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Silica Sol-gel NanoImprint Resist: a simple route to sequential patterning

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ABSTRACT

We have demonstrated that soft thermal nanoimprint of inorganically cross-linked sol-gel (ICSG) films is a powerful method to build up complex structures from simpler templates by sequential imprinting. A condensation threshold has been identified below which a methyl-silane film passes into a fluid state upon heating allowing for low pressure sequential imprinting. By controlling the condensation during a first imprint step, it is possible to tune the deformation incurred during of the second imprint step. Finally the material structured by sequential imprinting can be turned into pure silica by adequate annealing at high temperature.

KEYWORDS Sol-gel, nanoimprint, sequential patterning

Since the pioneering work of S.Y. Chou *et al*[1] Nano Imprint Lithography (NIL) has been established as a promising technique for surface nanopatterning, opening the way to numerous promising applications ranging from nanophotonics[2] to microfluidics[3]. NIL basically consists in the stamping of deformable films. Preferred materials for NIL are thermoplastics[4] and UV curable resists[5]. So far, most papers report on pattern transfer though single step imprint. However, many applications would benefit from a versatile *sequential* imprinting where simple features can be combined to create more complex structures for biomimetic materials[6] and photonics[7]. Sequential patterning strategies are an emerging topic in the field of NIL. An interesting method was proposed by the groups of Lee[8] and Low[9]: they demonstrated that for PMMA polymers the strain softening occuring during the first imprint step allows secondary imprints to be performed below the glass transition temperature without relaxation of the first imprints. The method, which is based on plastic deformations, requires that high pressure is applied during the imprinting process. However, when using a polymeric resist the resulting structure has a limited thermal and mechanical stability. Therefore for improved stability the imprinted layer is often used only as an etching mask to transfer the structures into the substrate. A major breakthrough for easier and faster processing, especially on brittle ceramic and glass substrates, would be a low pressure patterning technique on a directly functional resist omitting the final pattern transfer step. In that respect, inorganically cross-linked sol-gel (ICSG) resists appear as very attractive materials due to their low initial viscosity and outstanding final thermal, chemical and mechanical stability[10,11]. Very few authors have previously treated the imprinting of such materials[12,13]. For thermal imprinting of ICSG resists, we have recently shown a strong correlation between imprintability and sol-gel condensation[14]. Large aspect ratio inorganic structures have been obtained. In the present paper, we show for the first time that the specific thermal behavior of ICSG resists opens for low pressure sequential patterning: based on these principles, rectangular and diamond shaped structures were obtained from simple line gratings, demonstrating the potential of these materials.

In a previous work we reported that ICSG resists can be imprinted and the materials can be cross-linked at moderate temperatures to replicate nanoscale features from an elastomeric stamp. Features

with aspect ratios at least as large as 4 can be transferred with limited shrinkage even after annealing at high temperatures (700 °C). We also showed that there is a complex interplay between the condensation and the rheology of the films[14]. Depending on the imprinting conditions the films can pass into a fluid state upon heating whereby the imprinted patterns relax. Control of this property is essential for successful patterning of these systems as in many circumstances it will prevent thermal stability of the imprinted patterns. In contrast, in this paper, we demonstrate that a regime of moderate fluidity can be exploited to perform sequential imprinting by a careful control of the condensation of the imprinted structures.

Flexible stamps were obtained by casting liquid Polydimethylsiloxane (PDMS) on nickel or silicon nanopatterned master molds. Our templates consisted of gratings with 340 nm linewidth, 1 μm pitch and a depth of about 160 nm. The elastomer stamps were treated by Trichloromethylsiloxane (TMCS) against adhesion.

The ICSG resist was prepared from a Methyltriethoxysilane (MTEOS) sol: this hybrid precursor exhibits inorganic crosslinking through siloxane bonds while the methyl group, which is non reactive, can be oxidized by a thermal treatment above 550 °C. The MTEOS resist is prepared by aqueous approach, with a molar concentration of 1:14, under acidic conditions (acetic acid) at pH=3.1 for a total hydrolyzis of alkoxyde-silanes groups and a moderate condensation[15,16]. The ICSG resist is aged for one day before use. MTEOS films of about 300 nm thickness were deposited by spin-coating (at 3000 rpm) on silicon or glass substrates. All imprints were carried out at low pressures (<0.2 MPa) due to the low viscosity of the films. The flexible PDMS stamp allows a good compliance even at these low pressures.

The sequential nanoimprint process is described in Figure 1. A stamp containing line gratings is pressed, at ambiant temperature, into the ICSG resist. The system is heated at temperature T_{1imp} for a period of time t_{1imp}. The stamp is then removed and reapplied to the pre-patterned region after an in-plane rotation. The sample is then imprinted again at temperature T_{2imp} for a period of time t_{2imp}.

For successful double imprinting, special care must be devoted to the first imprint step parameters (T_{1imp} and t_{1imp}). In our previous work, we observed that the thermal stability of patterns imprinted on

ICSG film was highly dependent on the imprinting temperature T_{imp} and time t_{imp}. Atomic Force Microscopy (AFM) investigation of the structures after annealing at 130 °C suggested that a sufficient condensation threshold was needed to maintain the features and avoid relaxation due to fluidity of the gel. The condensation in the film after spin coating was monitored by transmission Fourier Transform Infrared (FTIR) spectroscopy at normal incidence. The temporal variation of the absorption peak intensity for the silanol SiOH groups at 895cm^{-1} was measured for temperatures T_{imp} comprised between 80 °C and 140 °C. The silanol groups condense into Si-O-Si siloxane bonds and the decrease of the silanol signal is proportional to the condensation[16] and quantifies the cross-linking of the ICSG resist. An example of condensation kinetics at T_{1imp}=110 °C is given in Figure 2. Raw spectra are displayed on Fig. 2a which features the marked decrease of the silanol group intensity and the appearance of distinct siloxane stretching resonances at 780 and 1020 cm^{-1}. Figure 2b displays the intensity of the silanol peak normalized to the value at ambient temperature τ_{SiOH} as a function of the imprint temperature T_{imp}. The parameter region of structures stable towards thermal annealing is indicated by the shaded area. Clearly, stability is acquired at a condensation threshold τ_{SiOH}~0.3. Patterns which are imprinted in conditions where the final value of τ_{SiOH}<0.3 are stable while they are unstable for τ_{SiOH}>0.3. In the former case the condensation is high enough to rigidify the features during annealing while in the latter case the film passes into a fluid state because of insufficient cross-linking. The value of the threshold does not depend on temperature and appears to be a material related constant.

This control of the ICSG resist viscosity has been exploited to perform a second imprint step. The strategy for double imprint is to control the condensation at the end of the first imprint so that during the second imprint the viscosity allows structuration by the PDMS stamp but prevents relaxation of the first features under the action of surface tension. This is achieved by tuning the thermal treatment temperatures T_{1imp} and T_{2imp} (between 80 °C and 140 °C) and times t_{1imp} and t_{2imp}. Several double imprints were performed. AFM observations were used to evaluate the quality of the second imprint. Our control parameter was the value of τ_{SiOH} reached at the end of the first imprint, as determined by IR

spectroscopy. The insert in Figure 2b displays the results of test experiments for double imprints as a function of the imprinting parameters for step 1: temperature T_{1imp} and time t_{1imp}. Successful double imprints are marked as filled squares while unsuccessful cases where the second imprint step did not modify the intitial pattern are indicated by open triangles. The region where the second imprint is feasible coincides with the fluid regime of the gel after the first imprint step. However, the features resulting from the second imprint depend on the value of τ_{SiOH} reached at the end of the first imprint. Figure 3 depicts four samples where τ_{SiOH} was 30.5%, 32%, 33% and 37% respectively after the first imprint and the second imprint parameters were fixed at T_{2imp}=130 °C and t_{2imp}=300 s. Figure 3a shows barely noticeable reliefs added to the first imprint: close to the condensation threshold, the gel is too viscous to be affected by contact with the PDMS stamp during the second imprint step. Figures 3b and c depict cases where the second features have been partially imprinted to produce a ripple structure superimposed on the first pattern. Figure 3d displays a case where it was possible to obtain a complete second imprint. In this case, the total heights of the structures of the mold and the replica are identical. Thus starting from simple gratings different dot patterns can be achieved such as squares and diamonds (Figure 4). In all cases, it was possible to finally remove the organic methyl groups by annealing to 700 °C leading to a pure silica material while maintaining the doubly imprinted structures. These results clearly demonstrate that an in-depth knowledge of ICSG condensation provides an essential adjustment parameter of the heights of the second patterns made by sequential imprinting.

We demonstrated that soft thermal nanoimprint of ICSG films is a powerful method to build up complex structures from simpler templates by sequential imprinting. On MTEOS resists, an intrinsic material-related condensation threshold was identified. Below the threshold, the fluid state of the material allows low pressure sequential imprinting. By adjusting the condensation during the first imprint step, it is possible to tune the heights resulting from the second imprint step. This is illustrated by the variety of features obtained from simple gratings ranging from simple amplitude-modulated lines to dot patterns. The structured material can be turned into pure silica by adequate annealing at high temperature. In

conclusion, enhanced knowledge about the relation between the structure and the rheology of ICSG materials opens for new and versatile patterning techniques.

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FIGURES

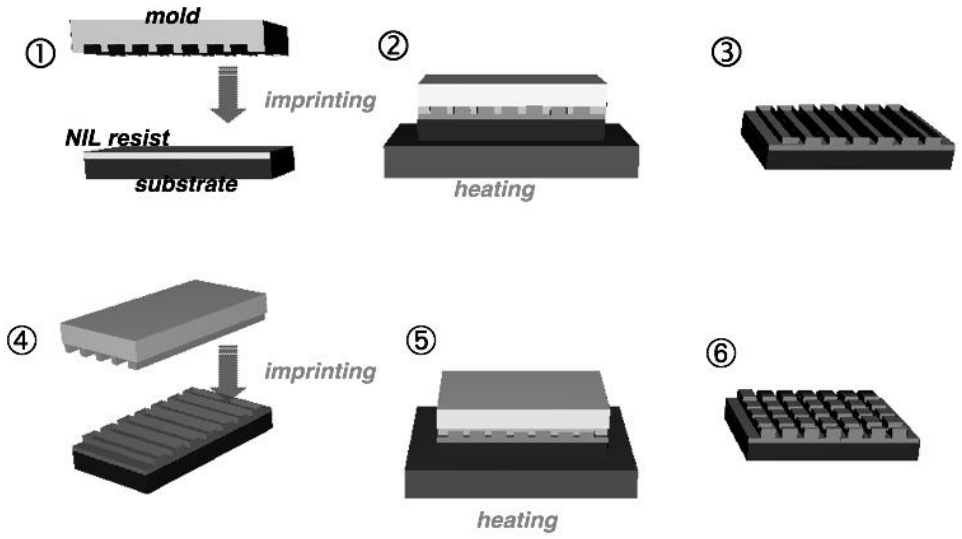


Figure 1: Schematic presentation of the sequential NIL process: 1) the stamp is applied on the resist 2) the first imprint step is performed at temperature T_{1imp} and a time t_{1imp} 3) separation between stamp and sample 4) the stamp is again pressed on the sample 5) the gel resist is re-annealed at T_{2imp} during t_{2imp} 6) complex structures are generated from simple templates.

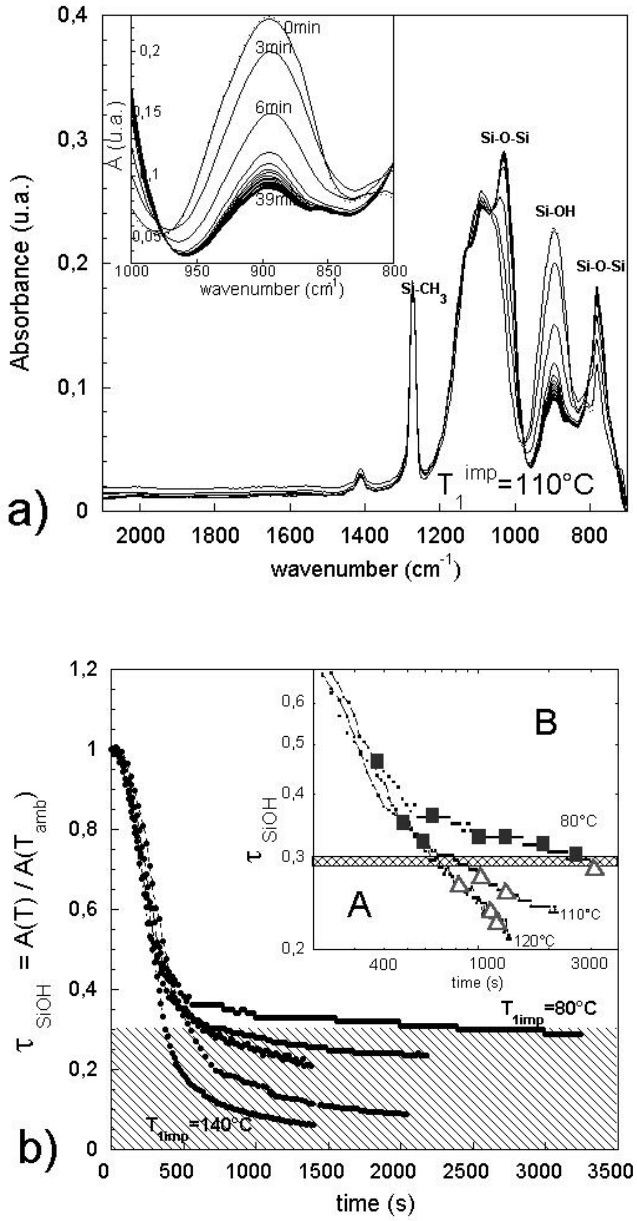


Figure 2: a) Time-dependent FTIR absorption spectra of ICSG resists at T_{1imp}= 110 °C in the range 2100-700 cm^{-1} (3 minute interval between spectra). Details on the time-variation of the silanol peak are reported in inset. b) Variation of the amount of silanol groups (peak at 895 cm^{-1}) normalized to the value at ambient temperature, τ_{SiOH} as function of time for different temperatures T_{1imp}=80, 110, 120, 130, 140 °C. The inset brings into relation τ_{SiOH} and the possibility to perform double imprints. Square (zone B) and triangle (zone A) symbols refer to samples where it is possible or not to imprint two times respectively.

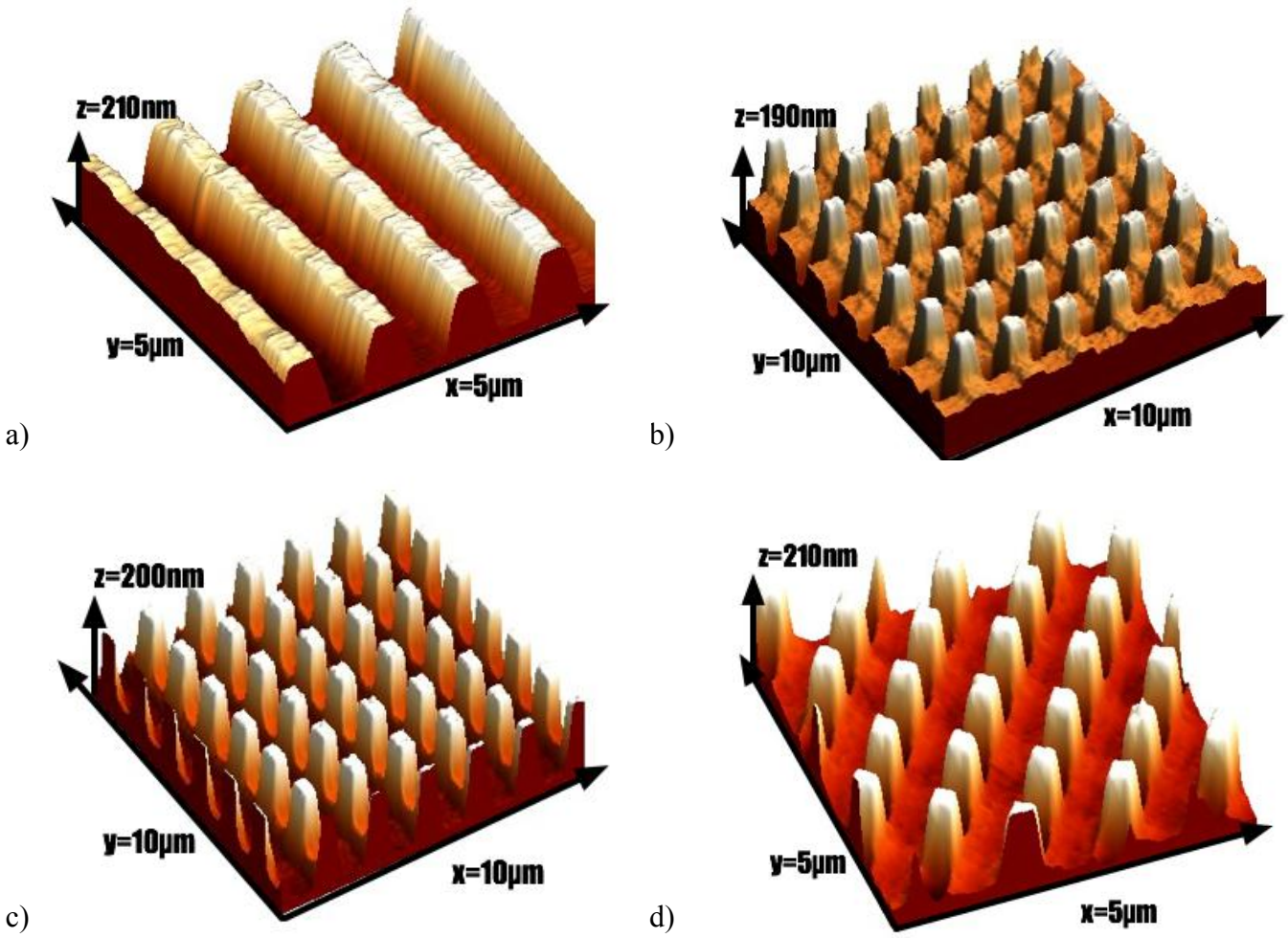
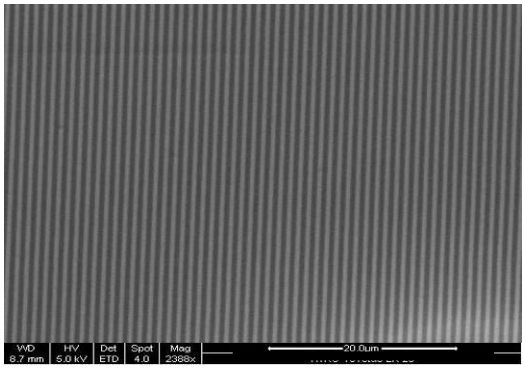
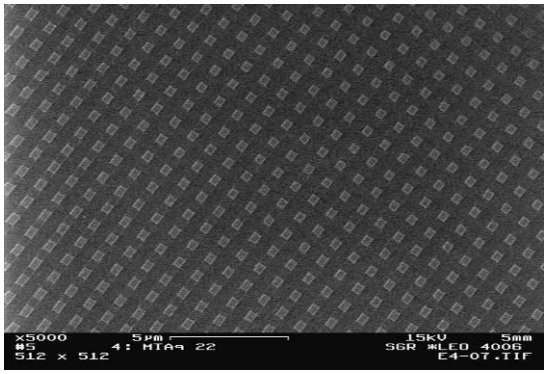


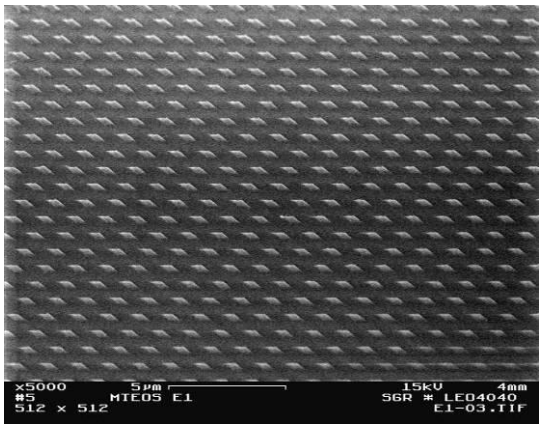
Figure 3: AFM images of double imprinted nanostructures prepared for different imprint time t_{1imp} at a constant temperature of T_{1imp}= 110 °C : the condensation ratio τ_{SiOH} at the end of the first imprint is a) 30.5% , b) 32% , c) 33% and d) 37% respectively. The PDMS stamp was simple gratings of 1 µm pitch, 340nm line width and a depth of 150 nm.



a)



b)



c)

Figure 4: SEM pictures of gratings and patterns imprinted in ICSG resists. (a) first imprint of gratings for T_{1imp}= 110 °C and t_{1imp}=240 s. (b) island array resulting from two successive imprints (T_{1imp}= 110 °C, t_{1imp}=240 s) for a stamp rotation between two imprints of α_{imp}=83 °. (c) diamond structures imprinted for a stamp rotation $\alpha_{imp}\approx$52 ° and T_{1imp}=110 °C and t_{1imp}=180 s.