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Patterning High-Aspect-Ratio Sol–Gel Structures by Microtransfer Molding

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Organic–inorganic silicon-based polymers can be tailor-made to obtain materials with mechanical, chemical, optical, or electric properties that suit a great variety of applications and are compatible with microfabrication technologies. Herein, this work reports on the one-step processing of microstructures of a sol–gel polymeric material on flat substrates by microtransfer molding. A careful selection of silanes and the experimental conditions for the generation of the three-dimensional polymeric network was of key importance to obtain structures of up to 70 μm high having an aspect ratio of up to 10:1 (height/width), with excellent periodicity and reproducibility. Besides, a very low degree of shrinkage of the sol–gel polymer was shown upon aging and drying steps, thereby enabling the perfect control over the fabrication of the final structure. Pillars, wells, and lines of different dimensions were fabricated and characterized by optical, scanning electron, and atomic force microscopy techniques. The controlled development of sol–gel microstructures using a simple fabrication technology may widen the range of promising applications of these materials in areas such as optoelectronics or chemical sensing.

Introduction

Mild temperature sol–gel fabrication processes have enabled the generation of homogeneous silicon-based polymeric matrixes with unique physicochemical properties. Since the early works in the field reported nearly four decades ago,[1,2] there has been a dramatic evolution in every aspect of this technology, from the almost unlimited range of precursors currently available to the great variety of polymerization and curing conditions.[3–5] One important issue that contributed to the widespread application of sol–gel technology was the introduction of organo-alkoxysilanes. These precursors bring organic functional moieties to the synthesized polymer matrixes, thereby providing attractive specific features to the so-called ORMOSILs[6] or ORMOCERs[7] resulting materials.[8,9]

The silicon sol–gel technology basically consists in the room temperature hydrolysis and polycondensation of (organo-)silicon alkoxides in a hydroalcoholic medium to give an inorganic polysiloxane network that may contain unreacted silanol moieties together with different organic side groups.[10,11] The kinetics of hydrolysis and condensation reactions depend primarily on both the nature of the precursors and the working conditions, such as use of acid or basic catalysts, temperature, type of solvents and water: silane ratio. A careful selection of these parameters enables the fabrication of innovative materials with a perfectly controlled physical and chemical morphology from the nanometric to the micrometric scale.[12]

Provided the inherent versatility of the sol–gel technology, organic–inorganic silicon-based materials can be fine-tuned to suit particular applications in different fields including integrated optics, electronics, coatings, catalysis or sensors,[13–15] for which they can be easily attained in a wide range of shapes such as films, rods, particles, membranes or monoliths.[16] Moreover, they can be doped with or work as host phases of active organic molecules[17] and labile biomolecules[18] which have contributed to a more expanded range of applications of these materials.

In addition, silicon-based polymers can be easily adapted to and integrated with microfabrication processes. Herein,

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many of these smart polymeric materials can be patterned using lithography techniques in order to obtain well-defined specific microstructures on various substrates.[19–37] Polymer matrixes containing photoactive and/ or thermocurable organic groups, such as methacrylic and epoxy moieties,[19–25] have been used for the fabrication of miniaturized devices by mask-assisted UV lithography[19,20,25] and laser writing UV lithography.[21–24] Working as negative resists, silicon-based materials can be developed into 3D passive optical structures, i.e., waveguides[20–22] and photonic crystals,[23] at wafer level. Other nonoptical micropatterned structures have been reported. This includes the fabrication of sol–gel microneedles for transdermal drug delivery[24] and the development of an organic thin film transistor using a patterned sol–gel hybrid material as a gate dielectric.[25]

Soft lithographic techniques, pioneered by Whitesides et al.,[26] have been applied to the fabrication of sol–gel 3D microstructures in a one-step process. Microtransfer molding[27] (μ-TM) and micromolding in capillaries[28] (MIMIC) enable the development of replicas of polymeric materials on planar and nonplanar substrates by using a relief pattern of a flexible mold, common to all the soft lithographic techniques. These nonphotolithographic approaches are available to a wider range of organosilane precursors, since the patterning process is not dependent on the presence of active functional groups in the selected monomers, like the ones mentioned above. In addition, they do not require complex equipment, are cost-effective, and can equally be applied over large substrate areas, thus making them very attractive for high-throughput microfabrication processes. Regardless of the reported pros and cons of each of these techniques,[26] both of them have been applied to the development of micrometer- and submicrometer-sized structures of inorganic[27–30] and functional organic–inorganic[31–34] sol–gel silicon-based materials. This includes passive waveguides,[28–30] mesostructured laser waveguides,[31,32] membranes,[30] microstructures for protein patterning,[33] and active patterned surfaces[34] for sensor purposes.[35]

Replica molding[36] and embossing[37,38] are alternative nonphotolithographic approaches that make use of a mold and appear to be suitable for the fabrication of polysiloxane diffractive optical elements[36] and selective recognition structures in sensor devices.[38] Combined mask assisted photolithography/embossing processes have also been reported on the development of silicon-based microlenses.[39]

This work describes how tailor-made sol–gel processes using organic–inorganic precursors afford the one-step fabrication of functional siloxane 3-D patterns by μ-TM. Perfect replicas of relief patterned molds were attained with excellent periodicity and reproducibility. A careful selection of the silane precursors and the corresponding experimental conditions for the preparation of the sol–gel enabled the fabrication of structures with dimensions down to 1 μm wide and up to 70 μm high, exhibiting maximum aspect ratios of 10:1 (height/width). It is shown that, tuning the hydrophobic/hydrophilic nature of the sol–gel materials by combining appropriate proportions of functional alkoxysilanes containing phenyl and methyl side groups, smooth and crack-free surfaces of these structures were achieved. Regarding the previous works on the field outlined above and to the best of our knowledge, the one-step simple fabrication of such high-aspect-ratio patterns has not been reported before. Possible applications of such structures are envisaged and commented.

Experimental Section

Materials. Tetramethoxysilane ($\geq$99.0%, TMOS), methyltrimethoxysilane ($\geq$98.0%, MTMOS), and phenyltrimethoxysilane (purum, PhTMOS) were purchased from Sigma-Aldrich Química S.A. (Spain) and used as received. SU-8 5005 and 5025 photocurable polymer and propylene glycol methyl ether acetate (PGMEA) developer were from Microresist Technology GmbH (Berlin, Germany). Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 were from Dow Corning Corp (Midland, MI). All other chemicals were of analytical reagent grade. Ultrapure water (resistivity, 18 MΩ cm) was also used.

Preparation of Masters and Molds. Masters were fabricated with the negative photoresist SU-8 by one photolithographic process.[40] A layer of SU-8 was deposited by spin-coating at 4000 rpm for 15 s, on a 4-in. SiO_2-coated Si wafer. SU-8 5005 and 5025 were used to obtain layers with thicknesses up to 25 μm and above this value, respectively. Following a bake step at 95 °C for 6 min, the SU-8 layer was exposed to UV light through a mask for 8 s. A postexposure bake at 95 °C for 5 min was then carried out, before developing the SU-8 in PGMEA to obtain the master.

PDMS prepolymer solution was made by thoroughly mixing 5 mL of the silicon elastomer 184 and 0.5 mL of the curing agent

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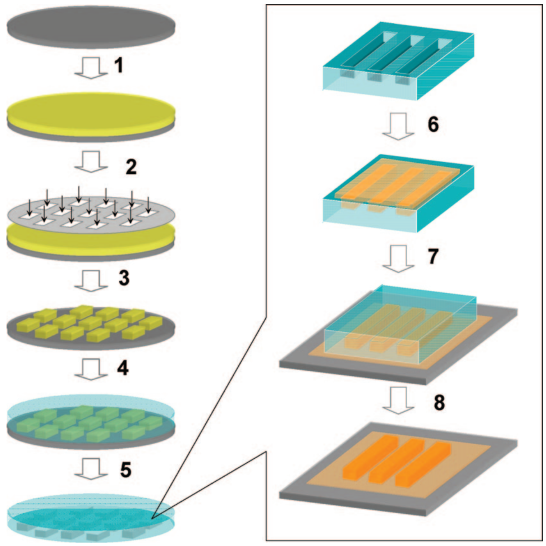

Figure 1. Fabrication of master and μ-transfer molding lithographic process. (1) SU-8 spin-coated on wafer. (2) UV exposure through a mask. (3) SU-8 developed to release the patterns. (4) Master coated with PDMS. (5) PDMS peeled off the master. (6) Sol solution cast on piece of PDMS mold. (7) PDMS transferred to substrate. (8) PDMS peeled off the substrate after polymerization.

184 (10:1 (v:v) ratio), respectively. The mixture was put under vacuum to remove air bubbles. Then, it was carefully poured onto the SU-8 master to cover its entire area, and finally cured at 80 °C for 30 min. Using these experimental conditions, the thickness of the PDMS was always less than 2 mm. The fabricated PDMS mold was peeled off the master with the aid of tweezers and stored in a closed container under clean room conditions. The resulting PDMS was the size of the master (4 in.). Before use, the PDMS was cut in pieces containing the desired patterns, having areas around 1 cm^2, using a scalpel. Figure 1 depicts the steps described above.

Sol–Gel Silicon-Based Materials. Some 615 μL of MTMOS, 60 μL of TMOS, and 75 μL of PhTMOS stock solutions were mixed in a plastic beaker, under constant stirring. Then, 900 μL of ethanol, 280 μL of water, and 25 μL of hydrochloric acid (0.1 M HCl) were sequentially added. These volumes gave a 10:1:1 MTMOS:TMOS:PhTMOS and a 1:3:3 silanes:ethanol:water molar ratios. The resulting mixture was gently stirred for at least four hours, at room temperature, until it lost around 30% of its initial weight. At this point, the resulting prepolymerization solution (the sol solution) was homogeneous and ready for the patterning process.

***μ*-Transfer Molding Process.** μ-TM was carried out on either glass or thermally grown SiO_2/Si substrates. Both of them were previously cleaned by immersion in concentrated sulfuric acid and then thoroughly rinsed with ultrapure water and ethanol, and dried under a stream of N_2. Some 4 μL of the sol solution were dropped on the PDMS mold (area around 1 cm^2), which was previously stuck to the base of a homemade press. This includes an XYZ micropositioner. The mold was brought down to contact the substrate. After that, a constant pressure was applied for 20 s. The PDMS/substrate system was then taken out from the press and left it undisturbed in air under Clean Room conditions (21 °C, atmospheric pressure) for at least three days to allow the polymer to gel, age, and dry. Finally, the PDMS mold was peeled off the substrate with the aid of tweezers in order to release the xerogel microstructures. A thin residual layer of the material, a few nanometers thick, coats the patterned area and so connects the polymeric features. This is inherent to the transfer molding process and, whether necessary, it can be easily removed by plasma etching.[27] Figure 1 shows the main steps of the μ-TM process.

Characterization of the Sol–Gel Microstructure. Bright-field optical microscopy images of the sol–gel patterns were initially taken to help assess the performance (periodicity and reproducibility) of our lithographic process. Profiles recorded with a PLμ Confocal Imaging Profiler from Sensofar-Tech. S.L. enabled the rapid evaluation of the degree of shrinkage of the sol–gel in the microstructure, upon aging and drying. The quality of the patterns was evaluated by recording scanning electron microscopy (SEM) images using a Hitachi S-530 microscope that detects secondary electrons, following the deposition of a 10nm-thick Au layer on top of the structures by vacuum evaporation. The topography and uniformity of the sol–gel surface was tested by atomic force microscopy (AFM) using a Nanoscope IV Dimension 3100 from Veeco Instruments, working in the dynamic mode.

Optical properties of some of the microstructures were evaluated by an end-fire coupling method. The input optical fiber had a diameter of 4 μm. A connectorized LED with a working wavelength of 678 nm was used as a light source. A x10 microscope objective was used to collect the light at the output side of the structure, which was imaged with a CCD camera. The alignment of the different components of the system was carried out with the aid of three XYZ micropositioners.

Results and Discussion

The experimental conditions to fabricate the sol–gel material were carefully studied. MTMOS, TMOS and PhTMOS were chosen on the basis of the different functional groups that they contain, which would provide specific properties to the final sol–gel material, as explained below. The room-temperature acid-catalyzed hydrolysis and polycondensation of MTMOS, TMOS and PhTMOS in a 10:1:1 molar composition gave rise to smooth, optically transparent, homogeneous and crack-free polymeric matrixes. Tuning the hydrophobic/hydrophilic balance of the sol–gel was essential in order to obtain a chemically and mechanically stable material that could be patterned over large surface areas by a soft lithographic approach. Indeed, it was shown that by applying the same polymer precursors but changing the silane proportions and silane:water:alcohol ratios, the resulting sol solutions proved unsuitable for the subsequent microfabrication process. MTMOS was used in a proportion above 80% of the total silane amount. This monomer was mainly responsible for the structural characteristics of the resulting material. MTMOS promotes the formation of hydrophobic sol–gel materials with a good degree of elasticity by introducing small nonhydrolyzable methyl side groups, which block one direction of cross-linking but without adding a steric hindrance effect for the formation of siloxane bonds. Besides, it avoids the formation of any cracks or defects on the polymer surface during processing.[11] The incorporation of TMOS in a proportion of around 8% was intended to introduce free silanol groups (Si-OH), which provide the desired level of hydrophilicity to the sol–gel material. This silane is commonly used as the backbone of hybrid polysiloxane materials. However, its use in high proportions is restricted due to the high degree of shrinkage that the resulting materials undergo during aging and drying steps.[41]

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PhTMOS introduces a phenyl side group to the polymer, which has an important influence on its optical properties. The refractive index of the sol–gel material can be tailored by adjusting the concentration of this organosilane. Increasing its concentration results in silicon-based polymers with higher refractive indices.[19,21] Here, PhTMOS was added in an 8% proportion of the total silane amount and it also contributed to the overall hydrophobicity of the resulting material. Besides, as well as MTMOS, the presence of the phenyl group makes the polymer network more flexible. The hydrolysis and polycondensation of these silanes was accelerated by the use of a catalyst such as HCl. Acid catalysis promotes the formation of homogeneous, dense xerogel structures with a rather limited porosity after solvent removal by evaporation at room temperature and under atmospheric pressure.[4,5,11]

The initial water:silane molar ratio was always 3:1, which is substoichiometric considering that TMOS requires four water molecules for its complete hydrolysis.[42] However, condensation reactions taking place simultaneously are an extra source of water for complete silane hydrolysis. The water content in the initial solution was kept low, which allows for a more cross-linked polymer network. EtOH was also necessary in the initial sol solution in order to obtain a rapid miscibility of all the components.

Weight loss of the initial solution before performing the patterning process was a key step in order to maintain the geometry of the desired microstructure. A 30% weight loss was appropriate for that and for keeping the sol solution fully transparent, homogeneous and with an optimum viscosity for the transfer molding process. The weight loss at this stage is likely to be related to the evaporation of both EtOH cosolvent and MeOH produced during the hydrolysis of the organosilane compounds.

Using the above optimized experimental conditions, different microstructures were patterned on either glass or thermally grown silicon oxide surfaces following the steps described in the experimental section. Polymeric pillars (Figure 2), microwells (Figure 3), and lines (Figure 4) were obtained on large surface areas, over a 1 cm^2, with excellent periodicity and reproducibility. Figure 2 shows an array of 7 μm high pillars with widths of 3 and 4 μm, having a separation of 2 μm. The optical image shows the good transition between both sets of structures. Amplifying pictures taken with SEM (Figures 2b and 2c) reveal the excellent performance of the molding process and the high quality of the resulting patterns, since no cracks or defects can be observed on the material surface. Besides, they show that well-defined densely packed structures could be easily obtained with this technique. Considering the pillars as "positive" patterns, 7 μm deep microwell structures (Figure 3) were fabricated with the aim of assessing the suitable fabrication of "negative" patterns within a thin layer of the xerogel material. No volume loss was observed in any of these experiments. The confocal microscopy image in Figure 3b also shows the fine definition of the side-walls of these microstructures.

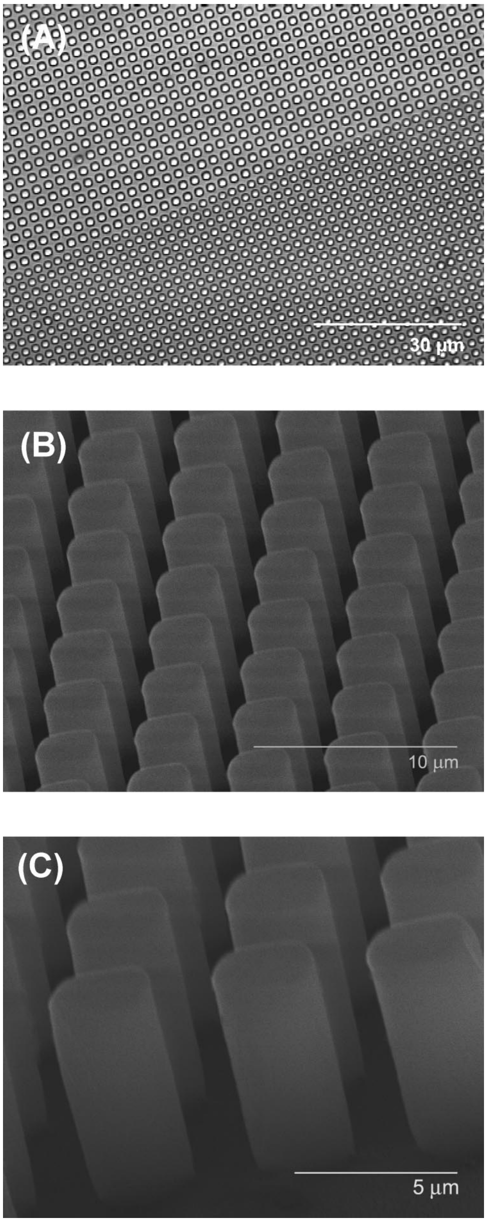

Figure 2. (A) Optical image of pillars 3 μm and 4 μm wide separated by 2 μm, printed over a large surface area. (B, C) SEM images showing 3 μm wide pillars.

Lines 500 μm long and 1 μm to 30 μm wide were also fabricated. Figure 4a depicts SEM images of densely packed lines with widths ranging from 4 μm to 7 μm. Also are shown isolated structures 1 μm to 3 μm wide (Figure 4b), 1 μm being the smallest lateral dimension achieved with this material. A 7:1 (height/width) maximum aspect ratio was attained in the fabrication of these microstructures. Another issue addressed here was the good definition of the overall structure when the separation was significantly smaller than the width of the printed structures. It should be pointed out that limitations due to the fabrication of the master and the PDMS mold are a shortcoming for the generation of even smaller features with this sol–gel composition.[26]

At this stage, the surface characteristics of the resulting sol–gel material were evaluated by AFM. Figure 5 shows a 10 × 10 μm^2 AFM topographic image of this material. The rms roughness is 1.27 nm. From these results, it can be said

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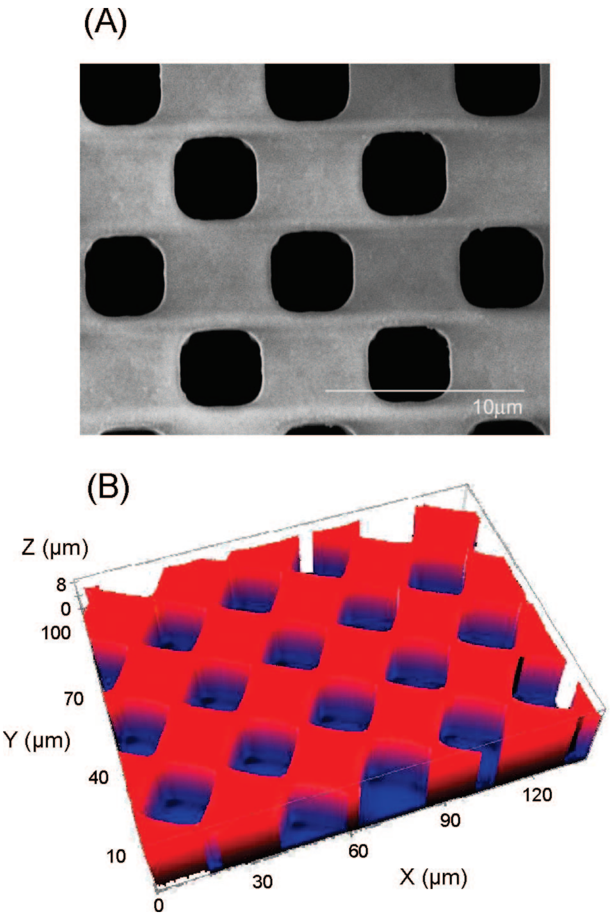

Figure 3. (A) SEM image and (B) confocal image of 7-μm deep, 4-μm wide microwells defined on a thin sol–gel layer.

that the material is smooth and uniform and does not show any cracks or defects. Studies of the porosity of these material structures were carried out by BET N_2 adsorption analysis. However, these studies proved unsuccessful. It has been reported elsewhere that sol–gel materials prepared by acid-catalyzed hydrolysis and condensation reactions, at room temperature and atmospheric pressure, exhibit a narrow pore size distribution in a normal range between 1 and 5 nm,[5] with mean pore diameters below 2 nm. Besides, it has been also described that BET N_2 adsorption analysis does not give accurate results when trying to measure pore diameters in this range.[43] Using other methods like thermoporometry analysis, pore size distribution of an acid catalyzed MTMOS-based xerogel material was studied. A mean pore size of less than 1 nm diameter was reported.[43] Therefore, it can be inferred that the sol–gel material described in this work may have a short-range pore distribution with a mean pore size roughly in the 1 nm range.

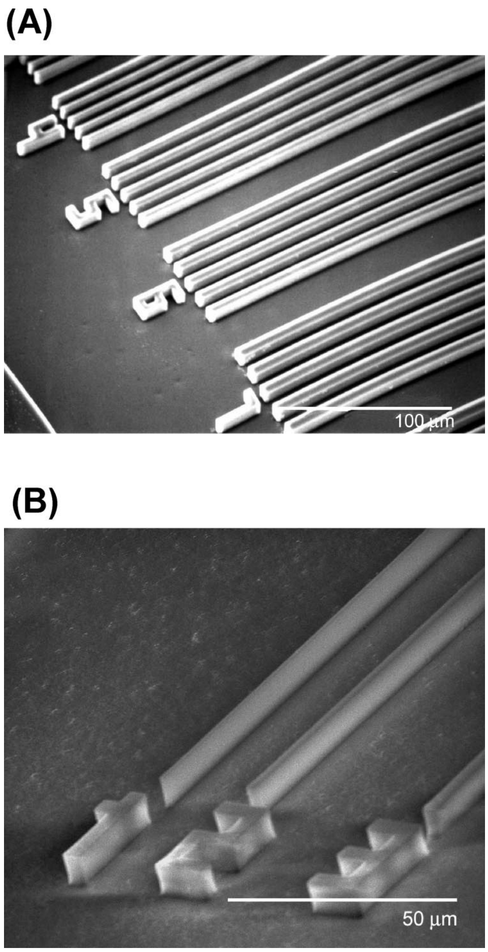

Figure 4. SEM pictures of sets of well-packed (A) 4−7 and (B) 1−3 μm wide sol–gel lines, all of them having a height of 7 μm.

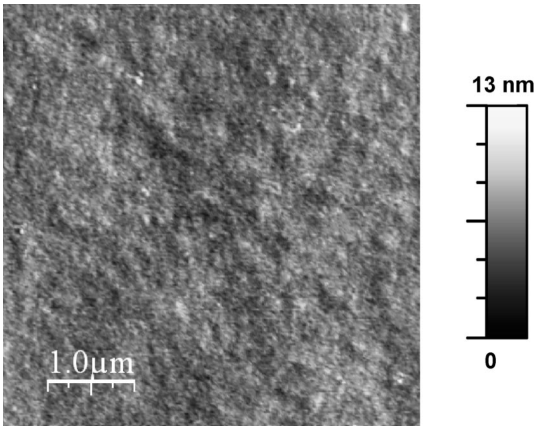

Figure 5. AFM topographic picture of the sol–gel surface of a microstructure fabricated by μ-TM process.

With the aim of fabricating higher structures, PDMS molds with patterns showing heights between 20 and 70 μm were obtained. Here, it was shown that loss of vertical dimensions in such high structures usually took place if the viscosity of the sol solution was not controlled. Thus, the typical meniscus appeared at the top facet of the microstructure. As described above, the initial solution was stirred for at least four hours until it lost 30% of its weight whereupon the appropriate conditions to develop these structures and to avoid the loss of the feature dimensions upon drying and aging were attained. Working with organo-alkoxysilanes allows for the anticipation of volume losses when the sol–gel is being processed. Control of the shrinking effect appears to be very difficult when developing inorganic glasses from tetra-alkoxysilanes such as TEOS or TMOS. Loss of lateral and vertical dimensions is commonplace here and, in addition, the resulting structures are more susceptible to cracking upon drying and aging processes.

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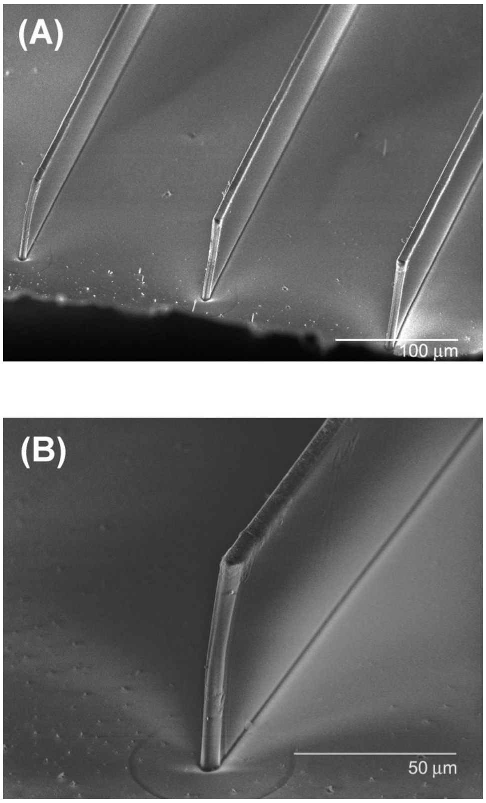

Figure 6. (A) SEM images of 7−9 μm wide sol–gel lines with a height of 70 μm. (B) A more detailed SEM picture of the 7 μm wide xerogel line.

Figure 6 depicts SEM images of lines 70 μm high and widths ranging from 7 to 9 μm. Such lines were fabricated up to 1 cm long. A 10:1 (height/width) aspect ratio was easily achieved. The confocal image and profiles in Figure 7 demonstrate the excellent definition of these structures. Besides, it should be pointed out that no loss of structural dimensions was observed upon removing the PDMS mold when working with this sol–gel composition and under the experimental conditions mentioned above. To the best of our knowledge, the one-step fabrication of such high aspect ratio sol–gel patterns has not been reported before. As stated by Whitesides et al.,[26] the fact that PDMS is an elastomer explains why soft lithography has not been used to make high structures with larger height to width aspect ratios. The sidewalls of high-aspect-ratio PDMS relief features tend to adhere causing lateral collapse or pairing and consequently destroying the structure.[44] This effect was not seen in the present work probably due to the large separation between neighboring features in the mold, which was kept around 150 μm. A two-layer structure made with "hard" PDMS (*h*-PDMS, polymer composite made of a vinyl PDMS prepolymer) and common PDMS is mechanically more stable and seems to be a good alternative for the fabrication of PDMS molds containing large aspect ratio features. Although this modification seems to be more suited for the fabrication of PDMS nanostructures it may be useful for microsized features too.[44]

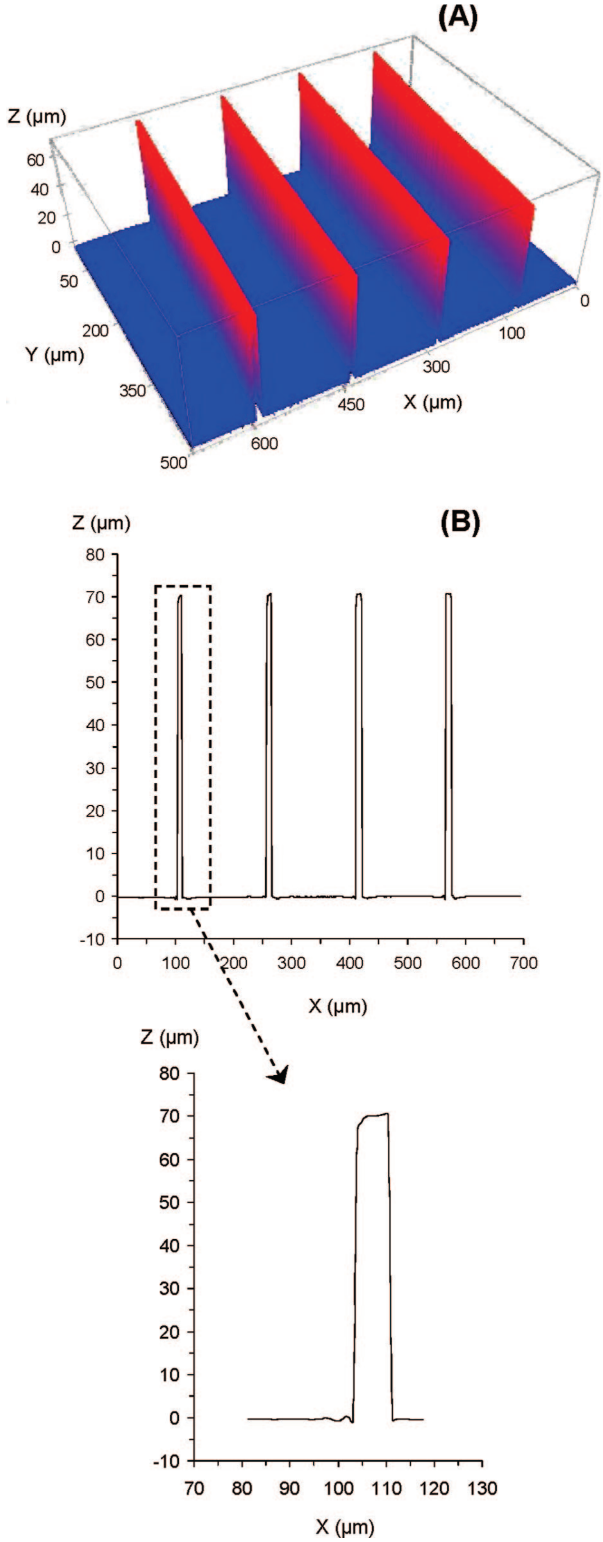

Figure 7. (A) Confocal image of the xerogel lines shown in Figure 6. (B) Profiles of these lines and full-scale real dimensions of the 7 μm wide line.

Regarding the influence of temperature on the overall structural properties of hybrid xerogel materials, all the patterns presented in this work were processed and further stored at room temperature. They were tested at room temperature operational conditions over a period of up to six months time and did not show any appreciable evolution.

To assess for the optical quality of this sol–gel material, we tested its applicability for the development of waveguides. Herein, 20 μm high waveguides with widths ranging from 3

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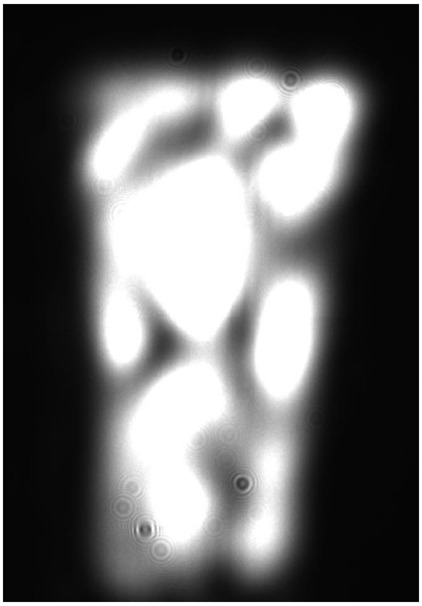

Figure 8. Recorded output signal of a sol–gel waveguide 12 μm wide and 20 μm high.

to 15 μm were fabricated and tested. They were first cleaved in order to remove the thick-film residual sol–gel layer generated on those areas not covered by the PDMS stamp during the μ-TM process and to obtain good quality input and output facets. Figure 8 shows an image, in near field, of the output light for a 12 μm wide 1 cm long waveguide. It is seen that the light was perfectly confined within the waveguide, with the expected highly multimodal behavior. These results confirm the validity of the proposed sol–gel material for the fabrication of single-step integrated photonic elements.

Conclusions

The versatility of the sol–gel process has been extensively demonstrated in the literature. The fabrication of patterns of controlled dimensions of a tailor-made sol–gel material may expand the range of applications of these polymeric phases within fields such as microfabrication, optoelectronics and sensors.[19–39] The use of soft lithographic approaches, mainly μ-TM and MIMIC has given rise to the successful fabrication of sol–gel microstructures with a variety of geometries.[27–35] However, these technique seemed to be restricted to the generation of sol–gel patterns with heights up to 10 μm[34] and aspect ratios not larger than 8:1 (height/width).[27] Here, we show the successful fabrication of standing structures of up to 70 μm and aspect ratios up to 10:1 (height/width). Negligible loss of either lateral or vertical dimensions during the patterning process was observed. This was demonstrated by a good structural characterization of such patterns carried out by optical, scanning electron and atomic force microscopy techniques. The successful implementation of this fabrication process relies on tuning the silane precursor composition and thus the hydrophobic/hydrophilic nature of the resulting sol–gel. Besides, the prepolymerization conditions should be carefully optimized, which includes the water to silane content and solution percentage weight loss before the patterning process. It is envisaged that such patterned microstructures could play a role in microfabrication technologies and in the development of a variety of applications in fields such as optoelectronics and chemical sensors. As an example of application, the guiding properties of a 20 μm thick sol–gel waveguide fabricated with the presented technology were shown.

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