

RESEARCH NOTES

Rapid Thermal Processing of Mesoporous Silica Films: A Simple Method to Fabricate Films Micrometers Thick for Microelectromechanical Systems (MEMS) Applications

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We are interested in constructing self-assembled mesoporous silica films several micrometers thick in a cost-effective way, for use as ionic conductors, membranes, and sensors for microelectromechanical systems (MEMS) applications. One way to construct films of micrometer thickness is to repeat the coating processes with each step, followed by calcination of the surfactants. However, conventional furnace calcination requires hours, which makes it impractical. In this paper, we report the use of a lamp-based rapid thermal processing (RTP) as a simple and fast way to remove surfactants and stiffen the silica framework. The RTP enabled us to save processing time (by an order of magnitude, in comparison to the time required for conventional furnace processing). Mesoporous silica films $\sim 2.5 \mu\text{m}$ thick were fabricated within an hour. Using microfabrication techniques, self-supporting mesoporous films were subsequently fabricated on patterned silicon wafers.

Introduction

Porous nanostructured films are of great interest in chip-scale analytical devices, because of their high surface area.¹ Presently, it is a challenge to fabricate such a porous nanostructure in cost-effective ways with current top-down micromachining. In this paper, we explore the use of self-assembly of nanoporous silica deposited via dip coating and rapid thermal processing to create a self-supporting film on a silicon wafer. Previous work has shown that self-assembled mesoporous silica films (which are defined as those having pores with diameters of 2–50 nm) can be an alternative to creating such nanostructure in a simple and controlled manner, because they can be easily coated using conventional coating techniques² (for instance, spin coating³ and dip coating^{4,5}), readily functionalized with functional organic groups, and are compatible with current silicon microfabrication technology.^{6–8} However, self-supporting films on substrates have not yet been demonstrated.

Self-assembled mesoporous silica materials have attracted much research interest over the past decade.^{9,10} Their uniform pore structures in nanometer scales enable them to find applications in separation,¹¹ catalysis,¹² encapsulation,¹³ chemical/biological sensing,¹⁴ low-dielectric coatings,¹⁵ and optical thin films.^{10,16} Mesoporous silica materials can form typically via cooperative interactions between the self-assembly of surfactants

(cationic or anionic) and the condensation of silica, leading to an organic/inorganic hybrid nanoporous framework structure.^{17–20} The chain length of the surfactant molecule determines the size of the pores, whereas the synthesis conditions (such as sol composition, temperature, aging, and reaction time) determines the crystal phase. Thin-film surfactant/silica composites can be produced by solvent evaporation methods such as dip coating and spin coating. Subsequent removal of the organic surfactants inside the nanopores—typically, via furnace calcination for several hours—opens the pores and stiffens the silica framework for practical usage, resulting in continuous nanoporous films with a thickness of $< 1 \mu\text{m}$.

However, it is desirable to create continuous films of a thickness in the range of several micrometers to find the mesoporous silica films in microelectromechanical systems (MEMS) applications that need functional nanostructures. It is believed to be a significant challenge to deposit a continuous sol–gel film of $> 1 \mu\text{m}$, because of the stress developed within the framework stemming from the capillary force induced by solvent evaporation.⁸ Repeated coating (dip or spin), followed by furnace calcination, may allow one to build films with a thickness greater than $1 \mu\text{m}$. However, it would be very costly, as well as inconvenient, in standard silicon processing, because of prolonged calcination process. To avoid such a high thermal budget, it is desirable to devise a new process to remove surfactants in a relatively shorter time period.

Here, we investigate a lamp-based rapid thermal processing (referenced hereafter as RTP) as a new calcination process to reduce the thermal budget. RTP

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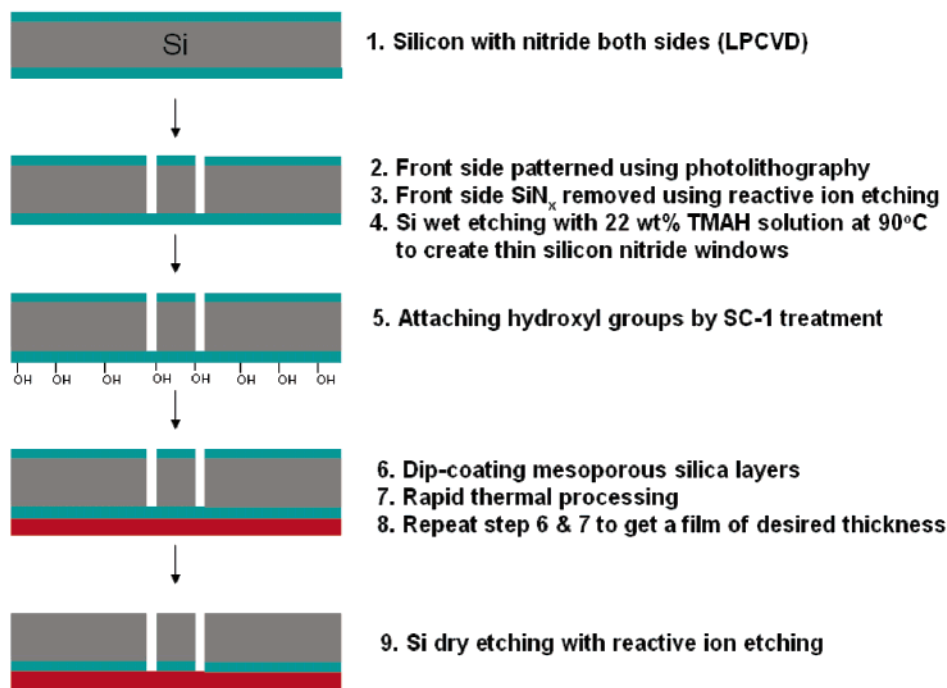


Figure 1. Procedure for the microfabrication of a self-supporting mesoporous film on a silicon wafer.

has been used in the integrated circuit (IC) and MEMS communities to relieve the residual stress of thin films.²¹ Unlike low-temperature processing techniques, this technique requires a high temperature; however, the processing time is only a few seconds, thus reducing some of the adverse effects.²² The RTP method typically uses electrical lamps (either incandescent or arc) to ensure spiking of the temperature.²²

In this paper, we report the use of RTP to remove surfactants and to stiffen the nanoporous silica framework, and to demonstrate that mesoporous silica films with a thickness of $\sim 2.5 \mu\text{m}$ can be built within a short period of time (minutes instead of days). Using microfabrication techniques, self-supporting mesoporous films prepared with RTP were subsequently fabricated on a patterned silicon wafer. Self-supporting mesoporous films on substrates (in particular, silicon wafers) are interesting, not only for some of the MEMS applications but also for the fundamental study of the structure–property relationships of the films.

Experimental Section

Preparation of Mesoporous Silica Films. Mesoporous silica films were prepared using a two-step sol–gel technique that was developed by Brinker and co-workers.²³ A prehydrolyzed solution was first prepared by refluxing tetraethoxysilane (TEOS), ethanol (EtOH), water, and HCl (at a molar ratio of 1:3.8:1:(5×10^{-5})) at 60 °C for 1 h. The surfactant (CTAB: $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$), water, and HCl then were added. After stirring at room temperature for ~ 5 min, the sol was allowed to age at room temperature for ~ 1 h. The final molar composition was typically 1TEOS:20EtOH:0.0056HCl:5.6H₂O:0.13CTAB.

Silica films were deposited on clean (100)-silicon substrates by dip coating at a rate of 5 mm/s and allowed to dry at room temperature for several hours. To remove the surfactant and stiffen the silica framework, two different calcination methods were applied: one using a conventional furnace processing (referenced

hereafter as FP) and the other using an illumination-assisted rapid thermal processing (RTP). In a conventional furnace, the films (FP films) were heated at 400 °C for 6 h with heating and cooling rates of ~ 1.5 °C/min under an oxygen flow. In RTP, the films (RTP films) were ramped up to 900 °C at the heating rate of ~ 450 °C/min and soaked at 900 °C for 30 s under an oxygen flow of 40 mL/min. The cooling was facilitated with cooling water but not controlled. Typically, several minutes were required to cool the assembly to 200 °C. A thermocouple was placed in contact with the silicon wafer to measure the temperature.

Microfabrication of Mesoporous Silica Films. Figure 1 illustrates the fabrication procedure used to create the self-supporting mesoporous silica films on silicon wafers. Prime-grade *p*-type (boron-doped) double-side-polished (100) silicon wafers with diameters of 100 mm and resistivities of 0.01–0.02 $\Omega\text{-cm}$ were used as substrates. To prepare patterned substrates, a silicon nitride film ~ 800 nm thick was first deposited on both sides of a wafer by low-pressure chemical vapor deposition (LPCVD). Photolithography was used to pattern four small circular openings with a diameter of 1.4 mm on the front side of each die on the wafer. Reactive ion etching with a Freon plasma was then applied to remove the silicon nitride, to expose circular areas on the front side, as shown in Figure 1. Silicon nitride membranes were formed by wet etching of the silicon in a 22 wt % tetramethylammonium hydroxide (TMAOH) solution. Prior to coating the mesoporous silica layer, the nitride membranes of the die were treated in SC-1 solution (100H₂O:10H₂O₂:1NH₄OH) at 73 °C for 2 h, decorating the nitride surface with hydroxyl groups. These hydroxyl groups help the wetting of mesoporous silica on the silicon nitride surface. Mesoporous silica was then dip-coated on the backside of the wafer and treated with RTP. The dip coating and RTP was repeated until films of the desired thicknesses were obtained. The silicon nitride windows were finally removed using a deep

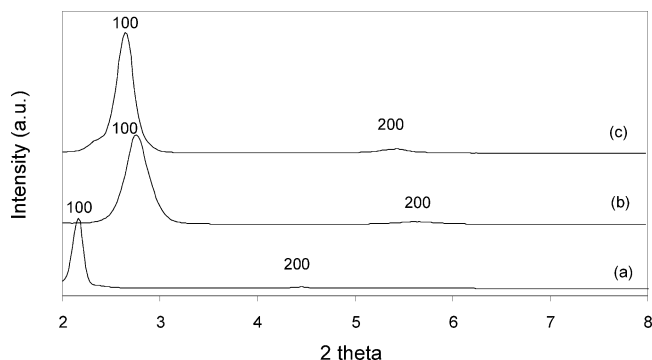


Figure 2. X-ray diffraction (XRD) patterns of mesoporous silica films: (a) as-deposited, (b) calcined using a furnace at 400 °C for 6 h, and (c) calcined using rapid thermal processing (RTP) at 900 °C for 30 s.

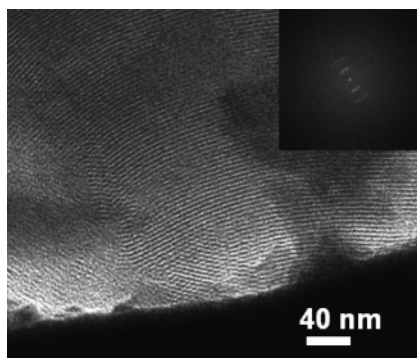


Figure 3. Transmission electron microscopy (TEM) image of a RTP mesoporous silica film scratched from the substrate. Inset shows the Fourier transformation of a selected area. The film was treated at 900 °C for 30 s.

reactive ion-etching (DRIE) technique, yielding self-supporting mesoporous silica windows.

Characterization Techniques. The rapid thermal treatment was performed using a lamp-based rapid thermal annealer (Model E4-10, Radiant Energy Research, Inc., Minneapolis, MN) that was equipped with a Micristar controller (828 series). The structures of the as-deposited and calcined films were examined by X-ray diffraction (XRD) (Rigaku D-Max) with Bragg–Brentano reflection sample geometry, using Cu K α radiation ($\lambda = 1.54056$ Å). Transmission electron micrographs were taken to image the pore structures of the films, using a high-resolution transmission electron microscopy (HRTEM) system (Philips CM-200) that was operating at 120 keV. For sample preparation, the silica films were scratched off the substrates and attached onto copper TEM grids with EtOH. The thickness of the film was measured using a surface profilometer (Sloan Dektak3). Scanning electron microscopy (SEM) (JEOL, model 6060LV) and optical microscopy (Leica) were used to investigate film morphology. A Nicolet Magna model IR-750 Fourier transform infrared (FT-IR) spectrometer that was equipped with a reflectometer (Harrick Scientific) was used to collect the reflectance spectra of the samples before and after various thermal treatments. All the spectra were collected using a liquid-nitrogen-cooled MCT-A detector. The measurements were performed using *p*-polarized light (wire grid polarizer, Harrick Scientific) at an angle of 65° to the normal. Given the reflective nature of the substrate, a polished gold mirror was used to collect the background spectra. Auger electron spectroscopy (AES) (Physical Electronics, model PHI 660) was used to probe residual carbon

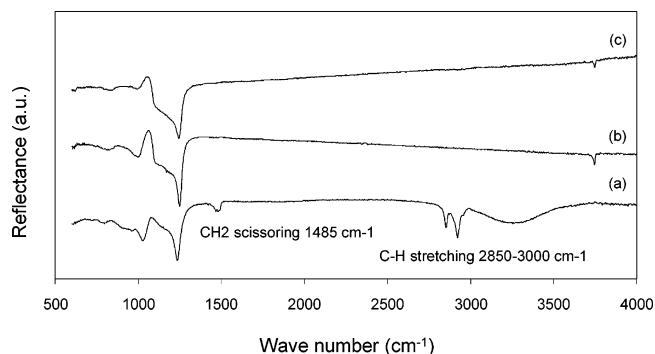


Figure 4. Reflectance Fourier transform infrared (FT-IR) spectra of mesoporous silica films: (a) as-deposited, (b) calcined using a furnace at 400 °C for 6 h, and (c) calcined using RTP at 900 °C for 30 s.

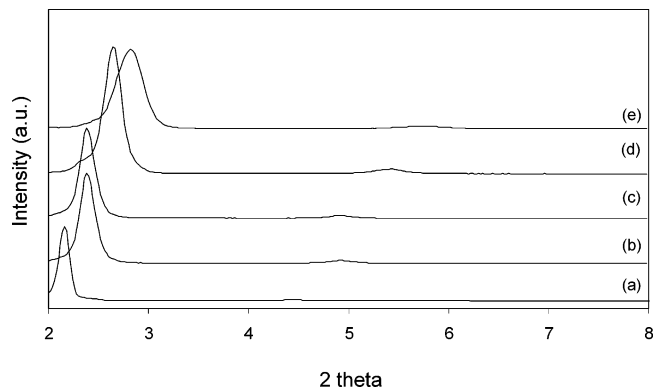


Figure 5. XRD patterns of mesoporous silica films calcined with RTP at different temperatures: (a) as-prepared, (b) 500 °C, (c) 700 °C, (d) 900 °C, and (e) 1000 °C. All samples were heated at a ramping rate of 450 °C/min and soaked at the desired temperature for 30 s.

Table 1. *d*-spacings of (100) Reflections, the Degree of Contraction along the [100] Direction, and the Full Width at Half Maximum (fwhm) of the (100) Peaks of the RTP Films at Various Temperatures

temperature (°C)	<i>d</i> -spacing (Å)	contraction (%)	fwhm
as-deposited	40.8	0.0	0.12
500	38.3	6.1	0.18
700	37.4	8.5	0.18
900	33.4	18.2	0.20
1000	31.0	23.9	0.32

species on the surface of the films. The presence of carbon at the surface was probed using the 272 eV carbon peak. To avoid surface contamination effects from handling, and to probe the presence of carbon in the bulk of the film, depth profiling (alternately sputtering using an ion gun and profiling using the electron beam) was performed.

Results and Discussion

The as-deposited and calcined films showed good optical quality, with thicknesses in the range of 200–300 nm. The XRD patterns of the FP and RTP films, in comparison with an as-deposited film, are shown in Figure 2. The intense Bragg diffraction peaks in the lower 2θ region and their second-order reflections indicate that these are highly ordered structures. The first peaks were assigned to the (100) reflection of a two-dimensional hexagonal lattice (p_{6m}) with the *c*-axis (the channel axis) preferentially aligned with the substrate.⁴ The lattice type was further confirmed by TEM analysis,

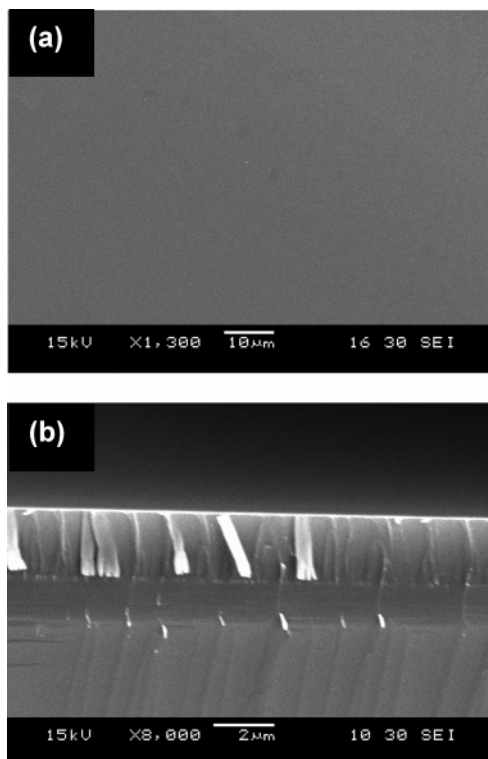


Figure 6. Scanning electron microscopy (SEM) images of a RTP mesoporous silica film: (a) top view and (b) cross-sectional view.

as shown in Figure 3. It was observed that, upon heat treatment, the d -spacings of the (100) planes were decreased to 31.9 Å for FP and 33.4 Å for RTP films, as compared to 40.8 Å for the as-deposited film. This decrease in d -spacing (equivalent to the increase in

Bragg angle) suggests that a contraction of the framework structure occurred in a direction perpendicular to the substrates, which resulted from the removal of the surfactant as well as additional condensation of silanol (Si–OH) species.²⁴ The removal of surfactant was further corroborated by the disappearance of infrared bands in the ranges of 2850–3000 and 1485 cm^{-1} , as shown in Figure 4. The absence of carbon species was also verified by AES (not shown here) for both of the calcined samples. As shown in Figure 2, RTP led to the less contraction (18%) than that observed for conventional furnace calcination (22%). This lesser contraction of the RTP sample could be explained by the fact that the degree of the condensation of the framework after thermal processing is expected to be higher for the FP sample, because of the substantially longer processing time (6 h, as compared to 30 s for the RTP sample) for the FP sample. The RTP sample showed the smaller full width at half-maximum (fwhm) value than the FP sample, indicating that the RTP produces mesoporous silica films of pore structures of less disorder. Figure 5 compares the XRD patterns of the mesoporous silica films treated with RTP at different temperatures, in comparison with the XRD pattern of an as-deposited sample. Table 1 summarizes the d -spacings of the (100) reflections, the degree of contraction along the [100] direction, and the fwhm of the (100) peaks. Figure 5 and Table 1 indicate that the d -spacings of the (100) reflections decreased as the RTP temperature increased, whereas their fwhm increased with increasing temperature. The decrease in d -spacing and the increase in fwhm with increasing temperature are due to the further condensation of silanol groups and the gradual degradation of pore structures, respectively. Clear structural degradation can be observed with the sample

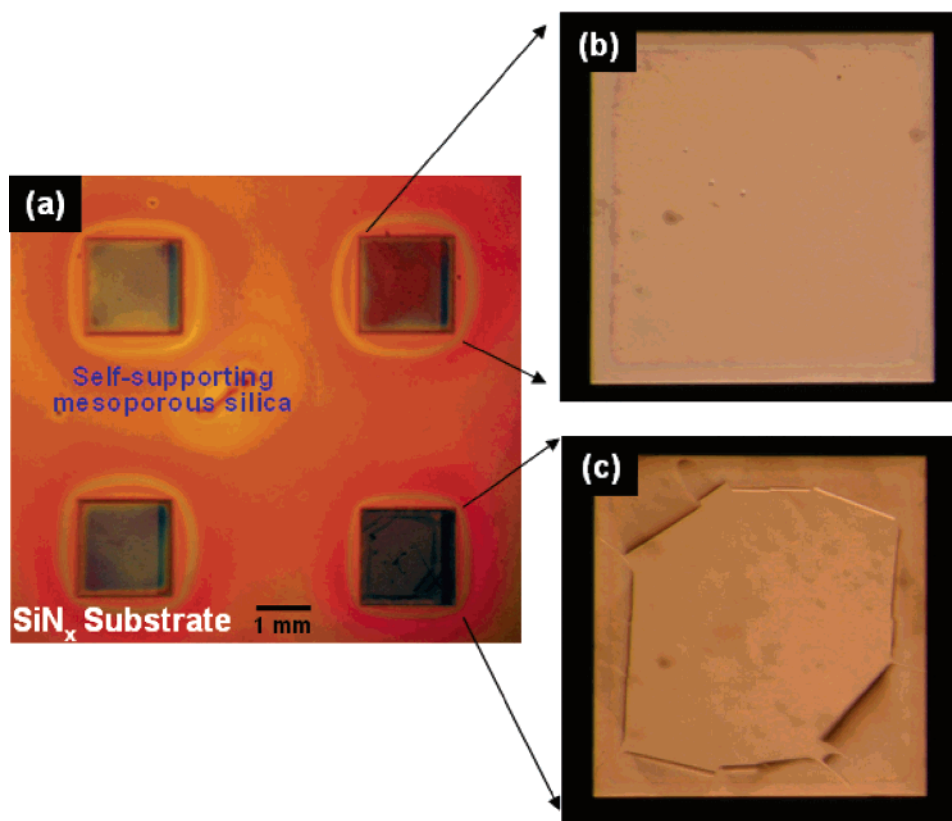


Figure 7. (a) Optical microscopy image of a self-supporting mesoporous silica film with four windows, and magnified images of (b) a good window and (c) a broken window.

treated at 1000 °C, showing large fwhm values and very small second-order reflection. Therefore, there is an optimal processing temperature (~900 °C in this case) that ensures complete condensation of silanol species and yet maintains the structural integrity. The FT-IR spectra for these samples (see the Supporting Information) indicate that the RTP at 500 °C is not enough to break the covalent bonds of the carbons within the processing time of ~2 min. The effect of processing time at 900 °C (given in the Supporting Information) shows the stiffening of the silica framework, according to the processing time. Mesoporous silica films ~2.5 μm thick were deposited by repeated dip coating, with each step followed by a RTP step within an hour. Films showed good optical uniformity, and no macroscopic cracks were observed via optical microscopy, although microscopic cracks were observed in some areas of the silicon wafer substrate using electron microscopy. Figure 6 shows SEM images of the film, revealing a continuous mesoporous silica film with a thickness of ~2.5 μm.

To demonstrate that RTP can produce mesoporous silica films with a quality that is suitable for MEMS applications, self-supporting mesoporous silica windows were fabricated using standard microfabrication techniques. The optical microscopy images given in Figure 7 show the self-supporting mesoporous silica windows. The mesoporous silica windows were optically clear, as opposed to the greenish silicon nitride substrate. A ruptured window shown in Figure 7c reveals the edge of the mesoporous silica film. A detailed study on the microstructures and transport properties of the self-supporting films is currently under way and will be reported in a separate article.

Conclusions

In this paper, we have demonstrated that lamp-based rapid thermal processing (RTP) is a cost-effective way to eliminate surfactants and stiffen silica framework. RTP has enabled us to save processing time by an order of magnitude, as compared to the conventional furnace processing. Continuous mesoporous silica films of ~2.5 μm have been created within an hour. Using standard microfabrication techniques, self-supporting mesoporous silica films have been subsequently fabricated on patterned silicon wafers. To the best of our knowledge, this is the first time mesoporous silica windows have been created on silicon wafers. This is an important step to apply self-assembled mesoporous silica films with a nanostructure to microelectromechanical systems (MEMS) applications.

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Supporting Information Available: FT-IR and XRD spectra of mesoporous silica films calcined with RTP at various temperatures and soak times (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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