

**NATuRal instability of semiConductors thIn SOLid films for sensing and photonic applications** [Horizon 2020](#)

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Leader partner	CNR
Author(s)	Marco Abbarchi, Monica Bollani
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1. Introduction

This deliverable is a report on the spectroscopic characterizations obtained in metal-oxides (MOx) patterned substrates after the nano-imprint processes detailing how the porosity depends on the composition, pH, polarity and inorganic condensation rate of the sol-gel components.

We distinguish between two kinds of porosity:

1) the micro- and meso-porosity of the material obtained via sol-gel dip- (or spin-) coating that is a structural property common to flat 2D-layers and to 3D structures realized via nano-imprint lithography (NIL). This intrinsic porosity of the MOx can be controlled a priori by adjusting the precursor concentration, adding Pluronic F127 (PEO-b-PBO). This nano-porosity changes the wettability of the walls of the micro-pores allowing to change at will the filtration properties.

2) the macro-pores determined by the topography of the 3D structures achieved after NIL process. These are exploited in microfluidic experiments when the samples are sealed at their top, with a transparent PDMS membrane (thus producing a channel for liquid propagation). The macro-pores are used to filtrate colloidal nano-particles and bacteria studying their mobility, trajectories, segregation, filtration, etc. Their features (e.g. size, shape, connectivity) can be tuned by changing the properties of the hard master used to replicate 3D structures in MOx materials during NIL process.

In what follows, we first address different realization of porosity in MOx studied via ellipsometry porosimetry. This is done on 2D flat layers (owing to the necessary absence of diffusion for this spectroscopic technique that does not allow to measure on rough surfaces). Then we show that via NIL we can shape the MOx in separated islands and connected structures forming the basis of a macro-porosity for micro-fluidic measurements.

2. Micro and meso-porosity of MOx

2.1 Environmental Ellipsometry Porosimetry

Environmental Ellipsometry Porosimetry is a convenient tool for the investigation of optical thin films porosity. It is non-destructive, highly sensitive, reliable and thus adapted for routine characterization. It relies on the measure of the refractive index evolution upon adsorption/desorption of water (or volatile organic solvents), from which isotherms can be deduced and used to obtain the mesoporosity characteristics (pore volume, pore size distribution, pore interconnection through adapted Kelvin models). It is also extremely convenient to independently assess the porosity of individual layers composing multilayer stacks systems or to address internal surface energy through co-adsorption of different adsorbates. Here the measurements have been carried out with a Wollam M200V (350nm – 1000nm) ellipsometer measuring in real time the

changes of refractive index of a porous layer kept in a chamber with controlled atmosphere where air and water are progressively mixed.

In the case of porous layers, increasing the relative solvent pressure, the adsorption and capillary condensation occur in the pores. By carefully monitoring the optical properties of the film evolution, it is possible to know the percentage of porosity and the pore size. Thus, Environmental Ellipsometry Porosimetry measures the refractive index evolution with the relative solvent vapor pressure (P/P_0 , as reported in Figure 1). The solvent used is generally water but can be switched to isopropanol in the case of hydrophobic films. The pore size distribution can be extracted for nanoporous films (up to pores of 50nm in diameter). Since pores are far smaller than the wavelength of light, the porous layer can be considered as a homogeneous media. The volume fraction of adsorbate is then deduced from the Bruggeman Effective Medium Approximation (BEMA):

$$f \frac{\widehat{\varepsilon_1} - \widehat{\varepsilon}}{\widehat{\varepsilon_1} + 2\widehat{\varepsilon}} + (1 - f) \frac{\widehat{\varepsilon_2} - \widehat{\varepsilon}}{\widehat{\varepsilon_2} - 2\widehat{\varepsilon}} = 0 \quad \text{Equation 1}$$

with $\widehat{\varepsilon_1}$ the dielectric function of the material, $\widehat{\varepsilon_2}$ the dielectric function of the pores, f the volume fraction of material 1 compared to 2 and, for transparent dielectrics, $\widehat{\varepsilon} = n^2$. During the adsorption, the pores first containing air ($n=1$) are progressively filled with solvent ($n_{\text{water}} = 1.326$, $n_{\text{isopropanol}} = 1.383$). During this step, the overall refractive index increases at a specific relative vapor pressure. The porous volume of the film (V_p) is first measured in dry atmosphere and then quantifying the refractive index of the film at each relative humidity (relative water pressure). The adsorption isotherm can be calculated as $V_{\text{water}}/V_{\text{film}} = f(\text{RH})$ from $V_{\text{water}}/V_{\text{film}} = f V_p$ (Figure 1). The pore size distribution is determined from the isotherm via Kelvin equation:

$$RT \ln \frac{P}{P_0} = \gamma V_L \cos \theta \frac{dS}{dV} \quad \text{Equation 2}$$

with P/P_0 the partial pressure, γ the surface tension, V_L the molar volume of the liquid, θ the contact angle between the solid and the adsorbate, dS and dV the surface and volume variations between the solid and the adsorbate. A modified Kelvin equation (not shown) is generally used to consider the non-spherical geometry of the pores and the thickness of the water layer adsorbed in the pores before capillary condensation as described by J. Lonzillon et al. J. Phys. Chem. C 2019, 123, 23479 (2019). This analytical treatment results in the curve visible in Figure 1 and gives the pore size distribution.

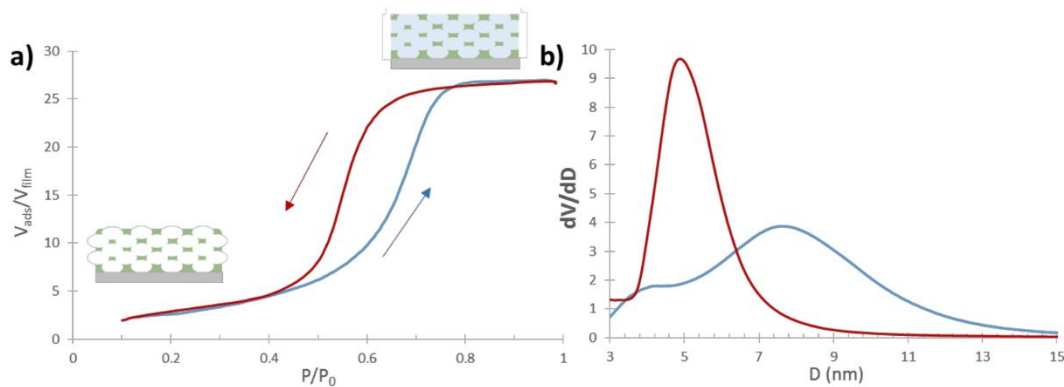


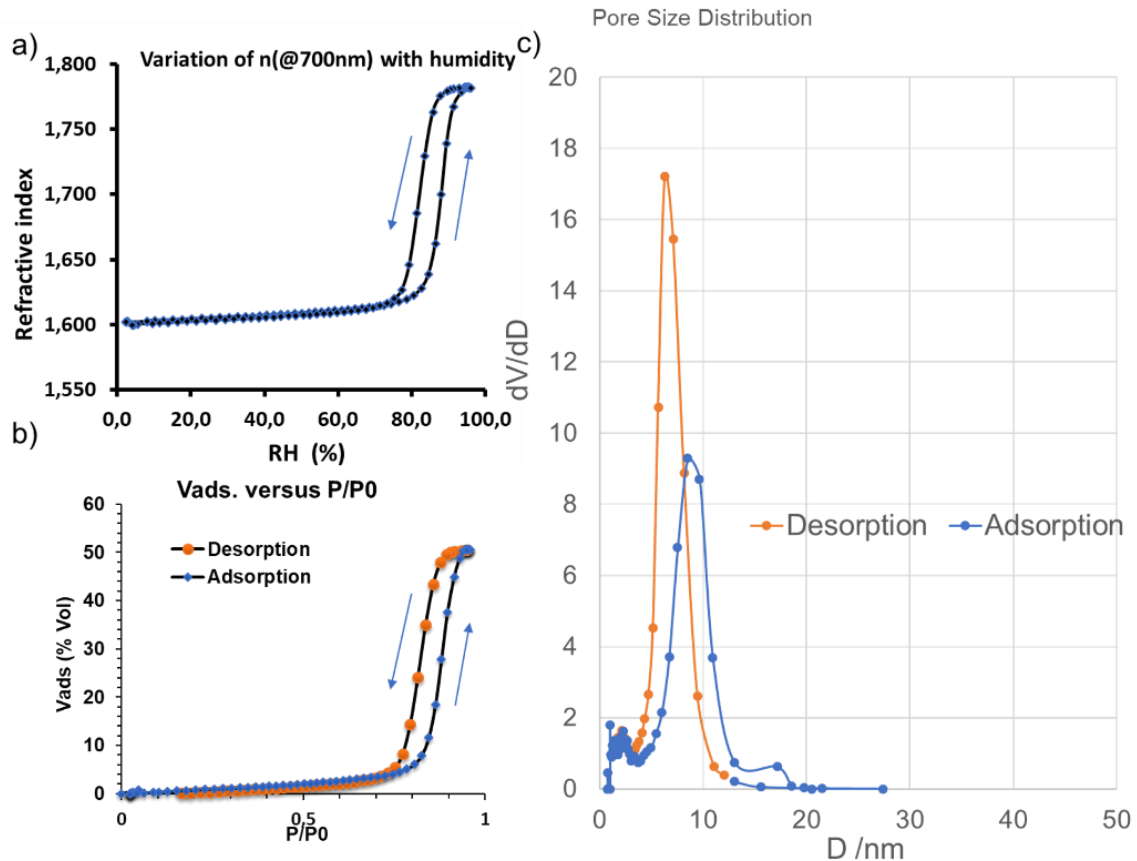
Figure 1. a) Adsorption (blue) and desorption (red) curves as a function of the relative vapour pressure (i.e. for water on a titania film). b) Pore diameter distribution (blue) and interconnections (red) extracted from a).

Note that the adsorption (blue) and desorption (red) curves do not coincide. Adsorption in mesopores generally occurs under oversaturation to overcome the thermodynamic barrier of the meniscus formation. The desorption, indeed, generally occurs under equilibrium conditions since the meniscus is already formed. However, when the interconnections are smaller than the pores (bottleneck pores), the hysteresis between adsorption and desorption curves is large. Owing to this well-known effect (pore blocking), the desorption branch is associated with the interconnection size and not with the pore size itself. Thus, for bottleneck pores, only the adsorption branch can be exploited to estimate the pore size, even if it occurs out of equilibrium, leading to an overestimation of the pore size. In J. Lonzillon et al. J. Phys. Chem. C 2019, 123, 23479 (2019) a new method involving desorption scanning is described to assess the complexity of interconnections between all the present population of pores in the film.

2.2 Example of porosimetry of a titania layer

As a first example we analyze the case of a porous titania layer obtained via sol-gel dip coating on a bulk silicon wafer. The solutions used for this sample is prepared from $TiCl_4$ precursor, Pluronic F127 block-copolymer porogene, water reactant, and ethanol solvent. As for the example previously shown in the introduction on ellipsometry porosimetry, Environmental Ellipsometry Porosimetry reveals the presence of two separate curves for the evolution of the refractive index upon adsorption and desorption (Figure 2 a). Exploiting Equations 1 and 2, it is possible to extract the corresponding isotherms for adsorption and desorption (Figure 2 b): owing to the different condensation in the pores during adsorption and bottleneck in the connections during desorption the two processes are not equivalent. Finally, exploiting the Kelvin equation (see J. Lonzillon et al. J. Phys. Chem. C, 123, 23479 (2019)) it is possible to estimate the pore and connections size that in this specific case are of the order of 9 nm and 6 nm respectively (Figure 2 c).

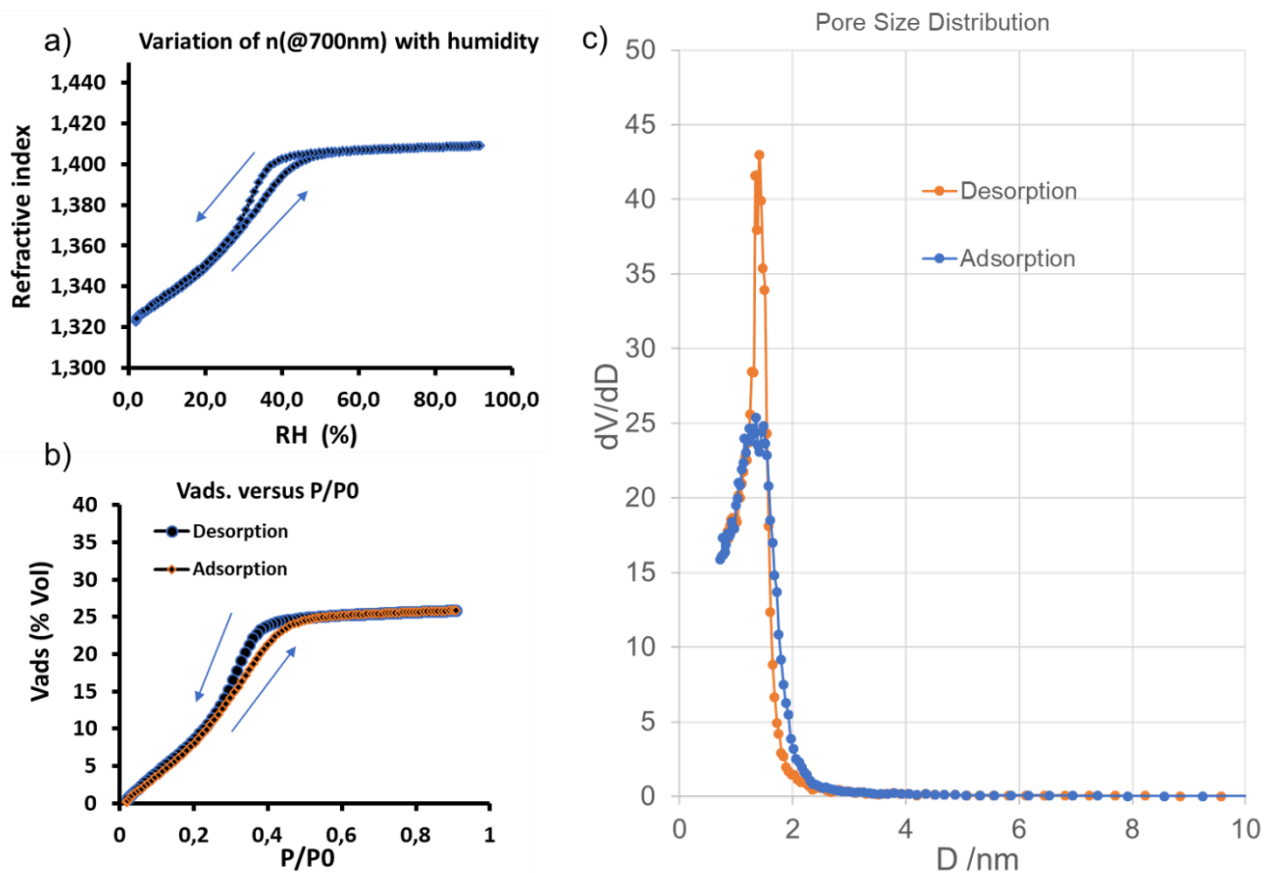
Figure 2. a) Refractive index changes upon water adsorption and desorption measured as relative humidity (%) for a TiO₂ layer about 100 nm thick, deposited on a Si wafer. b) Corresponding adsorption (blue points) and desorption (red points) curves as a function of the relative vapour pressure for water on a titania film. c) Pore diameter distribution (blue) and interconnections (red) extracted from b).



Further examples of titania layers with different pore size distributions can be found in T. Bottein et al. Adv. Fun. Mat. 2016 and in S. Checcucci et al., Adv. Optical Mater. 2019. Note that, for applications in optics, the possibility to adjust the mesoporosity of the sol-gel layers provides a fine tuning of the optical constant of the layers and it is thus a powerful tool to adjust n to a desired value (e.g., for anti-reflection coatings and Bragg mirrors). Furthermore, even if in Figure 2, the size of the pores is not that different with respect to that found in S. Checcucci et al., Adv. Optical Mater. 2019 the corresponding refractive index are rather different. This is simply due the fraction of pores in the layer volume that in the first case is about 50% determining a $n \sim 1.6$ and in the second case $\sim 16\%$ resulting in $n \sim 2.1-2.3$. Thus, the case presented here is representative of a rather porous titania layer with a low refractive index.

2.3 Example of porosimetry of a silica layer

Figure 3. a) Refractive index changes upon water adsorption and desorption measured as relative humidity (%) for a SiO₂ layer about 173 nm thick, deposited on a Si wafer. b) Corresponding adsorption (red points) and desorption (blue points) curves as a function of the relative vapour pressure for water on a titania film. c) Pore diameter distribution (blue) and interconnections (red) extracted from b).



A second example of porosimetry is provided for a thin layer of silica as reported Figure 3. The solutions used for this sample is prepared from TEOS (tetraethylorthosilicate) precursor, Pluronic F127 block-copolymer porogene, water and hydrochloric acid reactants, and ethanol solvent. As for the previous case, we study the behavior of n as a function of the relative humidity (Figure 3a), deducing the adsorbed volume (Figure 3b) and the size distribution of pores and interconnections (Figure 3c). For this specific case, the porosity is about 25% of the total volume, the pore diameter and connections are in the 1-2 nm range. The refractive index is about 1.32, thus rather smaller than the typical value of 1.5 found for dense silica.

As for titania, other examples of silica layer featuring a different porosity can be found in S. Checcucci et al., *Adv. Optical Mater.* 2019. In this latter case, an average pore size of about 7 nm is found with a porosity of 37% determining a refractive index of 1.28. More generally, a plethora of combinations of pore size distribution, interconnections and fraction of the total volume can be created providing a full control over the micro- and meso-porosity (J. Lonzillon et al. *J. Phys. Chem. C*, 123, 23479 (2019)).

3 Macro porosity of silica and titania obtained via sol-gel dip coating and nano-imprint lithography

3.1 Hard Master and PDMS mould preparation

MASTER 400 nm Ge layer on SOI, dewetted

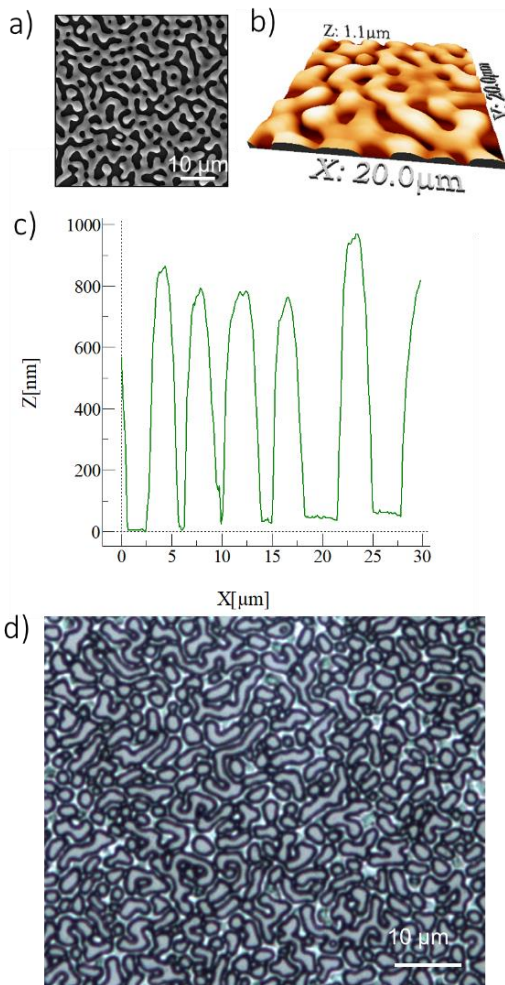


Figure 4. a) and b) SEM and AFM respectively, of 400nm Ge on thin SOI after dewetting. c) Height profile of the same sample obtained by AFM imaging. d) Bright field, optical microscope image (100X magnification) of the same sample.

(deposited via plasma enhanced chemical vapor deposition) to prevent sticking of the PDMS poured atop the PDMS of the negative mold. Images of negative and positive molds are provided in Figure 5.

A viable solution to create macro porosity in these MOx layers is to print 3D structures via nano-imprint lithography defining complex patterns that will serve as channels for mass transport (e.g., in micro-fluidic experiments). Here we address the cases of connected and disconnected objects featuring a disordered hyperuniform character provided by the hard masters in use (see M. Salvalaglio et al., Phys. Rev. Lett 2020) for nano-imprint lithography after sol-gel dip coating (see M. Naffouti et al., Science Advances 2017).

In Figure 4 is described a master obtained via solid state dewetting of a 400 nm thick Ge layer deposited via molecular beam epitaxy on an ultra-thin silicon on insulator wafer. The final morphology after dewetting at high temperature is composed by a spinodal like pattern in the scaling regime (see M. Salvalaglio et al., Phys. Rev. Lett 2020) with connected dendritic filaments about 800 nm in height and 2-5 μm wide.

From this hard master we create a negative mold by pouring PDMS in the cavities (to have a positive replica of the master via NIL) and in turn, from the negative mold we create a positive mold (in order to replicate the negative replica of the master via NIL). This latter step is performed using the negative mold previously passivated with a

thin
layer
of
SiO₂

Negative mold Positive mold

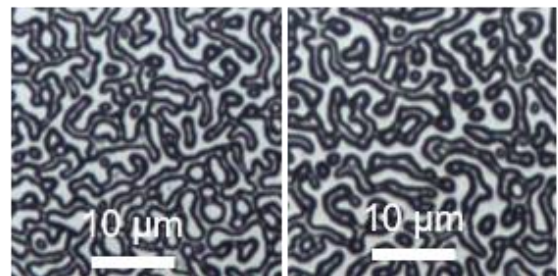


Figure 5. a) and b) Bright field, optical microscope image (100X magnification) of PDMS negative (left panel) and positive (right panel) mold used for NIL of titania

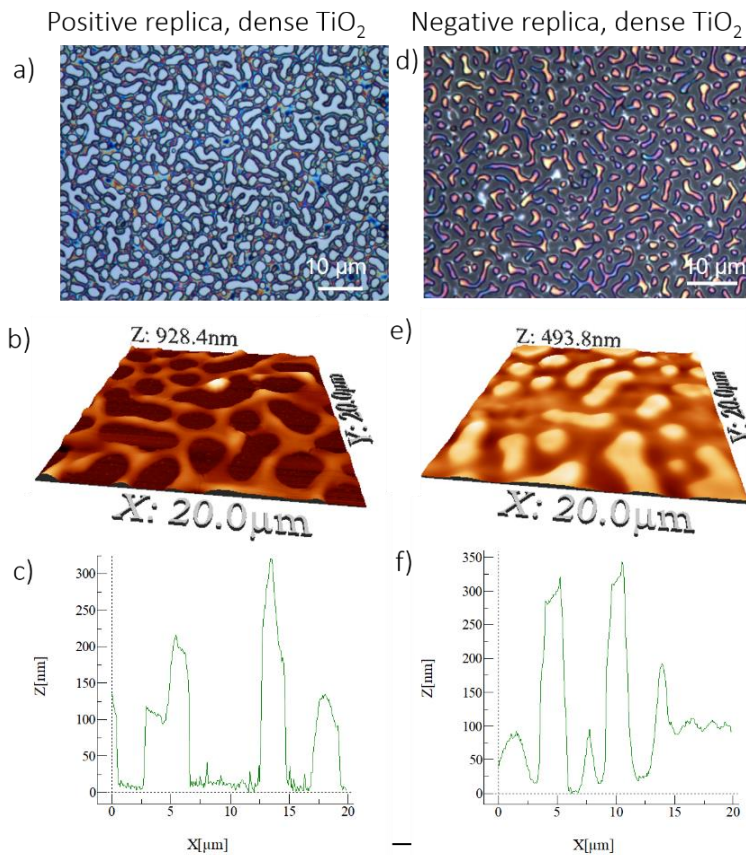


Figure 6. a) Bright field, optical microscope image (100X magnification) of dense titania positive replica of the master on glass. b) AFM image of the sample in a). c) Height profile from b). d) Bright field, optical microscope image (100X magnification) of dense titania negative replica of the master on glass. e) AFM image of the sample in d). f) Height profile from e).

Their very similar features reflect the fact that in spinodal structures in the scaling regime the fraction of filled filaments and empty parts are basically equivalent.

3.2 Positive and negative replicas in dense TiO_2

As an example, we show positive and negative replicas of the hard master in dense TiO_2 in figure 6. In these cases, the thicknesses of the flat titania layers are about 77 and 75 nm respectively for the positive and negative replica and were printed on a glass support. The porosity of these samples is of the order of 15% as for the cases shown in T. Bottein et al., Adv. Fun. Mat. 2016 and in S. Checcucci et al., Adv. Optical Mater. 2019. From AFM investigation we see the formation of connected (for the positive replica) or disconnected (for the negative replica) structures having a maximal height of about 300 nm. This value can be slightly increased by increasing the amount of initial sol-gel solution before NIL. However, the unavoidable shrinking of the printed titania results in structures rather smaller than the original master. The channels formed

between the 3D structures are about 2-10 micrometer wide.

3.3 Replicas in porous MOx

A second example of replicas in porous MOx are shown in Figure 7 for both titania and silica printed on a glass substrate. The thickness and porosity of the TiO_2 layer are respectively 160 nm and 50%, whereas for the SiO_2 they are 590 nm and 50%. The final morphologies are not different from what found in the previous case of dense materials. However, we remark that for porous materials a height in the range 500-600 nm can be obtained, accounting for a smaller shrinking upon evaporation of the volatile solvents. This difference can be justified by the larger fraction of Pluronic F127 block-copolymer porogene with respect to the volatile compounds used to obtain porous MOx and suggests a tradeoff between density (and thus refractive index) and shrinking.

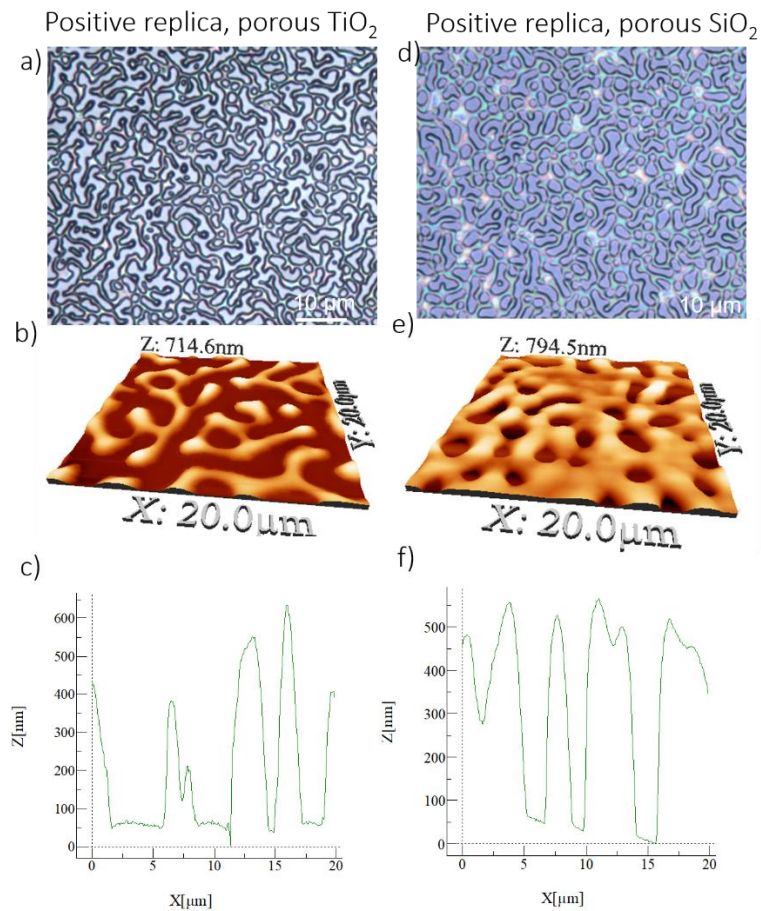


Figure 7. a) Bright field, optical microscope image (100X magnification) of porous titania positive replica on glass. b) AFM image of the sample in a). c) Height profile from b). d) Bright field, optical microscope image (100X magnification) of porous positive replica on glass. e) AFM image of the sample in d). c) Height profile from e).