



HAL
open science

Laser interference and nanospheres UV lithography to produce micro and nanostructured TiO₂ and TiN based sol-gel layers

Yves Jourlin, Nicolas Crespo-Monteiro, Victor Vallejo Otero, Marie Traynar, Maria Usuga Higueta, Emilie Gamet

► To cite this version:

Yves Jourlin, Nicolas Crespo-Monteiro, Victor Vallejo Otero, Marie Traynar, Maria Usuga Higueta, et al.. Laser interference and nanospheres UV lithography to produce micro and nanostructured TiO₂ and TiN based sol-gel layers. UV and Higher Energy Photonics: From Materials to Applications 2022, Aug 2022, San Diego, CA, United States. pp.1220107, 10.1117/12.2635170 . ujm-03818551

HAL Id: ujm-03818551

<https://ujm.hal.science/ujm-03818551>

Submitted on 18 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

PROCEEDINGS OF SPIE

[SPIDigitalLibrary.org/conference-proceedings-of-spie](https://spiedigitallibrary.org/conference-proceedings-of-spie)

Laser interference and nanospheres UV lithography to produce micro and nanostructured TiO₂ and TiN based sol-gel layers

Y. Jourlin, N. Crespo-Monteiro, V. Vallejo Otero, M. Traynar, M. Usuga Higueta, et al.

Y. Jourlin, N. Crespo-Monteiro, V. Vallejo Otero, M. Traynar, M. A. Usuga Higueta, E. Gamet, "Laser interference and nanospheres UV lithography to produce micro and nanostructured TiO₂ and TiN based sol-gel layers," Proc. SPIE 12201, UV and Higher Energy Photonics: From Materials to Applications 2022, 1220107 (3 October 2022); doi: 10.1117/12.2635170

SPIE.

Event: SPIE Nanoscience + Engineering, 2022, San Diego, California, United States

Laser Interference and Nanospheres UV Lithography to produce micro and nanostructured TiO₂ and TiN based sol-gel layers

Y. Jourlin^{1*}, N. Crespo-Monteiro¹, V. Vallejo-Otero¹,

M. Traynar¹, M. A. Usuga Higueta¹, E. Gamet¹

¹ Université de Lyon, Université Jean Monnet Saint-Etienne,

Laboratoire Hubert Curien UMR CNRS 5516, Saint Etienne (France)

*Yves.jourlin@univ-st-etienne.fr

ABSTRACT

In this paper, a direct and cost-effective sol-gel method to produce stable titanium dioxide and titanium oxynitride photoresists is described. This approach is compatible with many photolithographic techniques. We show that laser interference lithography and nanosphere lithography can be used, respectively, to obtain homogeneous TiO₂ diffraction gratings and periodic nanopillars over large areas. Further developments permit to transform TiO₂ microstructured based sol-gel to TiN metallic microstructured layer, with good optical properties, by using an innovative rapid thermal nitridation process, which opens the way towards plasmonics and NIR filters based on periodic metallic microstructured layers. Further technological processes were conducted to produce micro and nanostructured TiO₂ and TiN layers from a NanoImprint approach.

This work demonstrates the versatility of this complete process of soft chemistry new process of patterning TiO₂ and TiN thin films avoiding expensive processes (etching, lift-off...) while preserving their diffractive properties and a high thermal stability, up to 1000°C. It is thus compatible to various types of substrates (of different shape and size). These results open up the opportunity to develop a cost-effective and low time-consuming approach to address different fields of cutting-edge applications (metasurfaces, sensors, luxury and decorative industry...).

Keywords: UV lithography, Sol-gel Materials, Titanium oxide, Titanium nitride, Subwavelength microstructures Colloidal Lithography, Laser Interference Lithography, NanoImprint lithography

1. INTRODUCTION

Over the past 2 decades titanium dioxide (TiO₂) has been deeply studied for a wide range of fields such as solar cells¹, photocatalysis², optical filters³, anti-reflections⁴, wear coatings⁵. Another application of TiO₂ is its use as a decorative coating⁶⁻⁸. It is known that titanium dioxide has interesting optical properties. TiO₂ is considered a nonabsorbent material in the visible range with a high index. Thus, the color effect is associated with resonances or interferences in this high index film. Furthermore, TiN can be produced from TiO₂ film. This material is known to be a high reflectivity metallic layer with very good mechanical and chemical properties.

By doping these TiO₂ layers with nitrogen titanium oxide nitride TiO_xN_y or titanium nitride can be produced^{9,10}. Use of high index coating TiO₂ for everyday objects or in area exposed to strong meteorological, chemical and mechanical restrictions is made possible by its chemical stability and its relative hardness^{10,11}. Magnetron sputtering^{7,8}, and anodic oxidation^{12,13} are the most common to synthesize decorative TiO₂. Even though these techniques are mastered and well documented there are not adapted to the realization of complex patterns (shapes, micro-nanostructures...) which limits their usefulness. We recently presented a direct and innovative process of rapid thermal nitridation (RTN) which allows to produce crystallized TiN layers from photo-structurable sol-gel coating of TiO₂ using soft nitridation conditions¹⁴. One of the advantages of our technique is

its compatibility with a wide range of substrates. The TiN layers produced presents optical, electrical and mechanical properties comparable to the ones produced by standard process¹⁵. In this paper, we describe processes of production of complex 2D patterns in the micro and nano-scale from TiO₂ sol-gel and nanoimprint lithography. We will show that these processes are adapted to substrates of different nature and geometry and that a nitridation of these TiO₂ patterns is possible allowing the production of structured colored metallic TiN by using a direct nitridation technique. The thermal resistance of the patterns has been investigated so that it assures a stability up to 1000°C to address certain application requirements.

2. EXPERIMENTAL METHODS

2.1 TiO₂ sol-gel

The sol-gel used to form TiO₂ films has been elaborate in a previous study^{14,16-18}. This sol-gel contains a TIPT-BzAc complex degradable by UVA, which allows the photo-patterning of the TiO₂. The sol-gel is a mix of two sols. The first sol was prepared by mixing titanium tetra isopropoxide (TIPT from Sigma-Aldrich) with deionized water, hydrochloric acid (HCl from Roth) and butanol (BuOH from Sigma Aldrich) with a TIPT/H₂O/HCl/BuOH molar composition of 1/0.13/0.82/23.9. This preparation is then aged for three days at room temperature before being mixed with the second sol. The second sol is prepared from a reaction of TIPT (Sigma-Aldrich), methanol (MeOH, Sigma Aldrich) and benzoylacetone (BzAc, Sigma Aldrich) at a TIPT/MeOH/BzAc ratio molar of 1/0.75/20.4. The final product is obtained once the two sol are mixed. The final BzAc/TIPT ratio molar was 0.6. In this study films have been deposited by spin coating at 3000 rpm or by dip coating depending on the type of substrate. Once deposited a thermal treatment of 110°C for 90 minutes was applied to eliminate the solvent while conserving the photosensitivity of the film. This process results in the production of amorphous film called xerogel.

2.2 Photo-structuring process

Micro-nanostructuring of the TiO₂ xerogel can be done by UVA illumination at 365nm¹⁸. The xerogel films are soluble in different solvents such as alcohol, chloroform, and acetone, as long as BzAc remains complexed with TIPT. However, under UVA illumination, TIPT-BzAc complex in the xerogel layer will partially degraded into insoluble species (carbonates and/or carboxylates). By spatially controlling the illuminated and non-illuminated areas, it is possible to create a patterned layer of TiO₂. After that, the exposed film was developed by soaking it in ethanol for 30 seconds and rinsing it in deionized water for a further 30 seconds. Non-illuminated area will be dissolves by the ethanol. The water stabilizes the layer. The final pattern will be the area exposed by the UVA.

2.3 Laser interference lithography

Phase mask with a ring-shaped radial diffraction grating that converges at a central point has been used to structure the interior of a tube. This mask shown in Figure 1 has an inner radius (R_i) of 1mm and an outer radius (R_e) of 1.5mm. The details on the phase mask design and the fabrication are given in reference¹⁹. The phase mask is a radial diffraction grating designed to maximize the efficiency of the 1st transmitted orders over the entire range of the radial corrugation, while the 0th transmitted order propagates parallel to the tube axis and does not interfere

with the 1st orders at the cylinder wall. The 2nd diffraction orders are evanescent. The grating has a constant angular period (Λ) of 480 μrad which creates a variable spatial period as a function of the radial position R . This mask was used to structure the interior of a tube with an inner radius of 4mm. The period of the grating is therefore $\Lambda = R \cdot \Lambda_{\phi\text{-mp}} = 960 \text{ nm}^{20}$.

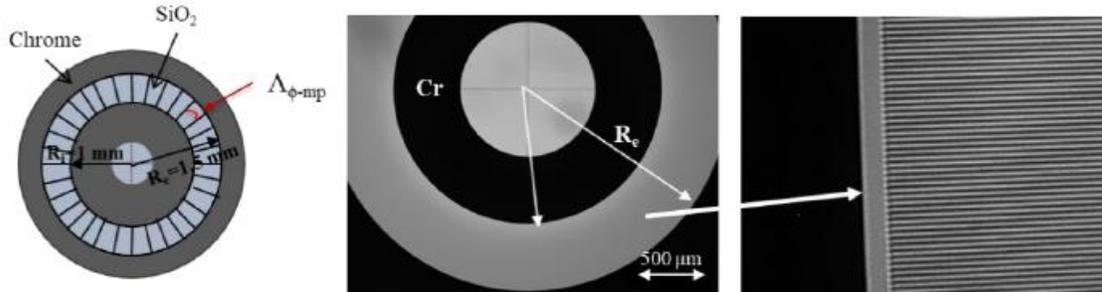


Figure 1. Radial mask illustration

2.4 Colloidal lithography

Silica microspheres of 1 μm diameter (in ethanol suspension (96% v/v) Micromod) functionalized with a hydrophobic acrylate surface were deposited on TiO_2 xerogel thin films covered with a poly(methyl methacrylate) (PMMA) layer according to the Langmuir Blodgett (LB) approach²¹. To realize this monolayer of silica microspheres an LB machine (KSV NIMA LB) (Biolin Scientific) was used. The silica microspheres monolayer were spread on the aqueous sub-phase at room temperature and left for 10 min for the solvent to evaporate. After compression of the silica microsphere monolayer at a barrier speed of 3 mm/min, LB was deposited on the thin film at a surface pressure of 40 $\text{mN}\cdot\text{m}^{-1}$ using the dipping method with a withdrawal speed of 3 mm/min. The TiO_2 xerogel layer was deposited by spin coating at 3000 rpm for 1 minute and the PMMA layer was deposited by spin coating at 6000 rpm for 1 minute. The PMMA layer was used to protect the TiO_2 thin film from water and to allow UV to pass through during film exposure. After deposition, the microspheres are illuminated at a wavelength of 365 nm for 90 seconds at 103,52 mW/cm^2 in order to obtain TiO_2 nanopillars with a 2D hexagonal arrangement¹⁶.

2.5 Nano-impression lithography

Polydimethylsiloxane (PDMS) stamps with sinusoidal micro-nanostructures of period 800 nm and depth 60 nm are used to micro-nanostructure the TiO_2 xerogel films. After deposition of the TiO_2 xerogel films by spin-coating at 4000 rpm during 30 sec, PDMS stamp was applied to the TiO_2 xerogel films in a humidity and temperature-controlled environment (20°C and 50% humidity) under 1 bar of pressure for 3 minutes using a press. Afterwards, a UV illumination at a wavelength of 365 nm for 5 minutes at 600 mW is used to stabilize the patterned TiO_2 films.

2.6 TiN films

The TiN films are produced by the nitridation of amorphous TiO₂ xerogel film by the RTN process previously published^{14,15}. This process consists of introducing pure NH₃ in a halogen infrared lamp-heated furnace (RTA As-One 100 from Annealsys). Initially, the reactor was purged with a cycle of N₂ (with the flow rate set at 1,000 sccm and 10 mbar) and vacuum. The TiO₂ xerogel layers were then irradiated for 30 seconds at 50% of the lamp power. Each cycle was repeated 10 times for one second at 1% of lamp power between each heat treatment cycle to protect the lamp and maximize its lifetime. The thermal exposure process based on 10 cycles lasted 10 minutes. During the process, the flow rate of NH₃ was at 1,000 sccm in the chamber at a pressure of 10 mbar.

2.7 Characterization

The optical transmittance and reflectance properties of the TiO₂ and TiN layers were analyzed in the infrared, visible and near-UV ranges using a Cary 5000 UV-Vis-NIR (Agilent Technologies). Reflection spectroscopy measurements were made in a specular configuration with an incident angle of 10°. The crystalline structure of the films was analyzed using Raman micro-spectroscopy (LabRam ARAMIS) with an excitation wavelength at 633 nm (He-Ne laser). The micro-nanostructured thin films were illustrated by atomic force microscopy (AFM) measurements (Dimension Icon from Bruker) in tapping mode with a tip AppNano (ACTA) and by scanning electron microscopy (SEM) using both high and low vacuum mode with JEOL JSM-IT800. Resistivity measurements were performed by the four-point probe method. The surface resistance has been measured in different places of each layers.

3. RESULTS AND DISCUSSION

3.1 Micro-nanostructuring of TiO₂ xerogel using laser interference lithography

The TiO₂ xerogel layer is deposited on the inner wall of a cylindrical substrate (tube), by dip-coating TiO₂ sol-gel at constant speed of 7 cm/min. Thickness homogeneity of the layers was ensured by a well control of the dip coating parameters during the withdrawal of the tube, thanks to an anti-vibrations table and a constant speed. The grating was printed on the inner wall of the cylinder using a phase mask, as described in References^{19,20}. The phase mask is illuminated under normal incidence with a circular polarization by a 100 mW laser at wavelength 355 nm. The photosensitive layer on the cylindrical substrate was illuminated during 10 minutes. The sample was developed in ethanol and rinsed in water during 60 seconds. After this process, the grating inside the cylinder was visible by the diffraction of white light (Fig. 2(a)). The depth of the grating was estimated at 170 nm and the period at 960 nm. The grating profile (Fig. 2(b), (c)) was analyzed using AFM and SEM analysis on a broken piece.

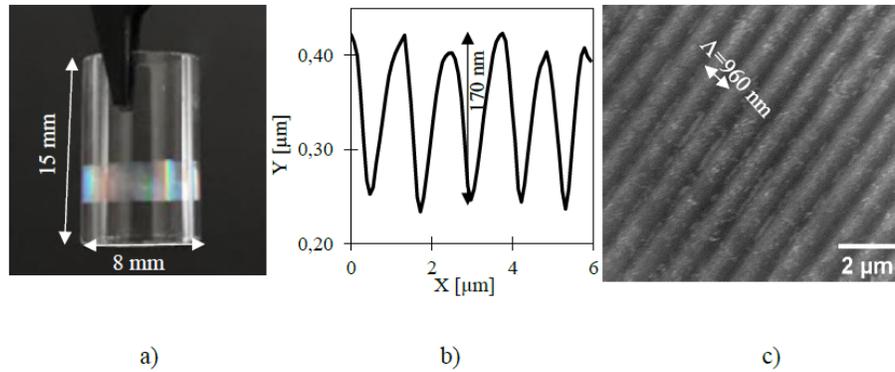


Figure 2. a) Radial Cylindrical grating inside a tube b) AFM profile and c) SEM image of grating

3.2 Micro-nanostructuring of TiO₂ xerogel using colloidal lithography

The realization of micro-nanostructures is also possible with this sol-gel by the colloidal lithography method (figure 3). A TiO₂ sol-gel layer is deposited at 6000 rpm and stabilized at 110°C. Then, a layer of polymethylmethacrylate (PMMA from Sigma Aldrich) was then deposited to protect the sol-gel layer from water for the rest of the protocol. The next step was the deposition of a layer of silica beads by the Langmuir-Blodgett method. This method involves transferring a floating monolayer of dispersed 1 μm diameter silica beads to the surface of a water bath. The silica bead layer is then deposited on the sample by dip-coating. After the beads were deposited, exposure was performed at a power of 300 mW for 5 minutes. The beads act as microlenses that focus the light creating what we call a "nanojet" or "photonic jet" of very intense light (Figure 2.43). The length of the nanojet in the Z direction is about 500 nm¹⁶. These dimensions depend mainly on the size of the beads, the exposure wavelength and the layer index.

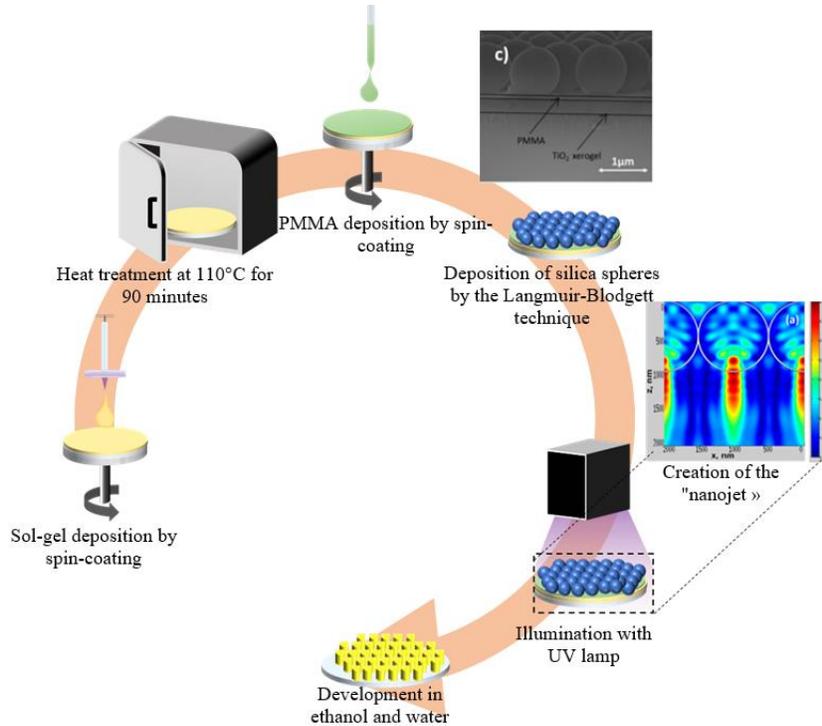


Figure 3. Illustration of the micro-nanostructuring process by colloidal lithography

Finally, the development of the sol-gel exposed layer is performed in ultrapure water using ultrasound to remove the silica beads, following which the sample is placed in chloroform to remove the PMMA layer. It is then immersed in ethanol which will develop the non-insolated areas of the sol-gel layer and then in ultrapure water for rinsing. The resulting nano-pillars have a height of about 300 nm, a period of 1 μm , and a diameter of about 550 nm (Figure 4)

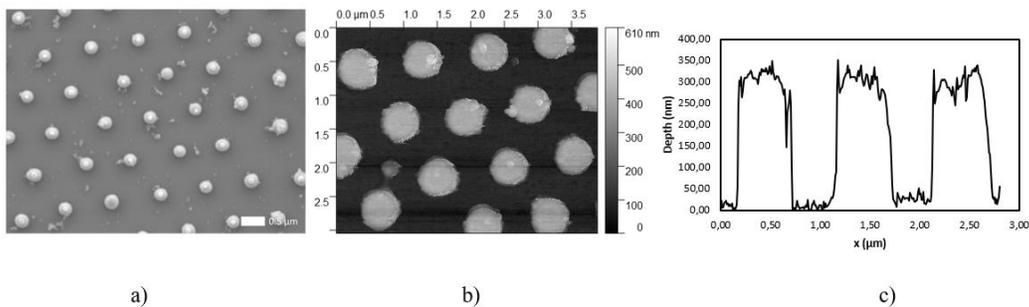


Figure 4. a) SEM image, b) AFM image et c) AFM profile of TiO_2 nano-pillars

3.3 Micro-nanostructuring of TiO_2 xerogel using nano-impression lithography

Another method for structuring this TiO_2 sol-gel is to use the direct UV nanoimprinting process to obtain, for example, amorphous TiO_2 diffraction grating. Figure 5 shows an example of structured TiO_2 xerogel thin layers

obtained by nanoimprint. From a PDMS stamps with a sinusoidal nanostructure of 800 nm period and 60 nm depth, it is possible to obtain replicas based on TiO₂ sol-gel with similar characteristics. Figure 5A and B show that the TiO₂ replica has a period of around 1 μm with a depth close to 150 nm. Figure 5C shows the grating pattern obtained with the nanoimprint method. A uniform structure was fabricated and allow us to obtain sample with diffraction phenomenon as shown Figure 5C inset.

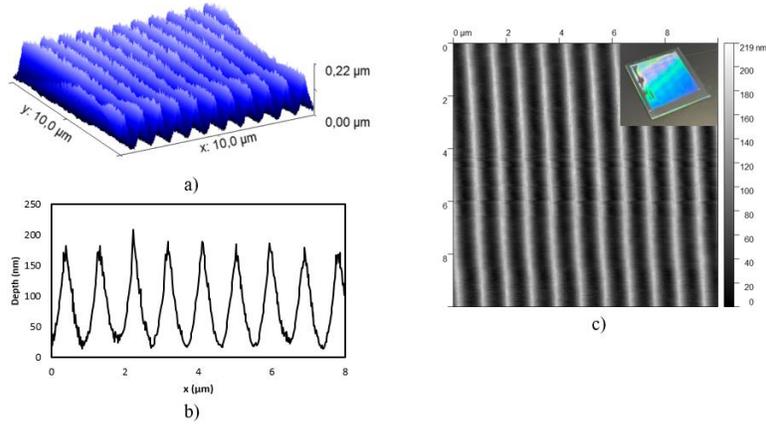


Figure 5. a) AFM TiO₂ xerogel sub-micronic diffraction grating. b) profile of the nanostructured TiO₂ thin film. c) AFM image of the TiO₂ diffraction grating with an inset picture showing the iridescence phenomenon of the structured TiO₂ layer.

3.4 Nitridation of TiO₂ patterns

As shown in figure 6 a), b), TiO₂ xerogel films are almost colorless in transmission and become purplish in reflexion. In order to obtain colored and more contrasting patterns, the TiO₂ samples were nitrided to obtain a metallic TiN pattern with a dark greyish color in transmission and golden based color in reflection figure 6 c), d), respectively. Amorphous structured TiO₂ xerogel by colloidal lithography was nitrided by rapid thermal annealing (RTA) under NH₃ gas. After RTN treatment, the multi-scale TiO₂ structured sample was converted to TiN according to processes detailed in recent works^{14,15}.

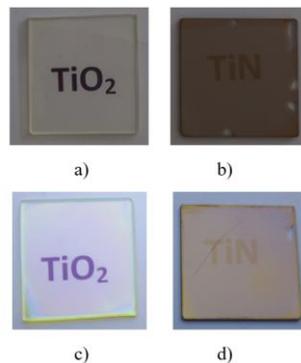


Figure 6. Optical images of TiO₂ xerogel films and TiN films in a), b) transmission and c),d) reflection, respectively.

Before nitriding, the period of the nano-pillars is 1 μm and their height is about 280 nm (Figure 7a). After RTN nitriding, the period is the same but the nano-pillars undergo a sharp decrease in height and reach about 60 nm, a decrease of about 70% (Figure 7b). The average diameter of the nano-pillars also undergoes a decrease.

Before nitriding, this diameter is about 550 nm and, after nitriding, it has been reduced to about 510 nm, a decrease of about 20%.

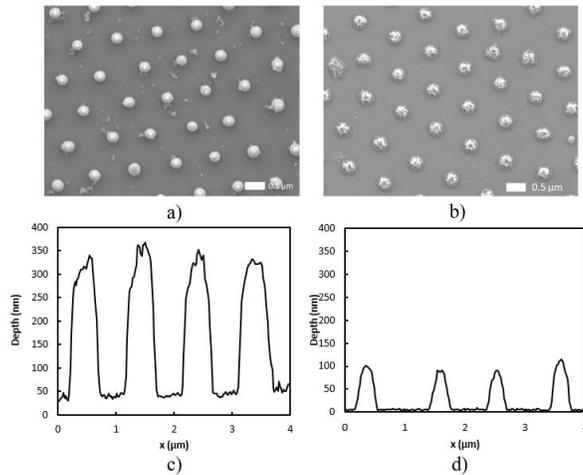


Figure 7. a), b) SEM images and c), d) AFM profile of TiO_2 and TiN nano-pillars, respectively.

3.5 Thermal resistance

In order to test the stability of the inscriptions, TiO_2 nanopillars produced by colloidal lithography were annealed under air to different temperatures (500 °C, 800 °C and 1,100 °C) for one hour. During the heat treatment, the period of the nano-pillars remains the same (1 μm) but their height and their diameter reduced (figure 8). Before annealing, the nano-pillars are a height about 300 nm and a diameter around 550 nm (Figure 8a). After 1h at 500°C the height is about 150 nm and their diameter around 450nm, at 800 °C the height is about 150 nm and their diameter around 400nm and at 1,100 °C their height is about 140 nm and their diameter around 400nm. Even if the structures decrease in height and diameter with temperature, they are still visible even after a heat treatment of 1 hour at 1,100°C.

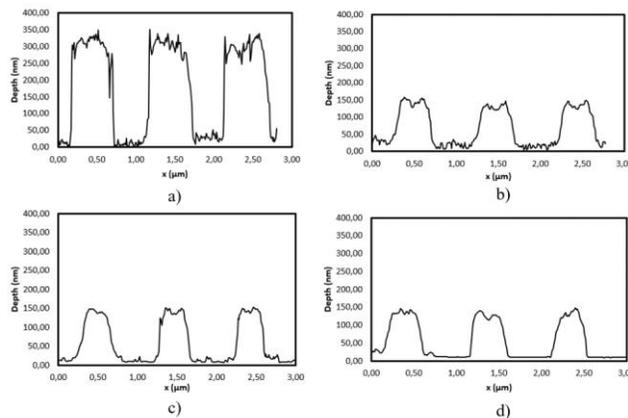


Figure 8. a) AFM profile of TiO_2 nano-pillars without thermal treatment and after 1 hour at b) 500°C, c) 800°C and d) 1,100°C

4. CONCLUSION

This work demonstrates the versatility of this complete process of soft chemistry new process of patterning TiO₂ thin films avoiding expensive processes (etching, lift-off...) while preserving their diffractive properties and a high thermal stability, up to 1000°C. It is thus compatible to various types of substrates (of different shape and size). These results open up the opportunity to develop a cost-effective and low time-consuming approach to address different fields of cutting-edge applications (metasurfaces, sensors, luxury and decorative industry...).

Periodic metallic microstructured layers is attracting more and more interest from industries nowadays, especially in the plasmonic materials field or optical metasurface devices where metal-nitrides are very promising new plasmonic materials to replace noble metals. Among them, titanium nitride (TiN) is one of the most investigated compounds to date, in particular thanks to its intrinsic properties which make it a first-choice material. Unfortunately, due to its notably hardness and chemical resistance, TiN cannot easily form micro- and nanostructures. Structuring techniques using lithography and liftoff and/or physical or chemical etching processes do exist but are encountering problems of either low speed, small patterning area or high cost equipment. The variety of potential applications in plasmonic devices, for example, in near infrared (NIR) range of patterned TiN thin films requires the possibility to easily structure periodically this plasmonic materials. An emerging solution to this technological lock-in consists of performing micro-nanostructuring on a titanium dioxide (TiO₂) sol-gel photopatternable film that is then converted into TiN using a thermal nitridation process in an ammonia atmosphere. Sol-gel process seems promising because of its simplicity of implementation, its low cost and its compatibility to various and unconventional substrates. The main advantage of the sol-gel-based processes is that they make it possible to achieve submicronic structuration with various reproducible shapes (like grating, pillars...) on large area.

ACKNOWLEDGMENT

This research was funded by French National Research Agency (ANR), grant number ANR-21-CE08-0042-0, within ANR JCJC project "NITRURATION as well as LABEX MANUTECH-SISE, grant number ANR-10-LABX-0075) of the Université de Lyon, within the program 'Investissements d'Avenir' (ANR-11-IDEX-0007).

REFERENCES

- [1] Shakeel Ahmad, M., Pandey, A. K. and Abd Rahim, N., "Advancements in the development of TiO₂ photoanodes and its fabrication methods for dye sensitized solar cell (DSSC) applications. A review," *Renewable and Sustainable Energy Reviews* **77**(C), 89–108 (2017).
- [2] Akpan, U. G. and Hameed, B. H., "Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: a review," *J Hazard Mater* **170**(2–3), 520–529 (2009).
- [3] Kitui, M., Gaiho, F. and Maghanga, C., "Optical properties of TiO₂ based multilayer thin films" (2012).
- [4] Lien, S.-Y., Wu, D.-S., Yeh, W.-C. and Liu, J.-C., "Tri-layer antireflection coatings (SiO₂/SiO₂-TiO₂/TiO₂) for silicon solar cells using a sol-gel technique," *Solar Energy Materials and Solar Cells* **90**(16), 2710–2719 (2006).
- [5] Bagheri, P., Farzam, M., Mousavi, A. B. and Hosseini, M., "Ni-TiO₂ nanocomposite coating with high resistance to corrosion and wear," *Surface and Coatings Technology* **204**(23), 3804–3810 (2010).

- [6] Chen, X. and Mao, S. S., "Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications," *Chem. Rev.* **107**(7), 2891–2959 (2007).
- [7] Skowronski, L., Wachowiak, A. A. and Grabowski, A., "Characterization of optical and microstructural properties of semitransparent TiO₂/Ti/glass interference decorative coatings," *Applied Surface Science* **388**, 731–740 (2016).
- [8] Skowronski, L., Wachowiak, A. A., Zdunek, K., Trzcinski, M. and Naparty, M. K., "TiO₂-based decorative coatings deposited on the AISI 316L stainless steel and glass using an industrial scale magnetron," *Thin Solid Films* **627**, 1–8 (2017).
- [9] Skowronski, Ł., Antończak, A. J., Trzcinski, M., Łazarek, Ł., Hiller, T., Bukaluk, A. and Wronkowska, A. A., "Optical properties of laser induced oxynitride films on titanium," *Applied Surface Science* **304**, 107–114 (2014).
- [10] Meng, Y.-L., Tan, J., Xu, K., Chen, J., Jin, G.-J., Sun, Y., Wang, L.-L., Zuo, Z., Qin, H.-Y., Zhao, Y. and Guo, J., "Salisbury screen optical color filter with ultra-thin titanium nitride film," *Appl. Opt.*, **AO** **58**(24), 6700–6705 (2019).
- [11] Diebold, U., "The surface science of titanium dioxide," *Surface Science Reports* **48**(5), 53–229 (2003).
- [12] Diamanti, M. V., Del Curto, B. and Pedeferrri, M., "Interference colors of thin oxide layers on titanium," *Color Research & Application* **33**(3), 221–228 (2008).
- [13] VAN GILS, S., MAST, P., STIJNS, E. and TERRY, H., "Colour properties of barrier anodic oxide films on aluminium and titanium studied with total reflectance and spectroscopic ellipsometry," *Surf. coat. technol* **185**(2–3), 303–310 (2004).
- [14] Valour, A., Usuga Higuaita, M. A., Crespo-Monteiro, N., Reynaud, S., Hochedel, M., Jamon, D., Donnet, C. and Jourlin, Y., "Micro-Nanostructured TiN Thin Film: Synthesis from a Photo-Patternable TiO₂ Sol-Gel Coating and Rapid Thermal Nitridation," *J. Phys. Chem. C* **124**(46), 25480–25488 (2020).
- [15] Valour, A., Higuaita, M. A. U., Guillonneau, G., Crespo-Monteiro, N., Jamon, D., Hochedel, M., Michalon, J.-Y., Reynaud, S., Vocanson, F., Jiménez, C., Langlet, M., Donnet, C. and Jourlin, Y., "Optical, electrical and mechanical properties of TiN thin film obtained from a TiO₂ sol-gel coating and rapid thermal nitridation," *Surface and Coatings Technology* **413**, 127089 (2021).
- [16] Shavdina, O., Berthod, L., Kämpfe, T., Reynaud, S., Veillas, C., Verrier, I., Langlet, M., Vocanson, F., Fugier, P., Jourlin, Y. and Dellea, O., "Large Area Fabrication of Periodic TiO₂ Nanopillars Using Microsphere Photolithography on a Photopatternable Sol-Gel Film," *Langmuir* **31**(28), 7877–7884 (2015).
- [17] Berthod, L., Shavdina, O., Vocanson, F., Langlet, M., Dellea, O., Veillas, C., Reynaud, S., Verrier, I. and Jourlin, Y., "Colloidal photolithography applied to functional microstructure on cylinder based on photopatternable TiO₂ sol-gel," *Microelectronic Engineering* **177**, 46–51 (2017).
- [18] Briche, S., Tebby, Z., Riassetto, D., Messaoud, M., Gamet, E., Pernot, E., Roussel, H., Dellea, O., Jourlin, Y. and Langlet, M., "New insights in photo-patterned sol-gel-derived TiO₂ films," *J Mater Sci* **46**(5), 1474–1486 (2011).
- [19] Berthod, L., Bichotte, M., Verrier, I., Veillas, C., Kämpfe, T., Vocanson, F., Langlet, M., Laukkanen, J., Parriaux, O. and Jourlin, Y., "Efficient reversible phase mask for TiO₂ submicron gratings directly printed on cylindrical surfaces," *Opt. Express*, **OE** **25**(8), 9003–9009 (2017).
- [20] Usuga Higuaita, M. A., Bruhier, H., Hochedel, M., Kämpfe, T., Vocanson, F., Valour, A., Jamon, D., Langlet, M., Crespo-Monteiro, N. and Jourlin, Y., "Resonant waveguide grating fabrication on planar and cylindrical substrates using a photosensitive TiO₂ sol-gel approach," *Opt. Mater. Express* **11**(1), 12 (2021).
- [21] Bardosova, M., Pemble, M. E., Povey, I. M. and Tredgold, R. H., "The Langmuir-Blodgett Approach to Making Colloidal Photonic Crystals from Silica Spheres," *Advanced Materials* **22**(29), 3104–3124 (2010).