry, decreases with temperature, and consistent with the polymer mass loss observed in TGA (Experimental Section).

Thermal miniaturization is also a versatile process which can be applied to any type of geometrical structures. As presented in Figure 2e and f, the size of imprinted nanopillars was easily reduced from 140 nm to 80 nm by simply heating the sample to 700 °C.

Remarkably, the thermal miniaturization cycle can be repeated to produce ultrasmall structures at different temperatures depending on the need. As illustrated in Figure 1b the first generation (1-G) pattern can be further functionalized with O₂ plasma and fluorosilane treatments to render structures with low surface energy suitable for NIL. Then it was used to imprint an SSQ resist previously poured on top of a transparent polyethylene terephthalate (PET) sheet in order to fabricate a flexible SSQ stamp (1G-stamp). A second generation (2-G) SSQ pattern was then fabricated with the 1-G stamp. The imprinted 2-G pattern can also be exposed to a thermal process to produce features much smaller than the original 1-G pattern. Although a multiple repeating process can be required to achieve significant shrinking, SSQ has been demonstrated to be an excellent material for nanoimprinting,²⁸ so pattern quality and yield is maintained over large areas and several repeating cycles.

The described cycle can be repeated several times in a sequential manner so structures with ultrasmall size can be created (Figure 1b). For example, with the use of a two-cycle process, a 2-G grating pattern with 20 nm line width structure was obtained (as compared with the initial line width of 55 nm) when a processing temperature of 350 °C was employed for the size reduction step (Figure 3a). Furthermore, the fabrication

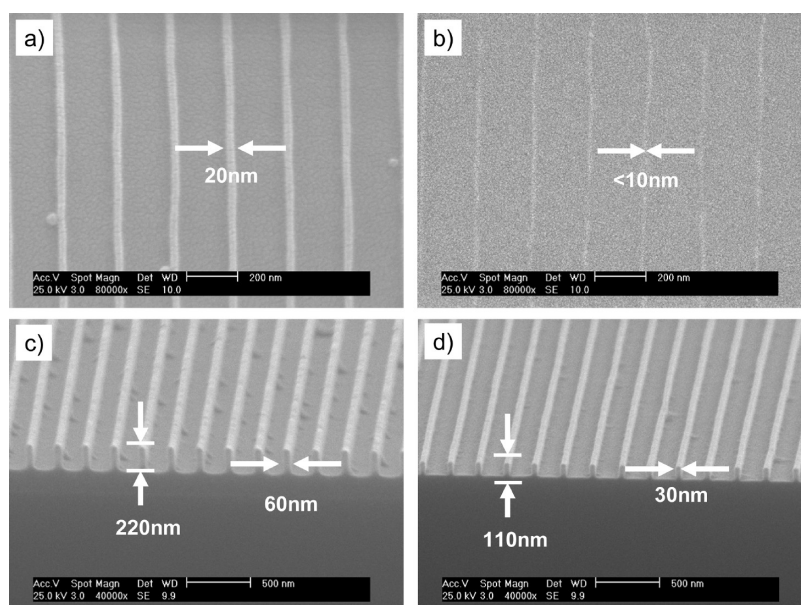


Figure 3. (a) 2-G nanograting pattern processed at 350 °C (line width is 20 nm), (b) 2-G pattern processed at 700 °C (line width is <10 nm); cross sectional view, (c) a 220 nm period 60 nm line width control sample, (d) a grating sample after being thermally treated at 700 °C (lines reduced to 30 nm).

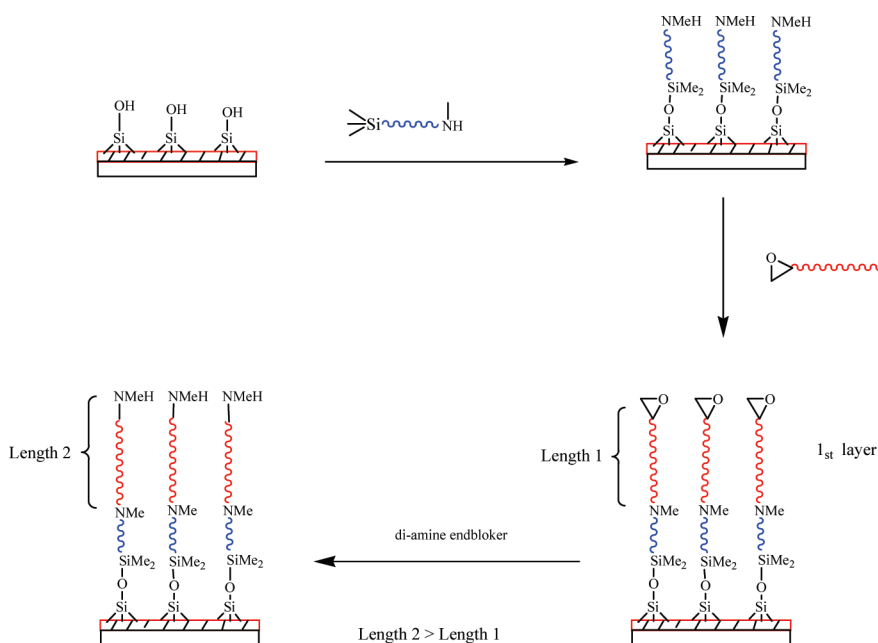


Figure 4. Reaction steps to build polymeric layers on top of SSQ surfaces; (1) silylamine is coated on a SSQ pattern to form an amine end block, (2) epoxy-terminated siloxane reacts with the amine end block (the process can be repeated multiple times to grow several layers).

of a 2-G pattern with sub-10 nm-structures was easily achieved with a higher processing temperature, 700 °C (Figure 3b).

Importantly, the miniaturized features maintain both the original profile contour and aspect ratio as the structure shrunk isotropically in this process. For example, a 220 nm period pattern with 60 nm line width maintained its initial structure profile when heated to 700 °C for 1 h, as displayed in Figure 3c,d, whereas the height and line width of the structure

was decreased to 110 and 30 nm, respectively, resulting in a minimal change in aspect ratio (~ 3.6 in both cases). These characteristics demonstrate that the thermal miniaturization is a high resolution structure fabrication technique with great simplicity and versatility.

Polymeric Layers Growth. In addition to pattern miniaturization, the versatility of SSQ materials also allows a simple approach to increase the size of nanoimprinted structures by a polymeric layer growth method. In this

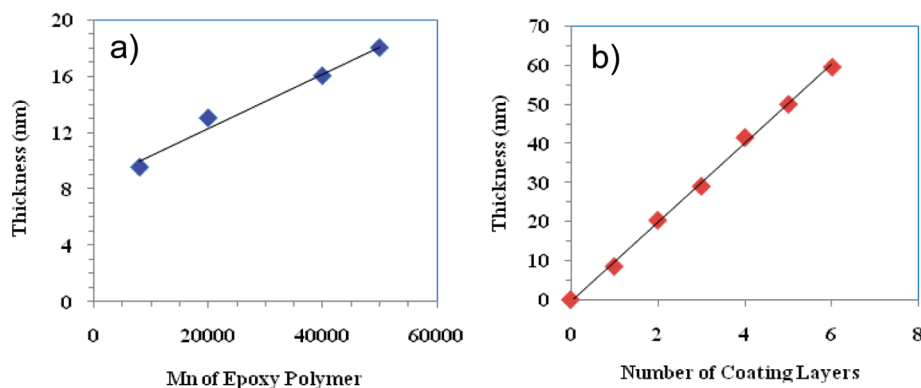


Figure 5. (a) Dependence of polymeric layer thickness on the molecular weight of the epoxy polymer used; (b) the thickness of the coating layers on the top of SSQ surface with the number of coating layers (Epoxy I).

method, the initial imprinted film employed to grow polymeric layers was a photocurable SSQ material²⁸ with hydroxyl functional groups on the surface. After the hydroxyl-rich (silanol-rich) surface of the SSQ material is treated with an anchoring silylamine monolayer, an epoxy-based polymer is grown on the top of the patterned film. An advantage of this simple process is the possibility to control the grown layer thickness in a single step by selecting an epoxy functional macromolecule (or alternatively, hydroxyl functional molecules) with appropriate molecular weight.

To illustrate the principle, a UV-curable acrylate-SSQ resin (SSQ-B), containing greater than 5.0% mole of silanol group in the resin as measured by ²⁹Si NMR, was used as the initial patterning material. The silanol groups were selectively introduced during the material synthesis under controlled reaction conditions so the resist material does not require any further surface modification.

The detailed process to grow the polymeric layers is as follows. First, the UV-curable SSQ resist was patterned *via* a UV-NIL process to form the desired structures. Next the surface of the patterned structure was treated with an aminosilane by a vapor deposition process (Figure 4); it reacts readily with the silanol groups on the surface to form an anchoring silylamine monolayer. Then the amine groups present in the anchoring molecule are brought into contact with an epoxysilicone polymer,³² whereby a strong covalent bond linkage is formed readily at moderate temperatures (50–100 °C). The unreacted or nonanchored siloxane polymers are removed selectively using organic solvents afterward.

Importantly, multiple layers can be grown controllably on the top of the original layer using a diamine coupling agent, which converts the epoxy enriched surface back into an amine functional surface. As a result, the deposition of a new epoxy polymer layer followed by the treatment using a diamine coupling agent can be repeated to build multiple layers on the patterned structure so the dimensions of the feature size can be precisely controlled accordingly.

The chemical reactions for polymeric layer growth are described as follows. At the initial surface treatment, the hydroxyl or silanol groups on the patterned surface are readily transformed into amine groups *via* a hydrolytically stable Si–O–Si linkage, by reacting with an aminosilane compound. The amine-enriched surface (I) is then coated with an epoxypropoxypropyl terminated polydimethylsiloxane (PDMS) polymer, whereby one of the amine groups reacts with the epoxy group forming a covalent bond linking the PDMS polymer chain on the patterned surface. After the first layer is built, the epoxy group on the opposite end of the PDMS chain (II) can be further treated with a diamine coupling agent to regenerate the amine-enriched surface (III). If an epoxysilicone polymer with more than two epoxy groups (functionality ≥ 3) is used as the epoxy growing layer, a hyperbranched molecular brush would be formed on the surface.^{33–35}

The thickness of the polymeric layers, measured by ellipsometry on flat silicon substrates, is found proportional to the molecular weight of the macromolecule used (Figure 5a). Importantly, multiple layers can be grown controllably on the top of the original layer. Thus, a series of sequentially repeated coating steps can lead to the formation of coating layers with any desired thickness. As an example, the same acrylate SSQ resin (SSQ-B) was spin-coated on a silicon wafer, and cured under UV-irradiation. The thickness of the coating on the top of the SSQ resin was then measured by ellipsometry, after growing each individual layer with an epoxypropoxypropyl-terminated polydimethylsiloxane (PDMS) polymer (Epoxy I) and subsequent treatments. The thickness of the coating layer increases linearly with the number of coatings, and each layer is approximately 10 nm thick (Figure 5b) for this particular molecular weight. It is worth notice that this sequential coating process works well only for lower molecular weight reactive oligomers (<10000 g/mol). When a higher molecular weight oligomer is used, the surface reaction usually takes a much longer time due to the relative lower concentration of the functional groups on the interface.

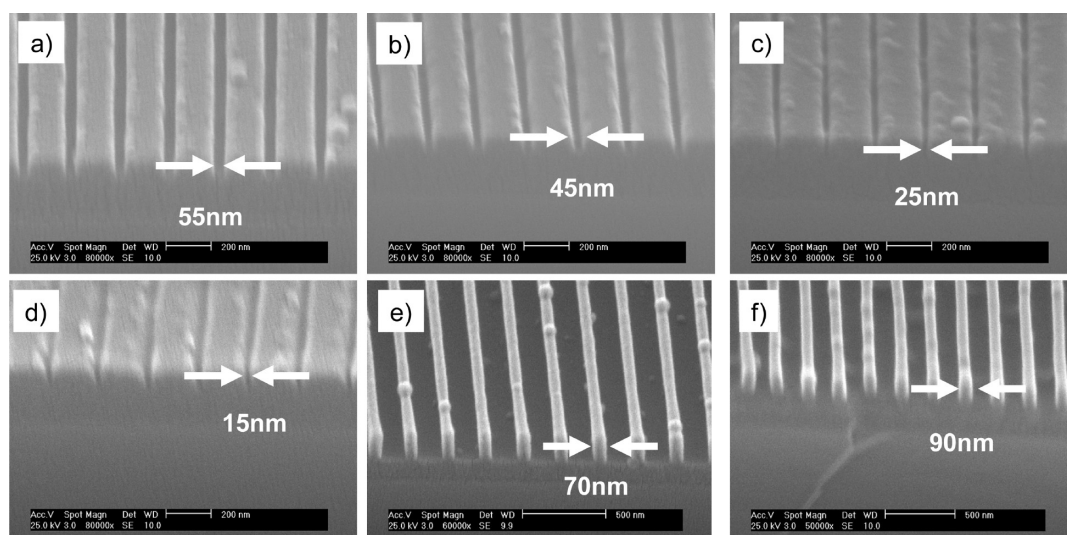


Figure 6. SEMs showing cross sections of (a) an original SSQ pattern, (b) a SSQ pattern where one layer of Epoxy I was coated, and (c) a SSQ pattern where a three layers of Epoxy I were coated and (d) a SSQ pattern with one layer of Epoxy II coating. SEMs of 200 nm period pattern showing that the profile is unchanged before (e) and after (f) the structure is coated with 2 layers.

This technique can be used for high resolution trench fabrication by reducing the gap between dense lines to less than 30 nm. As illustrated in Figure 6, the trench size of a SSQ grating pattern was reduced with the deposition of several molecular layers, and the gap size decreased almost linearly with the number of coating layers using Epoxy I. The original pattern (Figure 6a) having trenches with 55 nm width was reduced to about 25 nm after three coating layers (Figure 6b); each grown polymeric layer reduces the gap by ~ 10 nm. In addition, it was found that the space reduction between lines is also related to the molecular weight of epoxy polymers used. When Epoxy I was employed, the trench size was reduced to 45 nm (Figure 6c) after one layer coating and reduced to 15 nm by using a higher molecular weight polymer (Epoxy II, Figure 6d). These results are in agreement with the ellipsometry measurements (Figure 5).

Similarly to the size reduction approach, the growing polymeric layers also preserve the shape contour of the patterned structures so the modified patterns do not alter the original profile. For instance, the line width of another SSQ grating was increased from 70 to 90 nm with the successive deposition of two Epoxy I layers, as shown in Figure 6e,f, without affecting the profile of the structures.

Since the polymeric layers are grown on the patterns by using either vapor deposition or dip coating processes, the approach appears not to have physical size limitations; hence, structures with any desired dimensions can be constructed. We found that even a higher molecular weight epoxysilicone polymer (such as Epoxy II) can penetrate inside the nanoscale trenches (55 nm) by capillary forces. The same applies for the aminosilane molecules which are able to easily diffuse into the narrow trench due to their small

molecule size and the absence of intermolecular forces in the vapor phase.

An important application of this approach is the fabrication of nanoimprint molds having features smaller than the originally ones. For example, a SSQ mold with trenches narrower than originally patterned was fabricated with the aforementioned approach. Both molds, the original and modified ones, were used to imprint a SSQ resist (SSQ-B) under UV-irradiation conditions. As shown in Figure 7, the SEM pictures of SSQ patterns clearly reveal that the spacing between the lines was decreased from 150 nm (Figure 7a) imprinted with the original mold to 110 nm (Figure 7b) with the modified mold after four epoxysilicone layers were grown on the original mold. In the same manner, the trench of another replicated SSQ grating mold was reduced from 55 to 23 nm. The mold was then used to pattern a SSQ resist by a UV curing process; the imprinted SSQ resist is presented in Figure 7 panels c and d, respectively. This result shows that molds with any size nanostructures can be fabricated for NIL applications. Some increment in lateral edge roughness can be noticed in the pictures presented in Figure 7, which can be due to a difficulty in removing the excess material during the cleaning process. The use of an alternative and more effective cleaning process can smooth the structures walls.

CONCLUSIONS

Ultrascale structures were easily fabricated through a simple size modification of nanoimprinted SSQ patterns. Functional and versatile SSQ NIL resist layers with capabilities beyond an easy patterning were employed. A simple process to decrease the size of SSQ features following a thermal miniaturization protocol was demonstrated. Sub-10 nm-structures were fabricated combining thermal miniaturization and nanoimprinting

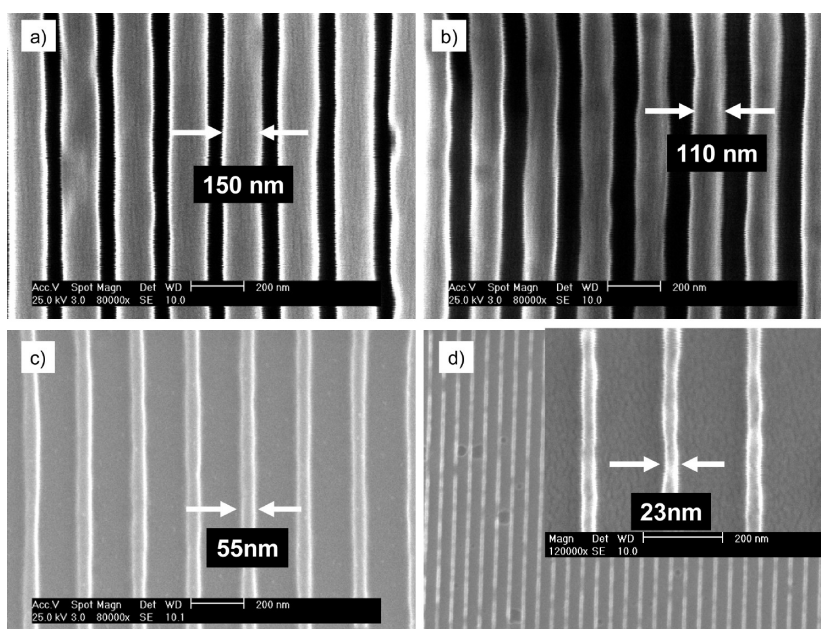


Figure 7. SSQ pattern imprinted by using (a) an original mold (150 nm trench width) and (b) a modified mold (four polymeric layers were added to produce 110 nm trench width); (c) an unmodified SSQ mold (55 nm trench width) and (d) a modified SSQ mold (23 nm trench width).

approaches. In addition, the gap size of highly dense grating arrays was accurately controlled and reduced from a few hundred to only tens of nanometers using a molecular layer growth approach. A fast top-down imprinting approach and high resolution bottom-up techniques could be combined to enable high resolution nanofabrications for a variety of applications.

Since SSQs have shown outstanding characteristics as stamps for nanoimprinting,²⁹ the replicated patterns

with reduced dimensions are easily transferred into other types of polymer films. In this fashion, high resolution NIL stamps can be made without having to rely on other expensive and low speed fabrication techniques. Finally, the methodology presented here can be used for several advanced applications such as the engineering of membranes with nanopore structures for separations and the direct fabrication of structures on silicon-based materials for the future microelectronic devices.

EXPERIMENTAL SECTION

Nanoimprinting of SSQ Material. Original silicon oxide master molds were vapor-coated with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (from Gelest) in order to achieve easy mold release after the imprinting and curing processes. Fluoro-SSQ stamps were fabricated using the original silicon oxide master mold.

The nanoimprint resist formulation was made by dissolving an epoxy silsesquioxane resin (SSQ-A), in propylene glycol monomethyl ether acetate (PGMA), followed by the addition of a photoacid generator (PAG) (about 3 wt % of the SSQ resin). The SSQ resin solution was spun on a hard silicon substrate, and the imprinting process was performed under UV light exposure within a few seconds at room temperature by a fluoro-SSQ stamp to produce a first generation (1-G) template. A Nanonex imprinting tool with vacuum capability and the wavelength for UV-curing is 365 nm or a light curing system ELC-430 from Electro-Lite Corporation was used for the imprinting.

Thermal Size Reduction Process. The nanoimprinted sample was placed on a hot plate (for temperatures below 370 °C) or a furnace for 1 h to produce a 1-G size reduced pattern. A 1-G stamp was fabricated by exposing a 1-G size reduced pattern to O₂ plasma for 15 s (60 Watts, 15 sccm, 250 mTorr) followed by a fluorosilane treatment (1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane) during 40 min at 120 °C. The 1-G stamp was then used to pattern a 2-G template as described above. The same process can be repeated several times to produce small size structures.

It is important to note that SSQ is a cross-linked organic–inorganic material with a chemical structure similar to SiO₂. SSQ inorganic core makes it highly resistant to O₂ plasma etching which is especially useful for using SSQ material as stamp for nanoimprinting; since the treatment required to fluorinate the SSQ stamp does not modify or degrade the structure profile. In contrast, regular organic polymers such as PMMA suffer physical distortions and degradation when exposed to O₂ plasma treatments.

Fourier Transformed Infrared (FTIR). FTIR of SSQ thin films spun on silicon substrates materials was obtained on a Perkin-Elmer BX FT-IR spectrometer (Figure 8).

Thermogravimetric Analysis (TGA). TGA was performed with a Perkin-Elmer TGA-7 thermogravimetric analyzer. For the measurements, a 20 mg sample was heated from room temperature to 800 °C at a heating rate of 20 °C/min.

Ellipsometry Measurements. SSQ thin films were heated at the required temperature with a hot plate or a furnace and then their thickness was measured with ellipsometry (Figure 9).

Polymeric Layers Growth. SSQ-Film and Structure Preparation. A 3-(trimethoxysilyl)propyl methacrylate monolayer was self-assembled on an oxidized silicon wafer through a vapor deposition process. Then, an acrylate-SSQ (SSQ-B) solution in propylene glycol methyl ether acetate (PGMEA) was spun cast on the surface treated silicon wafer to form a thin film. The SSQ thin

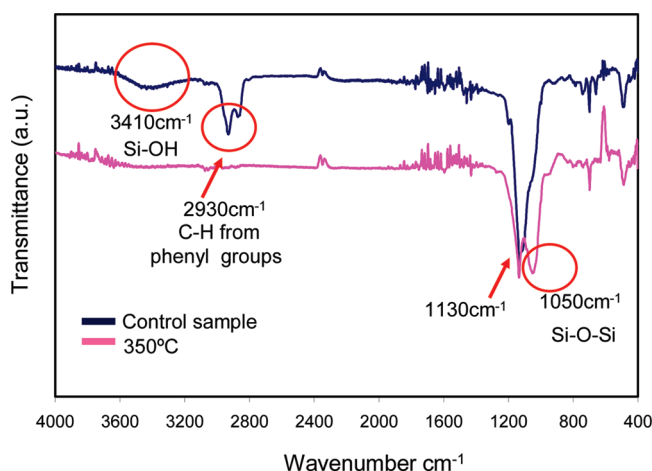


Figure 8. FTIR of epoxy SSQ material (SSQ-A) before and after thermal annealing at 350 °C.

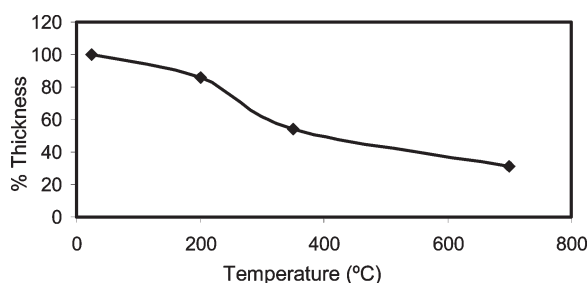


Figure 9. Thickness decrement of SSQ thin film with temperature; measured by ellipsometry.

film was either used to measure its thickness with ellipsometry or patterned using a flexible and transparent SSQ mold using a Nanonex imprinting tool (Princeton, NJ) under UV exposure.

Process and Conditions for Coating Epoxy Layer and Treated with Silylamine Coupling Agents. A silylamine anchoring monolayer was coated on the SSQ pattern by a vapor deposition process (100 °C for 20 min). Then, the silylamine treated-SSQ pattern was immersed in the corresponding epoxy terminated polydimethylsiloxane prepolymer liquid and heated at 100 °C for 40 min. Finally, the SSQ pattern was cleaned with isopropyl alcohol by sonication to remove unreacted siloxane prepolymer. The silylamine and siloxane prepolymer coatings were repeated several times to achieve desired thicknesses.

Fabrication of Dimensionally Modified SSQ Mold. The modified SSQ pattern according to steps discussed above was treated with O₂ plasma to create a reactive surface. Then, a low surface energy pattern was created coating a fluorosilane monolayer (1H,1H,2H,2H-perfluorooctyl-triethoxysilane) on the SSQ structures by vapor deposition. The low surface energy SSQ pattern was used as a mold to imprint on SSQ resists and fabricate grating patterns with narrower width.

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