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Eco-friendly soft nanoimprinting of TiO₂ nanostructures with a large range of pattern heights

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ABSTRACT

Nanoimprint lithography (NIL) is nowadays the most popular and effective method to develop new environmentally-friendly and low-cost photonic nanodevices. Combined with titanium dioxide (TiO₂) in the form of sol-gel, photonic nanostructures with low absorption and high refractive index can be produced, which can be of interest for many applications for which sustainability becomes increasingly important. In this paper, we present a patterning process based on soft NIL of TiO₂ sol-gel, and show that the very good pattern transfer has been obtained, which can be completed with independence from the feature size, shape and height of the patterns. We also propose a low-temperature (400°C) calcination process rather than 450°C or higher temperature to crystallize the TiO₂ nanostructures, which leads to very similar crystalline structures to higher-temperature processes, and a vertical shrinkage of about 61% compared to the imprinted pattern. Using this environmentally-friendly combined soft-NIL + calcination process, we show that submicron patterns with heights above 300 nm can be obtained. Such a large pattern height, combined with the wide range of pattern shapes and dimensions that can be fabricated, opens the possibility of a wide diversity of designs for the eco-friendly fabrication of TiO₂ nanostructures with highly-interesting photonic properties.

Keywords: photonic crystal, TiO₂ materials, nanoimprint, nanostructures, sustainability

1. INTRODUCTION

Nowadays, optical nanostructures have attracted growing interest for a variety of applications, ranging from telecoms/datacoms to displays, coatings, sensing or medical applications^{1,2}. The vast majority of photonic nanodevices are based on high-index material systems like silicon, which ensures high optical performances and direct compatibility with CMOS integration. However, the fabrication processes of such devices have a strong environmental impact, both because of the semiconductor substrate manufacturing, and of the oil-based lithography and etching technologies used for top-down patterning. In the current context of dramatic climate change, critical resources, and increasing particulate and chemical pollution, it has become imperative to bring sustainability into the equation, especially in the case of environmental applications and/or applications to health care where the photonic chips are often single-use consumables. Sustainability is a multidisciplinary concept that encompasses not only environmental sustainability, but also economic sustainability (cost-effectiveness) and social sustainability (end-user acceptance). Therefore, it is necessary to consider the development of optical nanopatterning/nanostructures in a holistic manner in terms of key aspects such as economic, ecological and technological (material, manufacturing and device life cycle) as well as societal (devices well adapted to the current societal needs and trends).

Among the potential materials for the development of sustainable optical devices, metal oxides are interesting for environment and health care applications. In particular, titanium dioxide (TiO₂) presents a variety of advantages such as good optical properties, with a refractive index above 2 and a good transparency up to near-ultraviolet frequencies. It has a low toxicity and a good biocompatibility. In addition, it is abundant, inexpensive, chemically stable, and has good photocatalytic properties and high mechanical strength. And last but not least, it offers the possibility of nanopatterning in the form of sol-gels. There are four natural TiO₂ polymorphs: anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic) and TiO₂ (B)³. In particular, anatase-TiO₂ is stable and known to be a high-purity single crystal with a

high proportion of reactive (001) facets that may cause improved catalytic activity and selectivity ^{4,5}. Thus, it has been regarded as a promising material for various applications. Among the environmental issues that can be addressed by the photocatalytic properties of TiO₂, Crespo-Monteiro *et al.* have shown that micro- and nanopatterning of sol-gel TiO₂ coatings leads to an increased photocatalytic efficiency for the degradation of formic acid under UV irradiation ⁶. In the broad area of optical sensing devices, Aki *et al.* developed a plasticized-poly (vinyl chloride) (PVC)/TiO₂ hybrid 2D photonic crystal for highly sensitive fluorescence-based ion sensing ⁷. In 2021, Modaresialam *et al.* fabricated a high sensitivity gas sensor by combining a gas-adsorbent silica layer with a dense TiO₂ metasurface ⁸. All these works are exploiting the possibility to micro- and nanopattern TiO₂ sol-gel layers via environmentally-friendly (resist-free lithography) and low-cost manufacturing processes.

In two of the works above, nanoimprint lithography (NIL) is proposed as a very promising cost-effective manufacturing process ^{7,8}, which highlights the increasing interest of NIL for the fabrication of optical nanostructures. NIL enables direct patterning of materials with a reusable stamp, hence offering nanostructure fabrication with high throughput and low environmental impact, as it avoids the polluting processes of standard oil-based lithography and etching. Moreover, nanoimprint is a scalable technique compatible with patterning over large areas at industrial scale ⁹. Several other groups have also proposed TiO₂ nanopatterns using NIL combined with sol-gel. Among them, Dinachali *et al.* successfully fabricated a 1D TiO₂ grating via direct NIL using a mold with equal line width and depth of 250 nm; after calcination at 450°C for 1h, a final height of 38 nm was obtained for the TiO₂ nanostructures ¹⁰. Kothari *et al.* fabricated crystalline TiO₂ from a Si master with 480 nm line height; after calcination at 500°C for 3h, the patterns reduced to a line height of 140 nm ¹¹. These two examples illustrate a current drawback of direct patterning of TiO₂ sol-gels: as the calcination process that is performed to crystallize the material induces a high shrinkage of the nanopatterns, the reported heights of the resulting TiO₂ nanopatterns usually are relatively small. For photonic applications, however, it would be of high interest to produce TiO₂ submicron features with increased heights in the 100-300 nm range.

In this context, this paper presents the development of a technological process that enables the fabrication of TiO₂ photonic nanostructures reaching a large range of pattern heights up to 300 nm or more. Our process is based on soft NIL, a technique that imprints patterns using flexible molds, usually made of soft materials such as polydimethylsiloxane (PDMS). Soft NIL was first proposed by Whitesides' group in the 1990s ¹². It has gained increasing interest as it is simple, easy to control and the required imprinting power is low, which means that it does not require the use of expensive apparatus. With the development of soft NIL techniques, the "degassed assisted patterning" technique has been proposed to obtain a better filling of the stamp features, taking advantage of the PDMS permeability to solvents. The key point of this technique is to use the pressure difference between the degassed PDMS stamp and the sol-gel substrate as a "sucking" mechanism inducing the infiltration of the solution into the PDMS voids, hence leading to a better filling of the patterns ^{13,14}.

Herein, we propose a soft NIL process for the patterning of spin-coated TiO₂ sol-gel layers, that allows for the low-cost and sustainable fabrication of photonic nanostructures with heights up to 300 nm or more. Our PDMS stamps are replicated from silicon templates and used for TiO₂ patterning, with very good transfer of the nanostructure heights and lateral dimensions from the silicon master to the TiO₂ sol-gel based structures. Using pattern arrays of photonic crystals with varying parameters, we will show that our NIL process is independent from the pattern size, shape and aspect ratio. In order to go one step further towards sustainability, we will also present a lower-temperature calcination process that leads to crystalline TiO₂ patterns with a stable shrinkage rate compared to the embossed patterns.

2. RESULTS AND DISCUSSION

2.1 TiO₂ nanostructures obtained via soft NIL

Our development of TiO₂ nanopatterning via soft NIL has been divided into several main steps that are all performed in a clean-room environment. The first and most critical of these steps deals with the fabrication of the silicon master. For the purpose of process development, electron-beam lithography has been used for the master fabrication. This enables the fabrication of photonic crystal arrays with varying parameters on the same substrate, i.e., one-dimensional (1D) and two-dimensional (2D) periodic nanostructure arrays with varying submicron feature sizes that cover a broad range of periods (from 400 nm to 2 μm) and different filling factors. After fabrication of the silicon masters, the next step is the fabrication of the flexible PDMS stamps by replication of the masters. And finally, the soft NIL step is performed using the PDMS stamps, to imprint the arrays of nanostructures into a home-made TiO₂ sol-gel based on alcoholic benzoylacetone-modified sol. More details about the Si master fabrication, PDMS replication and TiO₂ sol-gel are

presented in the experimental section. Between each step, the nanostructure arrays are characterized by complementary techniques, such as atomic force microscopy (AFM) and scanning electron microscopy (SEM), which enable us to determine the quality and reproducibility of the pattern transfers.

Our soft NIL process is shown in Figure 1. First, the TiO₂ sol-gel is spin-coated on a silica surface (glass or SiO₂/Si substrate). Then the degassed PDMS stamp is laid on the spin-coated TiO₂ layer. No external force is applied. The “PDMS + substrate” assembly is placed on a hotplate at a set temperature, T, for a given time, t, to remove the solvents and facilitate the filling. After the assembly has cooled down, the PDMS is demolded from the substrate.

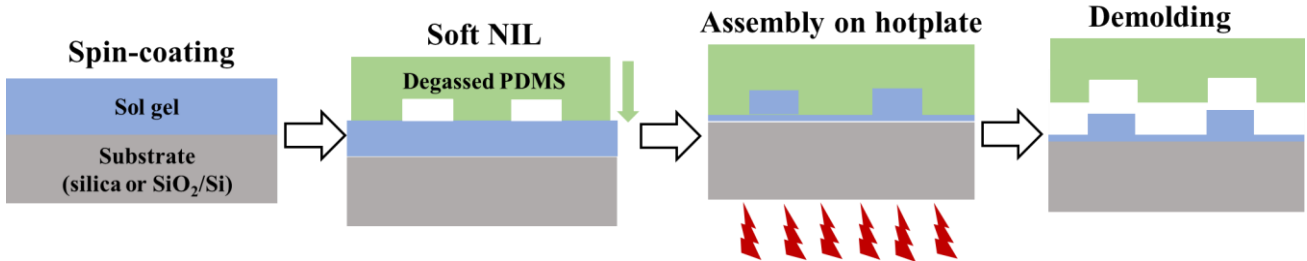


Figure 1. The 4 steps of the degassed-assisted soft NIL process.

Optimization of the process has shown that for a 3-minute heating time at a temperature of 120°C, the patterns are completely filled, leading to a very good transfer of the nanostructure arrays. Figure 2 shows two examples of SEM images of imprinted TiO₂ patterns prepared under these optimal NIL conditions. The 1D pattern (figure 2a) is made of a periodic array of TiO₂ lines with 700 nm period and 225 nm average line width. 2D pattern (figure 2b) consists of a square array of cylindric pillars with 700 nm period and 175 nm mean radius. In both cases, the standard deviation between features is about 5 nm. Despite the very different geometries, both patterns have heights of 190 ± 10 nm, which is the same as the height measured for the PDMS stamp. Similarly, the lateral dimensions of the lines and pillars are exactly the same for the TiO₂ structures as for the stamp. A perfect transfer of the features sizes and heights was also observed for the other nanostructure arrays with varying periods and widths. Hence, this result highlights the fact that the optimized NIL conditions can be applied to the fabrication of a large variety of photonic nanostructures.

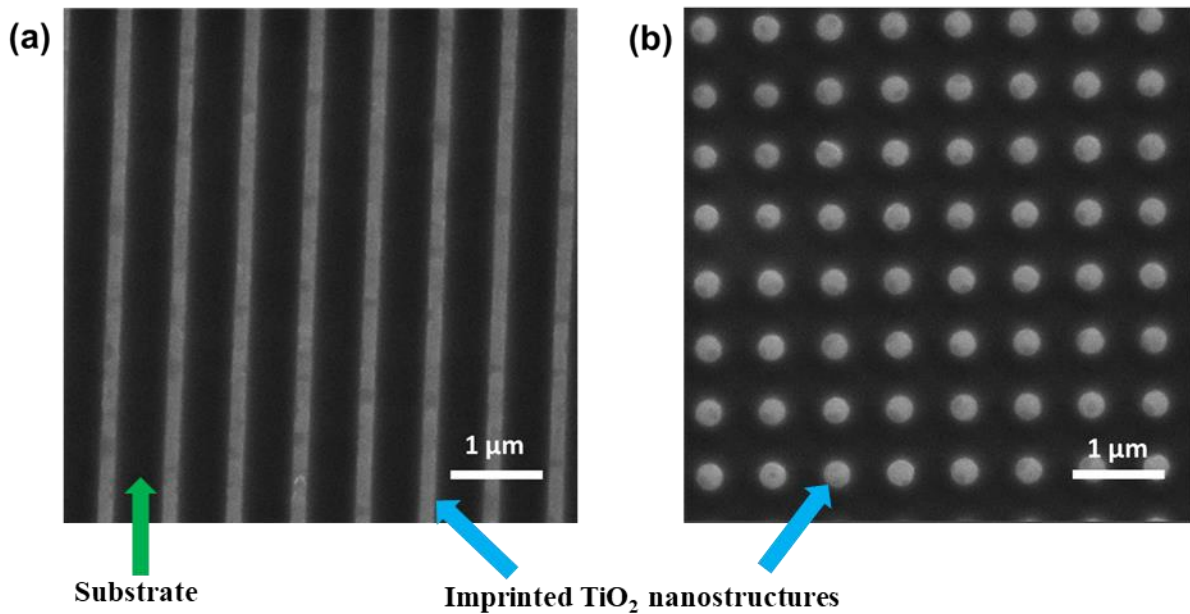


Figure 2. SEM images of imprinted TiO₂ patterns with 700 nm periods that were prepared with the optimized NIL conditions at T = 120°C for t = 3 min: a) 1D array of lines, and b) 2D square lattice of cylindric pillars.

2.2 TiO₂ calcination and induced shrinkage

For most applications, the imprinted sol-gel layer has to be crystallized, in order to gain high stability and a higher refractive index. The usual way for the preparation of anatase TiO₂ is via a thermal treatment (calcination) of the amorphous TiO₂ at high temperature. In general, the calcination process is performed at 450°C or slightly higher for a time ranging between a few tens of minutes to a few hours⁵. In order to keep the environmental impact of our calcination process as low as possible, we chose to perform the crystallization in a tube furnace at a slightly lower temperature (400°C) for only 20 min. After calcination, the TiO₂ layers were characterized by reflectometry and electron microscopy. Figure 3a shows a TEM (transmission electron microscopy) image of the material. We can recognize that the TiO₂ is made of small nanocrystallites with random orientation and an average size below 10 nm (a few examples are highlighted with red lines). This is confirmed by the electron diffraction pattern shown in Figure 3b, which shows a series of concentric rings corresponding to polycrystalline TiO₂ in anatase phase. The anatase phase was also confirmed by XRD (X-ray diffraction) measurements. The measured refractive index of the material is 2.1 and lies within the usual range of refractive indices obtained for polycrystalline TiO₂.

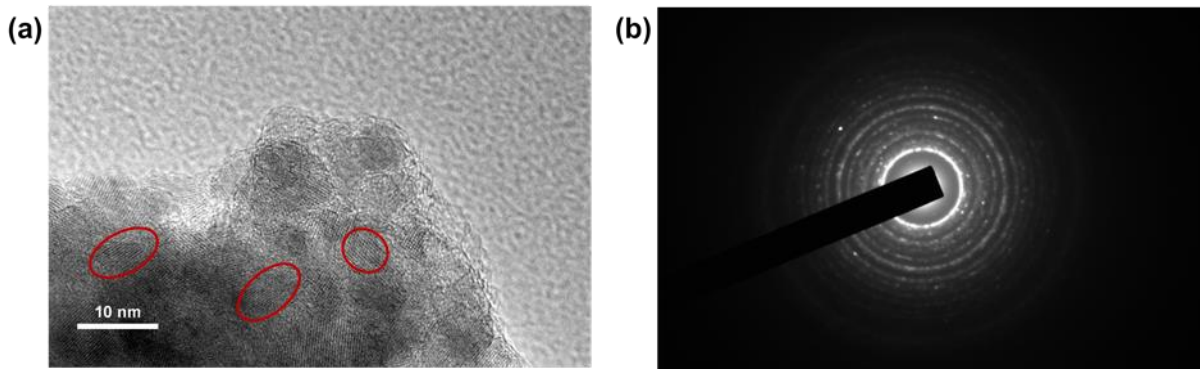


Figure 3. (a) TEM and (b) electron diffraction images of calcinated TiO₂ (at T = 400°C for t = 20 min).

As mentioned above, the crystallization process leads to a marked shrinkage of the imprinted TiO₂ patterns. This shrinkage occurs both in the lateral and vertical directions, and is mainly due to the evaporation of the solvent from the TiO₂ sol-gel during the calcination process, as well as the crystallite formation and the arrangement of the TiO₂ into a denser lattice. In order to quantify the shrinkage induced by our 400°C calcination process, systematic characterization by AFM has been performed. Table 1 shows a comparative measurement for a 1D TiO₂ pattern before and after calcination. The reduced size of the nanofeatures is clearly visible, both in the lateral and vertical dimensions. In this example, the TiO₂ lines have a width *w* and height *h* of 560 nm and 235 nm, respectively, before calcination. After calcination, the width and height of the lines are reduced to 260 nm and 90 nm, respectively, which corresponds to a lateral shrinkage of 54% and a vertical shrinkage of 62%. Similar shrinkages are observed for the other patterns with varying periods and feature sizes, both for 1D and 2D lattices. It can be concluded that the reduction of the imprinted pattern in the lateral and vertical directions does not depend on the lattice parameters. However, the reduction in the vertical direction is greater than the reduction in the lateral direction for both 1D and 2D patterns. The reason for this is not clear, but it could be an effect of the underlying residual TiO₂ layer.

Table 1. Measured feature sizes of imprinted TiO₂ (before and after calcination) for a 1D pattern of lines with width *w* and height *h* (mean values), with 2 μm period.

Samples	w (nm)	h (nm)
Imprinted TiO₂	560	235
Imprinted TiO₂ after calcination	260	90
Shrinkage (before and after calcination)	54%	62%

As a comparison, a similar study was conducted on identical TiO₂ sol-gel layers for the same time (20 min) at a “more standard” calcination temperature of 450°C. In this case, electron microscopy characterization showed that the resulting TiO₂ material is also polycrystalline in anatase phase with average crystallite size below 10 nm, which is very similar to

the results obtained at 400°C. The lateral shrinkage is also quite similar to the values obtained with the 400°C process, but the vertical shrinkage is slightly higher (68% for the 450°C calcination, vs. 62% for the 400°C process), which means that deeper patterns would be required in the initial masters to obtain the same pattern height in the final TiO₂ nanostructures crystallized at 450°C rather than at 400°C. However, the reflectometry measurements gave a refractive index of 2.2 for the 450°C process, which is slightly higher than the index obtained at 400°C (2.1); to obtain similar photonic properties, a usual way to compensate for the smaller refractive index obtained with the lower-temperature process would be a small adjustment in the parameters of the photonic structures, and in particular, a slightly larger pattern height; hence, we can deduce that the slightly larger vertical shrinkage of the 450°C process is more or less compensated by the slightly larger refractive index, and that both calcination processes should lead to photonic structures with very similar properties. Therefore, we have selected the process at 400°C for the further studies presented in the following, as it enables to reduce the environmental impact of the calcination.

2.3 Increasing the height of the TiO₂ patterns

In the process optimization that is presented above, the silicon master has an initial pattern height of about 245 nm. After PDMS replication, TiO₂ imprinting and calcination, the resulting pattern height is 90 nm. Such a pattern height is too low for most photonic applications, and needs to be increased. Ideally, a height of a few hundred nm would be of greater interest.

In order to investigate the quality and reproducibility of pattern transfer depending on the pattern height, different silicon masters have been prepared with varying etching depth of 245 nm, 400 nm and 874 nm, respectively. The masters were replicated to produce PDMS stamps that were used for TiO₂ imprinting followed by calcination, using the optimized process parameters described above. Figure 4 presents the measured heights of the patterns after TiO₂ imprinting (red circles) and after calcination (green triangles), for each one of the three initial master heights (black squares). The heights were all measured with AFM in the same conditions, and they are also summarized in Table 2. We can observe that the pattern heights of the imprinted TiO₂ are 235 nm, 380 nm and 845 nm, respectively, and are very close to the values measured for the silicon masters. This indicates that the filling of the patterns is almost complete, even for the very deep patterns. After calcination, the pattern height decreases significantly to 90 nm, 150 nm and 340 nm, respectively, which corresponds to a similar vertical shrinkage of about 61%. This result demonstrates that the vertical shrinkage does not depend on the pattern height. As we observed earlier that the lateral shrinkage does not depend on the feature size either, we can deduce that the overall shrinkage is relatively constant, independently from the feature size and height, for the whole range of parameters studied in this work (periods between 400 nm and 2 μm, heights up to 340 nm).

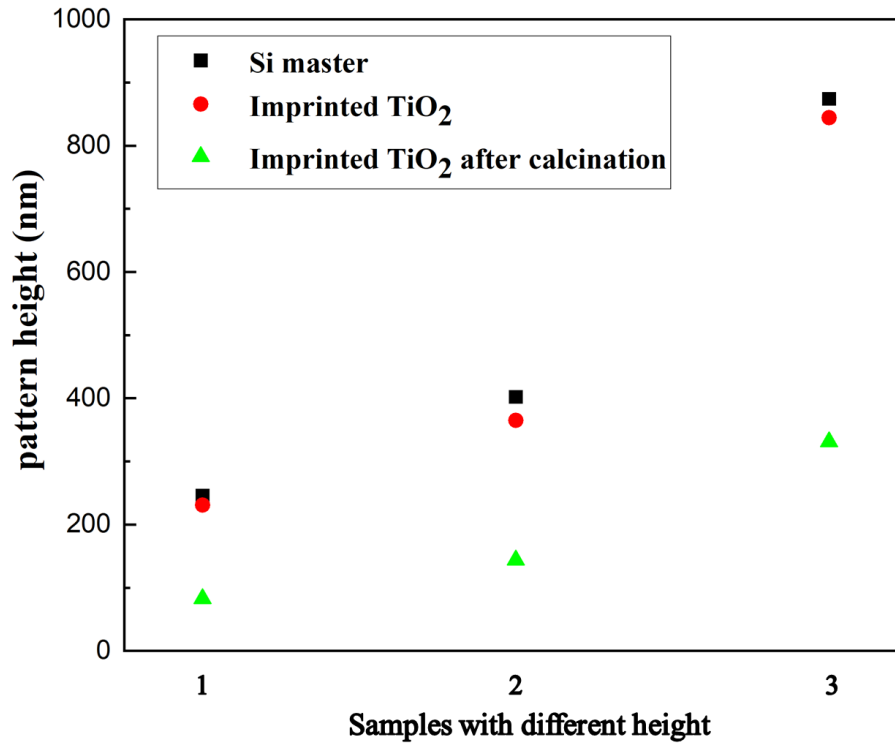


Figure 4. Measured pattern heights after master fabrication (black squares), after TiO₂ imprinting (red circles) and after calcination (green triangles) for 3 masters with different pattern heights.

Table 2. Pattern height of the master and imprinted TiO₂ (before and after calcination), for the 3 masters with different pattern heights.

Samples	S₁	S₂	S₃
Si master	245	400	874
Imprinted TiO₂	235	380	845
Imprinted TiO₂ after calcination	90	150	340
Height shrinkage (before and after calcination)	62%	61%	60%

In order to illustrate the quality of the fabricated high patterns, Figure 5 shows the surface and profile view of crystallized 1D TiO₂ nanostructures with 340 nm height. We can see that the imprinted TiO₂ surface (Figure 5a) is very smooth and homogeneous. The profile of the TiO₂ lines (Figure 5b) is vertical and well defined, hence highlighting the quality of the whole fabrication process. The small deep that can be observed at the top of some of the lines could be the sign of a beginning of collapse of the TiO₂ after filling; it is also present on some of the lower patterns on other samples, also barely visible. This indicates that a finer optimization of the NIL conditions might be required in order to increase the pattern height even further.

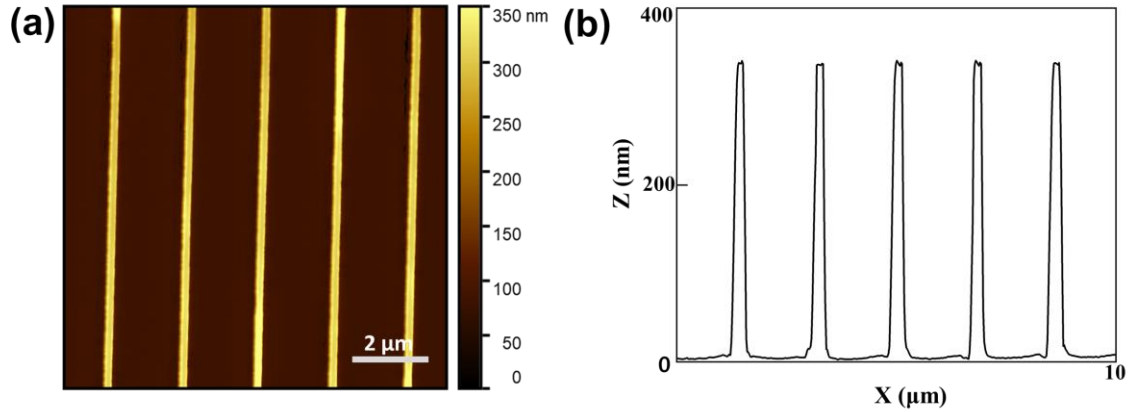


Figure 5. AFM images of imprinted 1D TiO₂ patterns with height of 340 nm: a) surface with top view; b) profile view.

The results described in Figures 4 and 5 and in Table 2 present a dual significance. First, they mean that TiO₂ patterns with height reaching 900 nm (and probably more) can be prepared by soft NIL, which enables to fabricate submicron patterns with a height above 300 nm after calcination. Secondly, the results also mean that pattern heights of any chosen value can be easily prepared without the need to re-optimize any of the process steps; the NIL conditions and shrinkage remain constant, independently on the initial pattern height.

3. CONCLUSIONS

In this work, we have shown the successful preparation of TiO₂ nanostructures using a fabrication process with reduced environmental impact that is based on soft NIL combined with sol-gel. We have shown that the optimized NIL conditions (3 min at 120°C) are independent on the feature size and shape of the patterns. We have also proposed a calcination process with a lower temperature (400°C) than the one commonly used for crystallization, and shown that this temperature is sufficient to obtain a polycrystalline material with a refractive index of 2.1. The influence of the heat treatment on the shrinkage of the imprinted TiO₂ patterns was also investigated. We could show that the shrinkage in the lateral direction (about 54%) is smaller than that in the vertical direction (about 61%), regardless on the size, shape and height of patterns. In addition, we have also explored the possibility of increasing the height of the embossed TiO₂ patterns after calcination, via an increase of the etching depth of the silicon masters. Using a silicon master with 874 nm feature depth, we have successfully demonstrated the fabrication of crystallized TiO₂ patterns with 340 nm height. Such a large pattern height, combined with the wide range of pattern shapes and dimensions that can be fabricated, opens the possibility of a wide diversity of designs for the eco-friendly fabrication of TiO₂ nanostructures with highly-interesting photonic properties.

4. EXPERIMENTAL SECTION

4.1 NIL preparation

Prior to the soft NIL process, the sol gel and PDMS stamps have to be prepared. The PDMS stamps are fabricated by replication of silicon masters. The patterns on the Si masters are produced by electron-beam lithography on a modified FEI Inspect-F SEM working at 30 kV and 30 pA beam current, with a feature resolution of 6 nm. The patterns are arranged in arrays of periodic photonic structures that cover a whole range of parameters of interest for future applications: 1D (lines) and 2D (square lattice of cylindric pillars) features with periods ranging from 400 nm to 2 μm, and filling factors from 0.1 to 0.3. The lithography is performed in a methylmethacrylate (MMA)/polymethyl methacrylate (PMMA) C2 resist double layer to obtain overhanging profiles for subsequent metal deposition and lift-off. After electron-beam writing, the patterns are developed in methyl isobutyl ketone (MIBK): isopropanol (IPA) for 1 min followed by 1 min rinsing in IPA and 1 min in deionized water. After development, 50-80 nm of aluminum are deposited on the sample via a slow thermal evaporation process. The metal deposition is followed by a lift-off process at room temperature in an acetone bath. The purpose of the Al deposition and lift-off process is to form a metallic hard mask on the surface of the silicon samples, which will enable to etch deep patterns into the silicon, with a depth that can reach 1 μm. The subsequent Si etching is performed by inductively-coupled plasma etching in a Cl₂/O₂ mixture at 5 mTorr

pressure and 315 V self-bias. After fabrication, each master could be re-used several times for PDMS replication, without any noticeable damage of the nanopatterns. The masters were cleaned by acetone, ethanol and IPA in ultrasonic bath for 5 min respectively before re-use, and then silanized prior to PDMS molding to prevent the PDMS from adhering to the master. The silanization process is performed overnight in gas phase in a vacuum chamber, using 1H,1H,2H,2H-perfluorooctyltrichlorosilane.

The PDMS stamps are made of two-layered PDMS constituted of a thin top layer of hard PDMS (h-PDMS) and a thicker bottom layer of soft PDMS. The thin h-PDMS top layer is used for reproducing the accurate features of the master and for providing mechanical stability during molding. It is prepared by mixing room-temperature-vulcanized (RTV) silicone and a crosslinker in a 2:1 weight ratio, and deposited onto the silanized Si master by spin-coating before curing at 65 °C overnight. The bottom layer of soft PDMS provides flexible support for the h-PDMS and ensures pressure homogeneity during subsequent nanoimprint¹⁵. It is prepared by mixing RTV silicone and cross-linker in a 9:1 weight ratio. It is added to the back of the h-PDMS by injection molding and heated at 65°C overnight for stabilization. The total thickness of the PDMS stamp is typically between 0.5 mm and 2 mm, and can be adjusted through the soft PDMS manufacturing step.

The TiO₂ sol-gel used for soft NIL is based on alcoholic Benzoylacetone-modified sol¹⁶. The sol-gel is a mixture of two sols with different reactivities. The first sol has a very weak chemical reactivity, and is prepared by reacting tetraisopropylorthotitanate (TIPT from Fluka) with benzoylacetone (BzAc from Aldrich) in ethanol (EtOH from Alfa Aesar). The TIPT/BzAc /EtOH molar ratio is 1/0.91/20.4. The second sol is very stable when stored in a closed bottle, but very reactive once deposited. This sol is prepared by mixing TIPT with deionized water (H₂O), hydrochloric acid (HCl from Roth) and BuOH. The TIPT/H₂O/HCl/BuOH molar composition is 1/0.82/0.13/23.9. To improve the wettability of the spin-coated TiO₂ film, we also add pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆) polymer to the final mixed TiO₂ sol-gel, with molar ratio 1.6×10^{-3} (F127/Ti).

4.2 Soft NIL and calcination

The prepared PDMS stamps are first put under vacuum for 10 minutes in a desiccator. In the meantime, the TiO₂ sol is spin-coated at 3000 rpm for 1 second, which leads to the formation of a homogeneous sol-gel layer with a thickness around 600 nm. As soon as both the pumping and the spin coating are done, the degassed PDMS stamp is placed on the surface of the spin-coated TiO₂ sol-gel. After ensuring that the PDMS surface is in good contact with the TiO₂ sol-gel surface, the assembly is placed on a hot plate at a preset temperature of 120°C for 3 minutes, before being removed from the hot plate for cooling. Finally, the PDMS stamp is peeled off the TiO₂ layer and is cleaned with ethanol before re-use.

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