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Glass nanostructures fabricated by soft thermal nanoimprint

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An one-step, fast and potential low cost process has been developed to fabricate silica like glass nanostructures by combining sol-gel chemistry and thermal nanoimprint. An inorganic-organic sol-gel thin film is patterned at low pressure and temperature with flexible stamps. Various geometries are achieved with a patterning resolution of about 150 nm and patterns aspect ratio higher than 4. To obtain pure silica structures a thermal annealing at high temperatures is required. During this step most of the structures collapse due to fluidization of the sol-gel material. It is shown that if a suitable condensation level is obtained during imprinting, the nanostructures are thermally stable.

KEYWORDS: Nanoimprint, sol-gel, glass

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INTRODUCTION

Patterning of surfaces at the sub-micrometer scale is a key factor for the emergence of a wide variety of applications from physics to biology. Among several alternative methods, thermal nanoimprint lithography (TNIL) [1] is one of the most attractive due to its simplicity and capability to replicate nanostructures into various kinds of materials (thermoplastics or UV reticulated films). Standard TNIL technology is based on the solidification of polymeric materials (resist) in contact with a structured stamp and resolution down to 5 nm has been demonstrated [2]. The direct imprinting of sol-gel films is very promising for both the diffractive and sub-wavelength passive optics components needed in solar panels, displays and waveguides [3] as the optical properties can be tuned to applications. Currently, most developments concerning such materials are focused on photo-sensitive resists based on hybrid materials obtained from sol-gel precursors with polymerizable organic groups (hybrimers) [4-6] and their application in electronics or photonics is emerging [7,8]. However, these materials have limitations when directly used as a functional layer in demanding thermal, mechanical and chemical conditions. The imprinting of the potentially more stable sol-gel films involving only inorganic reactions (no-hybrimers) has till now only been sparsely investigated. Under appropriate annealing these materials allow to obtain a completely inorganic highly resistant coating. The few previous papers treating this topic all reported time consuming and complex (high pressures and temperatures, plasma treatment) procedures [9-14]. Till example Marzolin *et al* reported in [10] on 60h predrying of the coatings and 12h printing time at 20°C while Rizzo *et al* [14] used 2 days imprinting at 80°C.

In this paper we deal with the patterning of low viscosity sol-gel films by TNIL using soft stamps. These stamps have the advantage of being compliant to the substrate surface which minimizes the pressure needed to obtain contact with the substrate and allow imprinting curved and irregular surfaces. This method based on PDMS stamp is largely developed for UV photoresist [15] and allows to reach 50 nm resolution [16]. We demonstrate that it is possible to define a simple and direct route to structuring, even though the rheological behavior of these materials is non trivial. Pure silica nanostructures are obtained after thermal annealing with a good conservation of initial features and sizes down to 150 nm, which is sufficient for most optical applications.

EXPERIMENTAL DETAILS

The soft thermal nanoimprint consists in replicating nanopatterns from a flexible stamp into a liquid sol-gel resist. The TNIL process is schematically depicted in the Figure 1. Soft PDMS stamps are simply replicated by casting

of liquid PDMS (Poly-dimethylsiloxane) on nickel or silicon nanostructured master-molds. After solidification at 80°C for two hours and peel-off, the PDMS stamps are treated by TMCS (Trichloromethylsiloxane) vapor deposition to develop an anti-sticking surface. The sol-gel thin films were prepared from a MTEOS (Methyltriethoxysilane) sol prepared under acidic conditions to guarantee a total hydrolyzation of ethoxy groups and a low condensation rate. Sol-gel films of 300 nm thickness were spin coated on silicon or glass substrates. The imprinting step is performed at low pressures ($P_{\text{imp}} < 1.5$ bar) as the cavities fill mainly by capillarity. To rigidify the patterns the sol-gel films are condensed by adjusting the imprint temperature (T_{imp}) and the imprint duration (t_{imp}). The stability of the process was explored over a large range of imprint parameters ($3 < t_{\text{imp}} < 90$ min, $110 < T_{\text{imp}} < 180$ °C) in more 20 cases. After cooling to ambient temperature, the stamp and substrate were separated and the patterns were investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Finally, the imprinted MTEOS films were annealed in a furnace in air to densify the silica network and to assure a total oxidation and decomposition of the methyl CH_3 groups [17]. The annealing was typically performed at 700°C for two hours. To follow the silanol condensation level in the films, Fourier transform infrared (FTIR) spectroscopy in normal incidence transmission mode was performed for different values of the TNIL parameters ($T_{\text{imp}}, t_{\text{imp}}$).

RESULTS AND DISCUSSION

Scanning electron microscope (SEM) images show that different types of nanopatterns could successfully be replicated using low pressure TNIL in MTEOS thin films. Gratings with 340nm linewidth, 1 μm pitch and 150nm depth were obtained (see figure 2a) as well as dot arrays with aspect ratio higher than 4 (600nm period, 160nm diameter and 650nm height, see figure 2b). The features are imprinted with a good homogeneity over several square centimeters and the actual patterning area is limited by the size of the stamp. The feature sizes are in good accordance with initial stamps and defects are related to our initial master mold. At room temperature the features are stable over several months. Nevertheless, upon annealing two different behaviors are observed which reveal the importance of the imprint parameters ($T_{\text{imp}}, t_{\text{imp}}$) for the thermal stability of the patterns. For some conditions the patterns are preserved and for other the structures disappear. An example can be seen in figure 3. Type A samples losses the imprinted patterns when heated, figure 3a, for the imprint parameters ($T_{\text{imp}}=130$ °C, $t_{\text{imp}}= 3$ min). Type B samples maintain the features during annealing, as seen in figure 3b and 3c for a sample imprinted at ($T_{\text{imp}}=130$ °C, $t_{\text{imp}}= 85$ minutes). Visual inspection and AFM imaging of samples exhibiting the A type of

behavior revealed that the patterns disappear during annealing because the film fluidizes. To understand the physico-chemical mechanisms behind the stability of the features in the type B behavior, the condensation of silanol groups in the film was followed in FTIR. The evolution of the SiOH silanol IR band at 920 cm^{-1} peak [17] was investigated as function of annealing and Figure 4 shows an example of resulting spectra. The condensation ratio varies as the inverse of the amount of silanol groups [18] and indicates the number of Si-O bonds formed. Figure 5 depicts the decrease of SiOH groups as a function of the imprint temperature T_{imp} while t_{imp} is kept constant at 3 min. As expected the results indicates that the condensation ratio increases with T_{imp} .

Our observations show that the type B behavior maintaining patterns during annealing occurs for high T_{imp} ($T > 170^\circ\text{C}$) at $t_{\text{imp}}=3\text{min}$. For lower T_{imp} , longer duration imprint time t_{imp} is needed otherwise the unstable type A behavior is taking place. This is schematized in Figure 5 where the shaded gray area indicates the imprint conditions for which a stable B type behavior is obtained. The gray square indicates the condensation ratio of the stable type B sample shown in Figure 3b while the unstable type A sample in Figure 3a) corresponds to the point at 130°C . Outside the shaded zone, the imprinted films will relax during annealing whatever the pattern. These results show that there is a complex interplay between the imprint conditions and stability towards annealing. The condensation level of the films after imprinting governs evolution of the patterns upon annealing: when a sufficient condensation level is reached, the coating is crosslinked enough to ensure the mechanical stability of the pattern, whereas it fluidizes under the effect of temperature when the condensation ratio is too low. The degree of fluidization is highly dependent on the history of the sample and the preparation conditions for the sol-gel film. The origin of this intriguing phenomenon still needs to be elucidated, to our knowledge it is the first time that this type of mechanisms has been observed in sol-gel films. A possibility is that a certain threshold in the degree of percolation of the silica network must be attained before the sol-gel film exhibits a solid like behavior.

For a sufficiently condensed sample (type A), it is possible to perform an adequate annealing to burn the organic CH_3 present in MTEOS. This densifies the silica network leading to completely inorganic silica glass nanostructures. Figure 4 compares FTIR spectra for imprinted sample before and after annealing at 700°C of a stable type A sample. Absorption peaks of Si- CH_3 (1280 cm^{-1}) and C- H_3 (2950 cm^{-1}) bonds have disappeared as well as silanol groups (920 cm^{-1}) after annealing. The inorganic nature is clearly shown by the presence of the SiO_2 absorption band (see Figure 4). Interestingly, there is no modification of periodicity and silica glass nanostructures are crack-free. We observe a smoothing of the sidewalls and the amplitudes of the pattern decreased from 140 nm to 105 nm corresponding to a sizes shrinking of about 25%.

CONCLUSION

We have developed a direct process to nanopattern sol-gel films over centimetric areas by thermal NIL technology with elastomer PDMS stamps. To obtain a completely fully condensed inorganic structure a thermal treatment was applied after imprinting. The rheology of the sol-gel materials proved to be complex and depending on the imprint conditions the obtained structures can either fluidize and relax or remain stable. Maintaining the structures demands proper control the condensation ratio of the material during the imprint process. This is to our knowledge the first physico-chemical study of the link between the condensation ratio and the imprint process of a mainly inorganic sol-gel. When sufficient condensation is achieved various silica structures can successfully be obtained with a resolution of less than 150nm with little shrinkage and no cracks. We believe that surface patterning combining sol-gel and nanoimprint techniques is an attractive method for the development of new functional coatings.

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FIGURE CAPTIONS

Figure 1: Schematic view of the thermal nanoimprint process.

Figure 2: SEM images of imprinted nanostructures : a) Gratings of 340 nm linewidth and 1 μm pitch. The inset shows a detailed view. b) Dots array of about 160 nm diameter, 650nm height and 600nm period. Imprinting are performed at 130°C and for a duration t_{imp} of 20min and 4min respectively for lines and dots. Samples were not annealed.

Figure 3: AFM profiles: comparison of non-annealed and annealed pattern profiles for sample A (figure 3a) and for sample B (figure 3b). c) AFM picture on $10 \times 10 \mu\text{m}^2$ for sample B after annealing at 700°C.

Figure 4: FTIR absorption spectra for sample imprinted at ($T_{\text{imp}}= 180^\circ\text{C}$, $t_{\text{imp}}= 6\text{min}$) before and after annealing at 700°C.

Figure 5: Variation of the amount of silanol group as function of temperature for a heating duration of 3 minutes ; square symbol: heating duration of 85 minutes corresponding to the imprinting conditions for sample B.

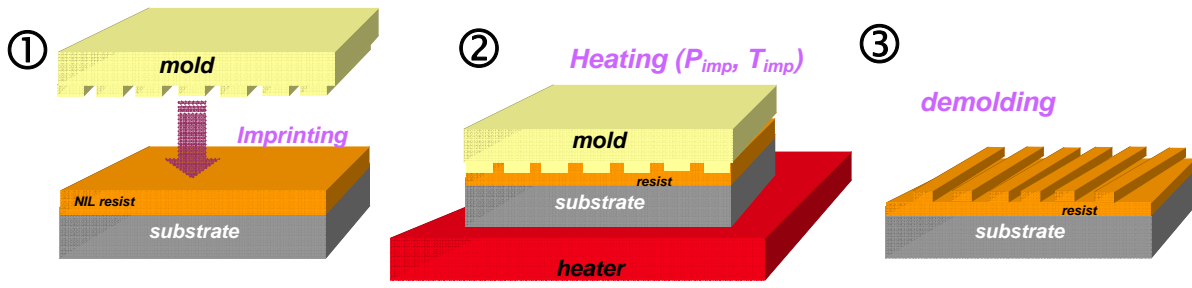


Figure 1.

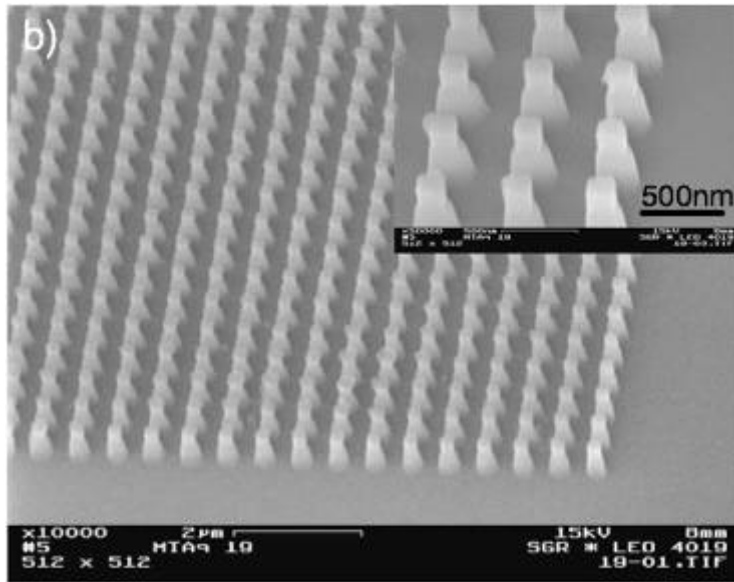
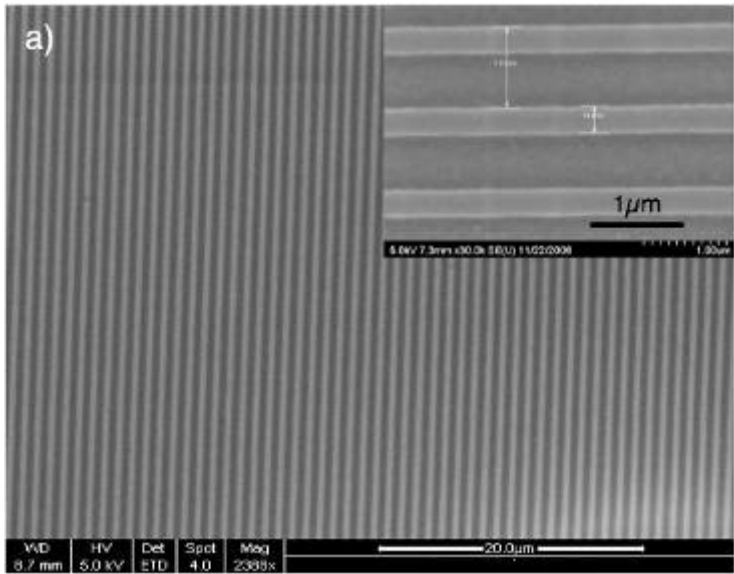


Figure 2.

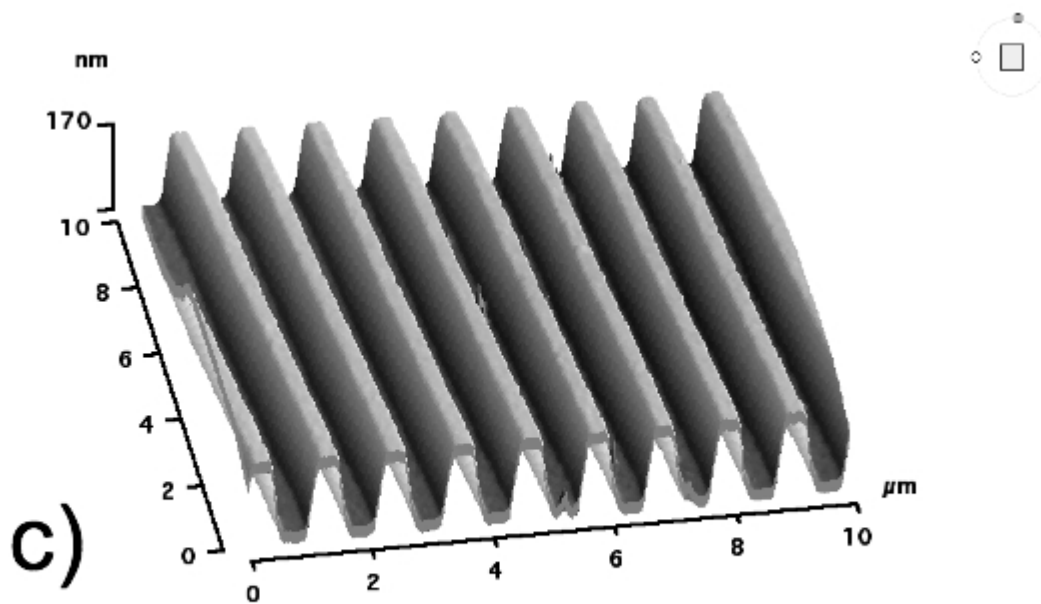
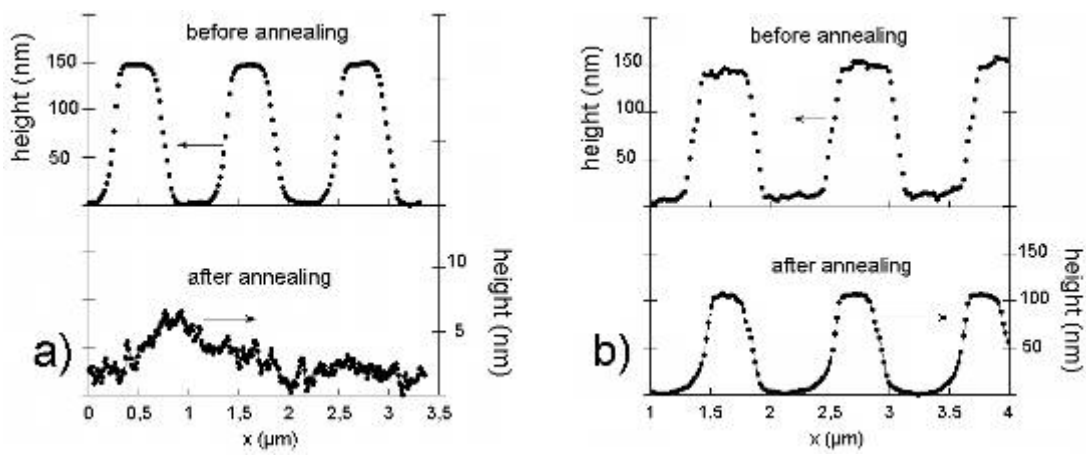


Figure 3 :

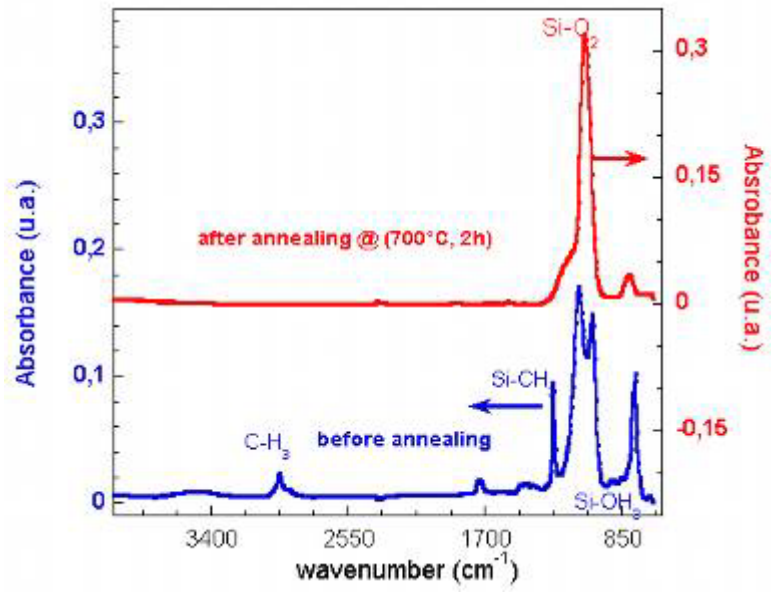


Figure 4

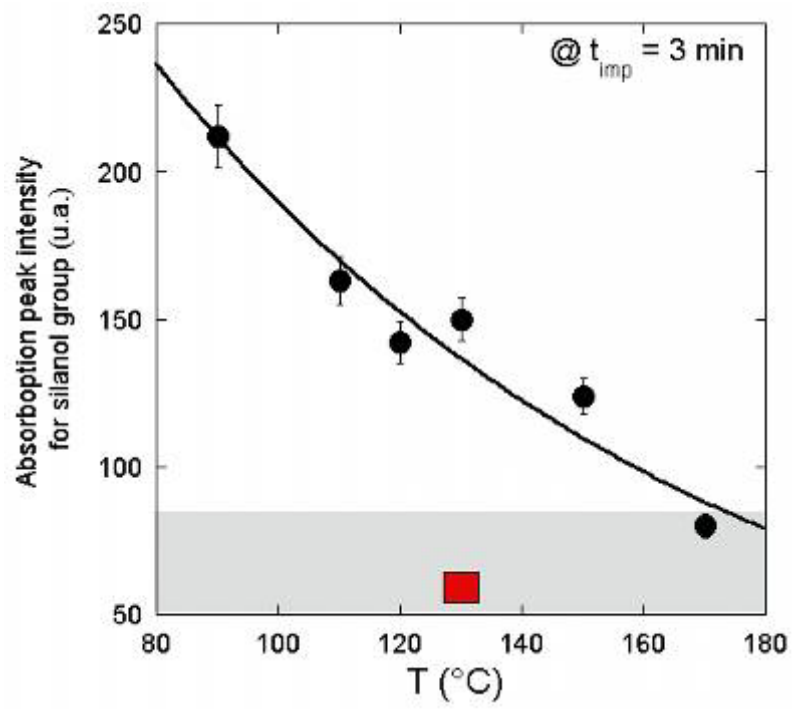


Figure 5