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Title: Definition of a roadmap for the scalability of the structures within the NIL process

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Contents

1. Introduction

This document is a deliverable of the NARCISO project, which is funded by the European Union's H2020 Programme under Grant Agreement (GA) No. 828890. It reports developments and optimization of soft NIL process, which has already developed by AMU and in part by CNR, into industrial scale-up process at Obducat (OTAB) and facilitate cost efficient as well as high throughput production.
The content of this deliverable has been developed within the tasks included in WP3, but it has already been applied for specific applications involved in other WPs (as, e.g., WP4 & 5).

The following flowchart targets for final industrial scale-up process via combining fabrication of large master via solid state dewetting (SSD), sol-gel dip coating and nano-imprint lithography (Soft-NIL) and OTAB NIL technique.

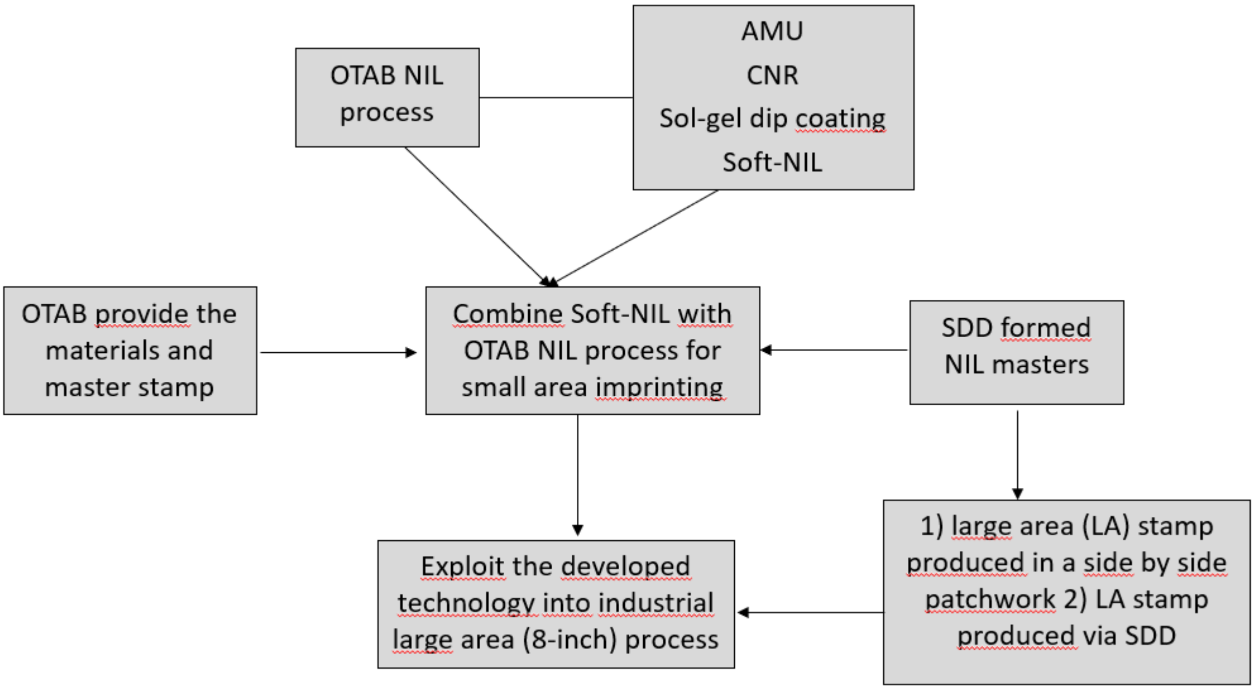

Figure1. Flowchart of NIL process development 1

2. Obducat NIL Process description

The NIL technique was first introduced in 1995 and then quickly recognized by researcher and industry as a potential low-cost, high-through put lithographic method for a wide range of applications. The NIL technique can be performed either by thermal or by UV curing process. Thermal NIL showed to be capable of reaching 5 nm resolution, but the high temperatures and temperature cycling resulted in wear of the template and anti-stick coating. Furthermore, the high temperature brought in more thermal stress into the patterned features. UV-NIL was soon to be invented enabling faster process for some applications.

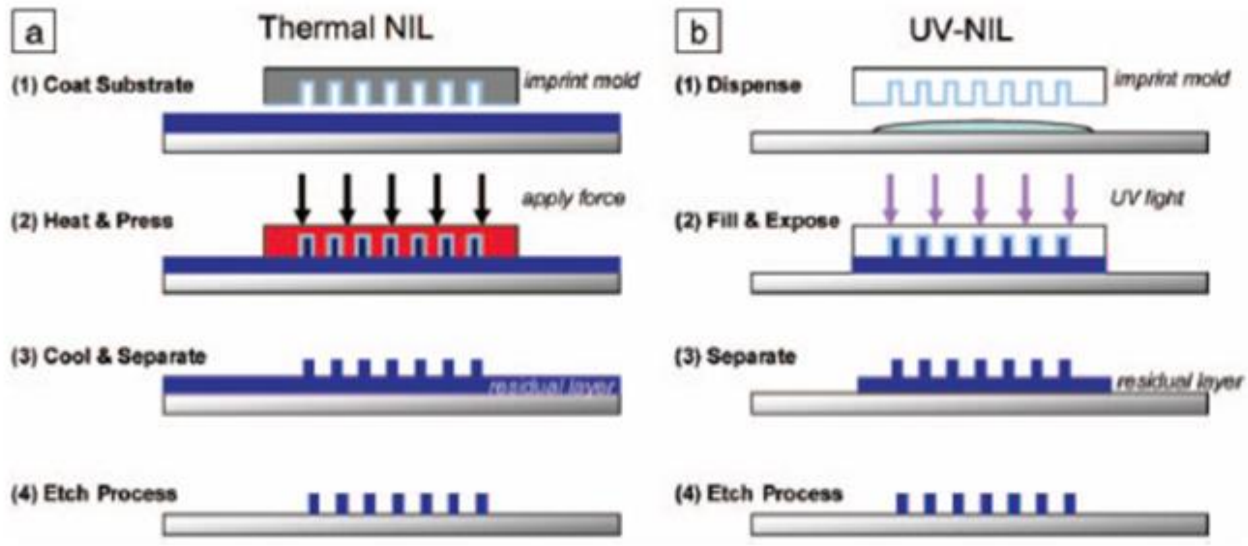

Figure 2 Two fundamental process types of NIL (Steward & Wilson, 2005)

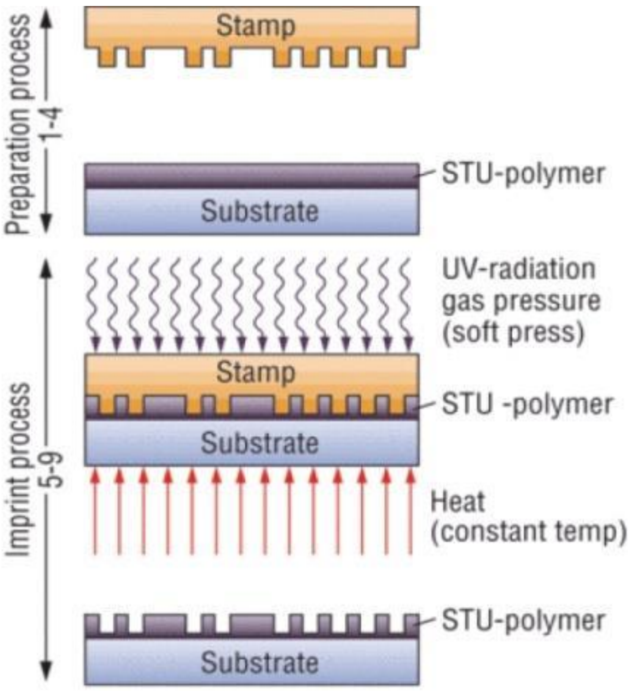

Figure 3. A simultaneous thermal and UV (STU) imprint process

With Obducat SoftPress® technology the pressure is applied to the stamp and substrate using compressed air, ensuring pressure uniformity over the entire imprint area. This allows stamp and substrate to conform to each other, eliminating negative effects from thickness variation, bow or waviness in stamp or substrate. SoftPress® enables thin and uniform residual layer over large areas, which is critical for high-resolution printing and pattern transfer fidelity. With Obducat NIL technique, simultaneous Thermal and UV (STU®) imprint was invented and Patented in 2005. In the STU process an elevated temperature is used simultaneously as pressure is kept and UV light cures the material.

Another key technique related to Obducat NIL is to use an Intermediate Polymer Stamp as a transfer step to overcome substrate unflatness, thereby extending the stamp lifetime, reducing stamp cost per imprint.

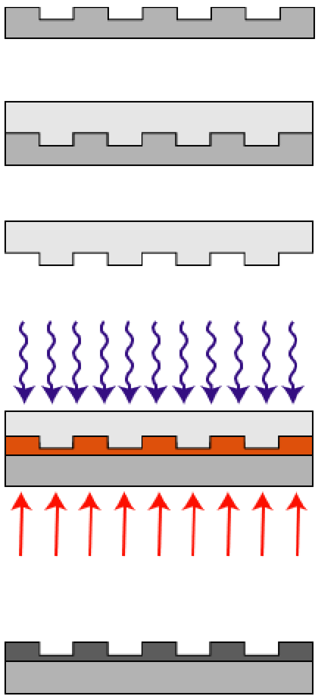

Figure 4. Imprint process with an Intermediate polymer stamp

The Obducat tools for R&D are operated manually with imprint substrate size up to 500 mm.

The fully automated Sindre imprint lithography provides a reliable, high volume manufacturing solution, combining high resolution with high yield, high throughput and enables cost-efficient production, with imprint size up to 8-inch wafers.

3. Combining sol-gel dip coating and Soft-NIL into OTAB NIL process

So far, the NIL process at Obducat has been used to print polymers **resists.** However, for many applications, this kind of materials are not optimal for the following reasons:
1) light-management is not very efficient with materials featuring a low dielectric constant;
2) polymers cannot be exposed to high temperature;
3) are easily delaminated from the host substrate by rubbing;
4) their porosity and composition are fixed after densification.
The soft-NIL process at AMU provides a realistic answer to the needs for more appropriated materials with adjustable (multi)functionalities such as what can be offered with **sol-gel-chemistry-compatible metal oxide (MO_x) materials** (e.g. binary MO_n such as SiO_2, Al_2O_3, TiO_2; ternary $MM'O_n$ such as $BaTiO_3$, $CaTiO_3$; or hybrids oxides such as all the family of organo-silicates). Tunable (multi)functionality concerns mechanical robustness, chemical resistance, thermal stability, but also adjustable properties such as dielectric constant (e.g. controlled composition and (nano)porosity), surface energy and reactivity (surface chemical grafting); photoactivities (e.g. composites with optically active nano-particles (QDots - perovskites), point defects (La^{n+} substitutions, or molecular emitters (dies)).

Thus, the collaboration between AMU, CNR and OTAB has been started to evaluate if materials and master stamps from OTAB can be used to perform Soft-NIL in MOx (SiO_2 and TiO_2 for a start) on arbitrary substrates (e.g. semiconductor, glass, metal). To this end, OTAB has sent four master stamps of nickel and silicon with different pattern design as well as the resist to produce moulds form these masters. On these masters are present structures with motifs ranging from ~10 nm to ~5 μm with different geometries and patterns.

The patterned area of the nickel stamps is 4-inch and contains a micropillar hexagonal array with dimension of pillar width of 2 μm, pitch 3 μm and height 3.4 μm. The nickel stamp with photonic crystal structures across a $55mm^2$ area, with dimension of 200 nm hole size, 460 nm pitch and 130 nm depth and arranged in a hexagonal array has been used.

In the case of the silicon stamp the typical pattern area is of 70mm X 20mm X 6mm and contains of an array of hexagonal moth-eye structures with dimension of 190nm width, 460nm pitch and 220nm height.

In parallel, masters obtained from solid state dewetting (SSD) over a large area are used to replicate functional MOx via combined soft-NIL and OTAB process.

One of the main differences of sol-gel soft-NIL of metal oxides compared to the standard process used by OTAB is bound to the fact that one has to use sol-gel chemistry to directly imprint this rich and interesting family of materials. Sol-gel chemistry involves the controlled nucleation growth of metal(oxy)hydroxides in solution to yield stable colloidal suspensions, with controlled size of solid (sub)nano building-blocks, that can then be used as a formulation in the NIL process. Since the sol-gel chemical reaction involves hydrolysis and condensation, the reactivity with water molecules is critical all over the various steps of the process. In addition, water plays the role of low viscous solvent that provides the desired fluidity to insure efficient infiltration into the mold cavities and faithful replication. As a result, the control of the relative humidity between the step of liquid deposition, to prepare the initial plain soft layer, and the nanoimprint is critical. The water chemical potential (relative pressure) applied in the atmosphere controls the composition of the soft layer in water through molecular dynamic equilibrium, and therefore the fluidity and network crosslinking kinetics responsible for the material rigidification. A systematic investigation has been performed in order to quantitatively establish the criteria for optimal replication of metal-oxide-based patterns (see Figure 5). The lateral dimensions and height of the structures were measured both on the master and on the replica by AFM (Fig. 5a) and were assumed to be identical between the mould and master (negligible shrinkage applied during PDMS cross-linking). TiO_2 structures exhibit the typical truncated square pyramids expected through imprinting from square cavities. More precisely, no replication occurs below 50% relative humidity (bottom panel of Fig. 5a), while imprinting is efficient above 50% relative humidity and a maximal vertical aspect ratio of the pillars is observed for 70% relative humidity. As an example of the impact of the aspect ratio on the optical properties we show dark-field images demonstrating the lack of colorization for very shallow structures (below 50% relative humidity) whereas taller pillars sustain resonant features providing neat structural colors (Figure 5 b). From the same optical images, it is also possible to detect the onset of surface roughness in the flat areas nearby the printed structures for relative humidity of 80%. A more precise assessment of this aspect is provided in Figure 5 c where the surface roughness is plotted against the relative humidity showing a steep increase above 70%. Thus, from this analysis we deduce that the optimal range of parameters for the best replication of the patterns is 50-70% relative humidity that provides large aspect ratio and reduce roughness.

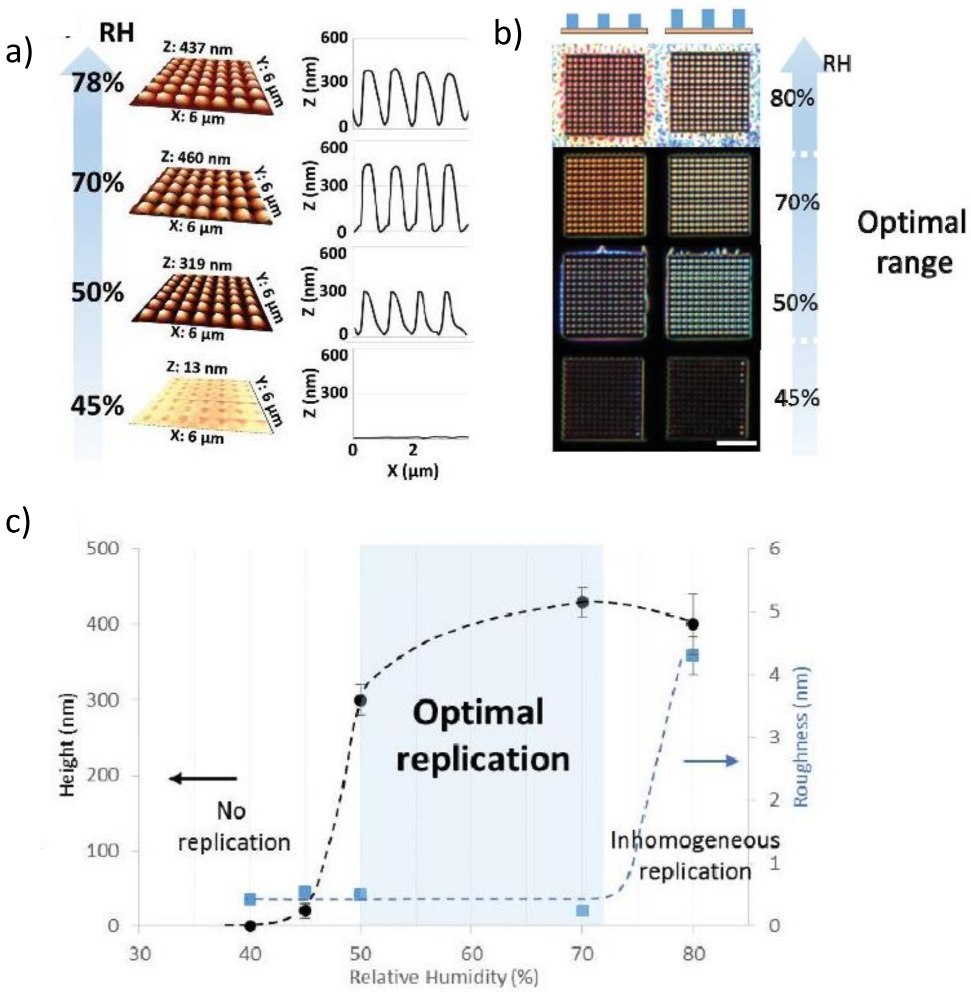

Figure 5: (a) AFM maps and profiles of the square arrays of square truncated pyramids with a 1 µm pitch imprinted at various relative humidities. (b) Optical microscopy dark field images of TiO_2 replicas imprinted at 45%, 50%, 70% and 80% relative humidity, replicated from a mould bearing arrays of pillars featuring 440 nm width, 1000 nm pitch and 700 nm depth (left array) or 1100 nm depth (right array). All the images are collected under the same conditions of illumination and detection to be directly compared. The color is homogeneous among the same array. Strong scattering around the structures due to cracks can be seen at 80% RH. Scale bar is 10 µm. (c) Motif's height (circles) and roughness (squares) after thermal curing as a function of humidity.

The composition of the sol-gel layer in water, seconds and minutes after liquid deposition has been carefully investigated by in situ ellipsometry (see Figure 6).

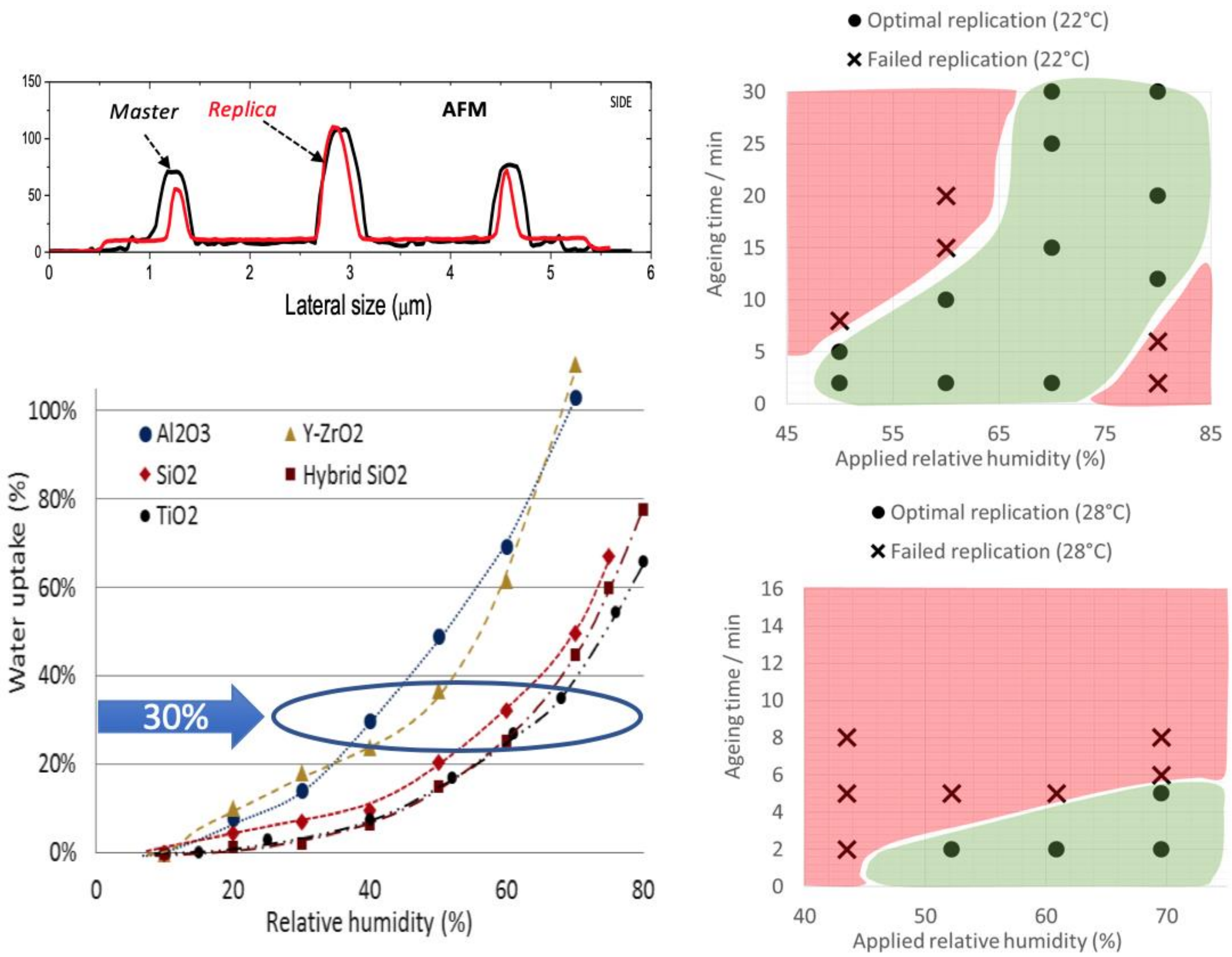

Figure 6: (bottom-left) In situ ellipsometry investigation of plain Sol-gel films swelling vs. applied humidity. (Right) processability of TiO2 sol-gel with respect to humidity, temperature and waiting time after liquid deposition. (top left) AFM profiles of features present on the silicon master and obtained after replication in silica.

It was demonstrated that the optimal quantity of water required in the layer previous to nanoimprinting corresponds to 30 % volume and is achieved through relative humidity control. Furthermore, one notices that obtaining such an optimal volume fraction for different sol-gel systems requires different applied humidity, that depend on the chemical potentials of the moieties composing the soft layer and the external temperature. As a result, discussions between AMU and OTAB have already started to exchange requirements and limits of respective technologies and to start proposing technical solution to implement controlled humidity on standard OTAB NIL equipment.

As mentioned previously, the control of the relative humidity between the step of liquid deposition, to prepare the initial plain soft layer, and the nanoimprint is critical, therefore at OTAB we designed a humidity control chamber used during the nanoimprinting process (see Figure 7), which is an accessory to OTAB standard NIL machine. The humidity chamber is sealed by a polymer membrane on top. As the substrate was layer coated via sol-gel assisted dip coating or spin-coating method, the polymer stamp replicated from master stamp was applied onto the substrate at a humidity, temperature-controlled environment, and then the nanoimprinting will be performed in the humidity-controlled chamber (see fig. 7) with desired temperature and pressure.

Figure 7: Humidity control chamber used during the nanoimprint process*, the high humidity water can be introduced into the chamber by inlet.*

For soft-NIL process, the nano-impression on metal oxides (MO_x) was conducted at 70% relative humidity and PDMS mold was applied onto the sol-gel film at 60°C for 10min. The soft-NIL process parameters can be easily adopted into OTAB NIL process, however, to replace PDMS with OTAB standard IPS (intermediate polymer stamp) material might not be work, due to the PDMS's unique properties, such as elasticity, durability, surface hydrophobicity and high gas permeability. Even though we might fail to use OTAB standard IPS material, we can still adopt the PDMS as an IPS into OTAB standard NIL process.