3D nanopatterning of photosensitive hydrogels

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Hydrogels are crosslinked polymers that swell in water forming soft and elastic materials. The length and flexibility of the polymeric chains can be controlled and their deformation allows the entry and retention of solutes into the 3D-network. Hydrogels are indispensable for many chemical and biological applications, especially in sensing and actuating devices [1, 2, 3]. The ability to pattern the topologies of gels at the micro and nanoscale is desirable in these applications especially to develop optical devices based on this sensitive nano and micropatterned surfaces. We have previously reported on the development of a new library of hydrogels modified in order to be photocurable and optimally nanoimprinted [4].

The work described is based on a tert-polymer PEGDMA-NIPAAm-AA: poly(ethylene glycol dimethacrylate-co-N-Isopropylacrylamide-co-acrylic acid). This stimulus-responsive or "intelligent" hydrogel shows promising applications, as it is sensitive to pH and to temperature. This tert-polymer **(PEG-co-NIPAAm-co-AA)** is obtained by combining the photoinitiator, IRGACURE 819 (Bis(2,4,6-trimethylbenzoyl) – phenylphosphineoxide) in a concentration of 0.1% w/w with the crosslinker **EGDMA: Etilenglicol dimetacrilato**, in 5% w/w. The NIPAAm is dissolved in the AA-PEGDMA solution, avoiding the introduction of another solvent. The minimum residual layer was obtained with the following combination: **10:40:50 P30** meaning a dilution in ethanol at 30%w.
We have developed a UV-NIL process to obtain 3D nanopatterns with this material. The optimization of the imprinting and etching processes was performed by Tecnalia with a 3D master-stamp developed at UG and replicated in Ormostamp in Tecnalia.

The 3D quartz stamp was fabricated using e-beam lithography. PMMA was used as a mask. Patterns from the PMMA mask were etched into quartz. Oxford 80+ RIE dry-etch tool was used for this purpose. CHF_3 gas was used to etch the quartz. Fabrication was done in two steps. In the first step 1 – 5 µm grating were fabricated on the quartz substrate and in the second step 100 – 500 nm grating were fabricated on 1 – 5 µm gratings. The result is a 1 – 5 µm gratings written on 300 µm x 300 µm patterns as shown in the fig 1. 100 – 500 nm gratings were also written in a 300 µm x 300 µm patterns on the top of 1 – 5 µm gratings. The Qz stamp was replicated in Ormostamp with good pattern fidelity as it can be observed on Fig.1

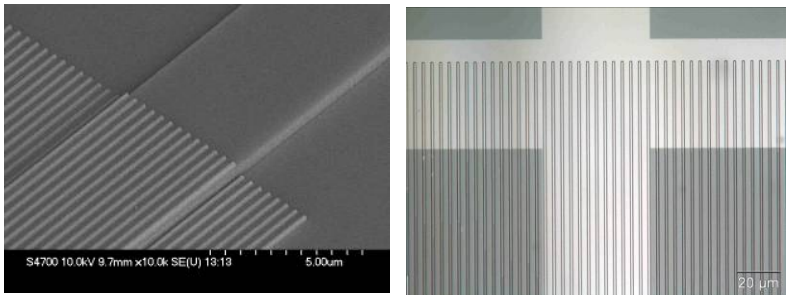

Fig 1. a) Qz 3D stamp and b) replication in Ormostamp

In order to avoid the adhesion between the sample and the stamp, a SAM (F_{13}TCS) is deposited over the stamp surface. TPM (3-(Trichlorosilyl)propyl methacrylate) is diluted in a solution of heptane:CCl4 (4:1) and the substrates are kept at room temperature for 5min under N_2 atmosphere in order to obtain good adhesion of the hydrogel on the oxidized silicon.

Table 1 describes the optimized process for 3D nanopatterning in an EVG620 mask aligner.

Materials	*Substrate*	Silicon oxide + TPM
	Resist	PEGDMA-co-NIPAAm-co-AA
	UMaster	OMS nanometer stamp
3µL drop		
Printing process	*Proccess*	UV NIL
	Contact mode	vacuum
	Applied pressure during exposure	600mbar
	Delay	10 min
	Exposition time	600seg

Complete filling was obtained as it can be observed on Fig 2.

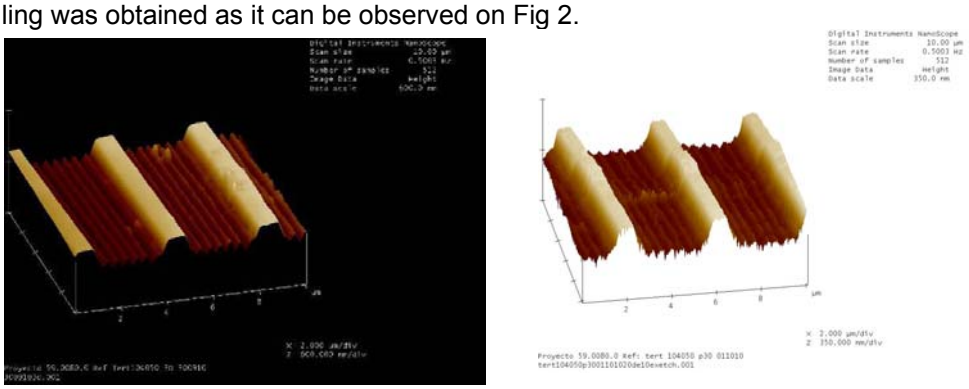

Figure 2. AFM images of the 3D topographies of the tert-polymer a) before and b) after etching

Fluorescein entrapment in the hydrogel after washing, was used in order to verify the complete etching of the residual layer. Hydrogel imprint materials before and after etching were observed under an optical and fluorescence microscope. In all cases, hydrogel imprint materials presented high fluorescence signal as it can be observed on Fig 3 a) optical and b) fluorescence.

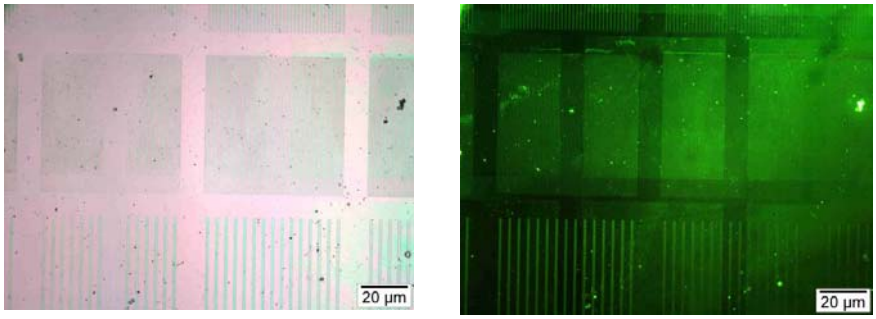

Fig.3. a) Optical and b) Fluorescence imaging of the 3D imprinted hydrogel after etching and posterior fluorescence adsorption.

References:

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