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# Direct patterning of functional materials using nanoimprint lithography

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## ABSTRACT

Nanoimprint lithography is a large area, high resolution and cost-effective replication technology for micro- and nanostructures. An interesting possibility in the nanoimprint process is the use of materials that remain a functional part of the final component or device. Such an additive approach offers interesting opportunities in terms of novel applications but also cost reduction and could also contribute to sustainability aspects. This paper is aiming at providing a short non-comprehensive overview on the direct patterning of various functional materials by using NIL for optics and life science applications.

**Keywords:** Nanoimprint Lithography, UV-NIL, functional materials, optics, life sciences

## 1. INTRODUCTION

Nanoimprint lithography (NIL) is a micro- and nanostructure replication technology, which offers high resolution on large areas and great process and application flexibility<sup>1-3</sup>. In a typical nanoimprint process in a first step a stamp is fabricated. This is made by preparing a negative copy of a master structure (e.g. ref<sup>4,5</sup>), which itself was made by electron beam lithography<sup>6</sup>, two-photon polymerization 3D printing or other micro and nanofabrication technologies. The stamp is often made either by a casting process (e.g. with PDMS (poly-dimethyl-siloxane)) or in a UV-NIL process (e.g. with OrmoStamp® see e.g. ref<sup>4</sup>). This approach reduces cost of ownership since the actual master structures is not used for a nanoimprint process and therefore is less in danger to get a defect. Additionally, with this approach, in general a higher flexibility is achieved in the master fabrication as well as in stamp fabrication and nanoimprinting. This aspect is especially relevant in the context of functional materials. We focus on UV-based nanoimprinting, where UV-curable materials, which are typically liquid at room-temperature are coated on a substrate and patterned using a UV-transparent stamp. To achieve this the stamp is brought into contact with the coated substrate. The liquid material fills the micro- and nanocavities in the stamp due to a capillary filling process. When this is done, the material is cured by UV-radiation (through the UV-transparent stamp). Finally, the stamp can be removed and reused for the next imprinting step. The UV-curing material can then remain as a functional component in the device to be manufactured. Such a material is a functional material in the sense of this contribution. We call such a process also an additive NIL process. Of course, the nanoimprint material can also be used as an etching mask or in a lift-off process<sup>7</sup>, in a subtractive NIL process.

## 2. OPPORTUNITIES, SUSTAINABILITY, CHALLENGES

The approach briefly described above offers several opportunities as far as applications and process design are concerned. Some examples will be given below. Additionally, it also has aspects in terms of sustainability. Considering sustainability, firstly, the nanoimprint process itself can be performed in a sustainable way. This is relevant for energy consumption and material consumption. Tools for optical lithography like DUV and EUV lithography often consume significantly more energy than nanoimprint tools<sup>8,9</sup>. Considering a growing market for semiconductor applications and the need to shift to fully renewable energy supply, reducing the energy consumption is important. The use of functional materials adds to this aspect, since a reduction of the number of process steps is possible. Furthermore, nanoimprinting can be performed in an additive way using functional materials, meaning that the patterned material does not serve as an etch mask, but remains an integral component of the final device. If such a process is possible for a certain application, it can reduce the number

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of processing steps and related energy and material consumption. Also cost and time savings could potentially be achieved with such processes. Additionally, inkjet printing can be used as a material deposition technology for NIL<sup>10, 11</sup> (see also figure 2), which produces less waste than typical spin coating processes and even provides additional opportunities. Secondly, the versatility of the nanoimprint process can contribute to many applications with sustainability aspects. In this context, often the structures are bio-inspired<sup>3</sup>. Friction reduction is an important topic. Nanoimprint patterning was used to replicate the reduce the friction on ceramic surfaces (see figure 2)<sup>12, 6</sup>. For airplanes sharkskin-inspired structures are investigated<sup>13</sup> and for ships surfaces are investigated that reduce the adhesion of marine plants and animals, which, when attached to a ship hull, increase the fuel consumption of the ship significantly<sup>14</sup>. In photovoltaic applications anti-reflective moth-eye structures<sup>15</sup> and self-cleaning structures inspired by the surface of rose petals<sup>16</sup>, both made by nanoimprinting, can be of interest. This can also be relevant for lenses<sup>17</sup>. Other examples where nanoimprinting plays a role can be found in the life sciences and lighting field. In the life sciences the use of in vitro tests to replace in vivo test with lab animals often is desired, both to reduce costs and animal suffering. Here, the capability of nanoimprinting to directly pattern biocompatible materials with complex structures can be of use (e.g.<sup>18, 19</sup>). The possibility to pattern micro-optical elements for indoor and outdoor lighting using nanoimprinting can help to reduce light pollution, which in turn benefits nocturnal animals and humans alike.

Not only but also and especially for the use of functional materials in additive nanoimprint processes the material properties are critical. The materials must fulfil the requirements for the nanoimprint process and has to fulfil the requirements of the final application, in terms of pattern fidelity, mechanical and optical properties, temperature and humidity requirements to biocompatibility, autofluorescence aspects, to name a few. In the following, a few examples will be given.

### 3. APPLICATION EXAMPLES

#### 3.1 Optics

The refractive index plays an essential role in the functionality and efficiency of devices in the field of optics. It determines the refraction, reflection, or in case of waveguides, the quality of light guiding. NIL offers the possibility of a fast-direct patterning of materials with different refractive indices. UV-curable nanoimprint materials come in a wide range of refractive indices starting around 1,3 (e.g. 1,34 for MD700<sup>20</sup> and going up to 1.9 (e.g. IOC-133<sup>21</sup>). In addition, some of these materials are now also available as inkjet versions (e.g. IPO-912). Table 1 below gives a few examples.

Table 1. Examples for nanoimprint materials with different refractive indices

| Material                      | Refractive Index (@ 589nm) | Curing mechanism |
|-------------------------------|----------------------------|------------------|
| IOC-133 (Inkron)              | 1.8-1.9x <sup>21</sup>     | UV curing        |
| OrmoClear (micro resist GmbH) | 1,56 <sup>22</sup>         | UV curing        |
| MD700 (solvay solexis)        | 1,34 <sup>20</sup>         | UV curing        |
| IOC-560C (Inkron)             | 1,1x <sup>21</sup>         | thermal          |

In our first example a multilayer multimaterial optical device has been fabricated. Figure 1 shows the result of preparing two nanoimprinted layers with different refractive indices on top of each other. The layer sequence is sketched in the inset. First a low refractive index material was patterned with a hexagonal pillar array, followed by a high refractive index material of the same pattern. The layer stack was protected with an unpatterned layer of the low refractive index material. The substrate that was used was glass. Although this special layer sequence only serves demonstrational purposes it shows the potential of preparing several nanoimprinted layers on top of each other. For nanoimprinting of optical components alignment in the range of 100nm has been shown<sup>23-25</sup>. For the sample in Figure 1 the high index material was just droplet dispensed, with the hexagon-shape developing due to the underlying micropattern, which consisted of a hexagonal array of pillars. Figure 2 shows an example, where the high refractive index material was inkjet printed to obtain the pattern of the butterfly in this case.

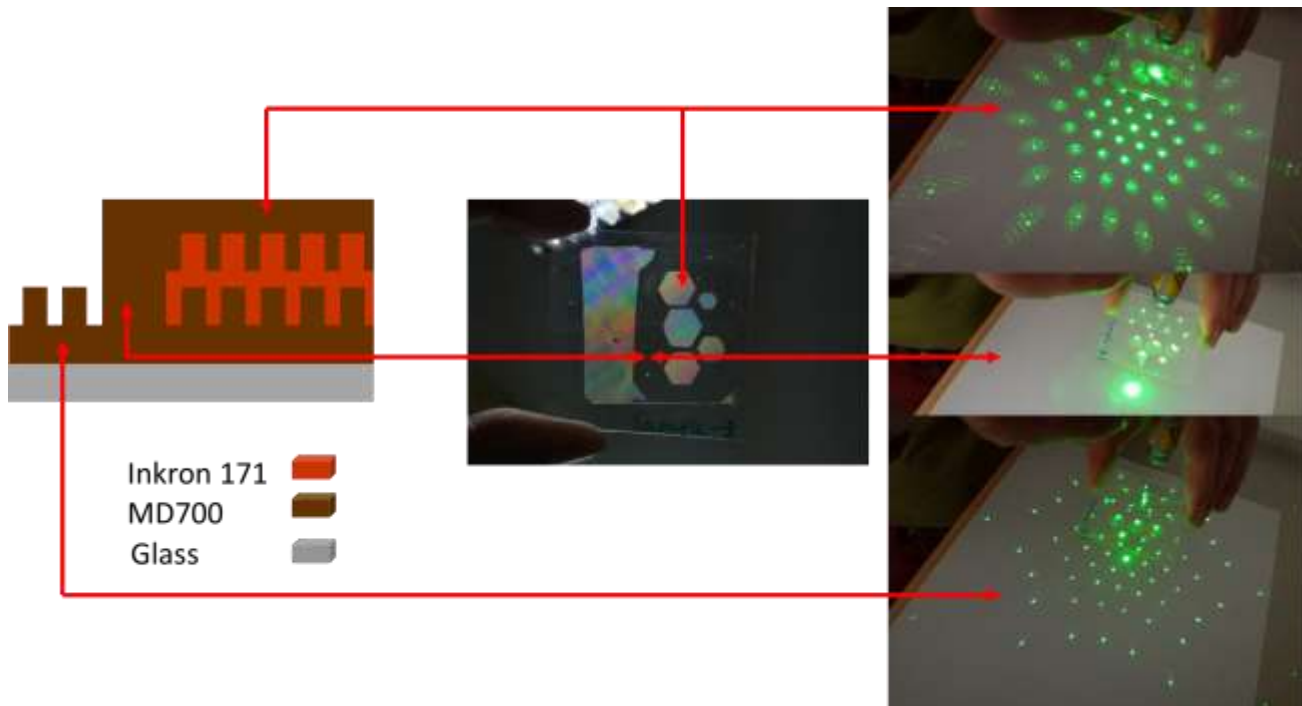


Figure 1 example for a multilayer multimaterial nanoimprinted pattern. On a glass substrate a low refractive index layer was nanoimprinted (MD700), followed by a high refractive index layer (Inkron 171). The layer stack was covered by a low refractive index protection layer, which was unpatterned. In the left the schematic layer stack is show, in the center a photograph of the sample, to the right the diffraction patterns resulting in the different regions of the sample. From top to bottom: all three layers, only unpatterned low refractive index layer, only the first patterned layer.



Figure 2: sample according to the layer stack in figure 1, but with inkjet deposited high refractive index material.

Another example in the field of optics is the fabrication of biomimetic anti-reflection moth-eye structure coatings as shown in Figure 3. Biomimetic anti-reflection moth-eye<sup>26,27</sup> structures are known to provide a gradual change in refractive index coming from the refractive index of air changing to the refractive index of the moth-eye (imprint) material. This leads to a significantly reduced reflection caused by the moth-eye structures. In our example, the nanoimprinting was performed on a curved lens-like surface. The ability to pattern the surfaces of non-flat objects is an additional interesting feature of nanoimprinting<sup>28</sup>. Figure 3a shows a photograph of a watchglass patterned on both sides (lower part of the substrate) and an unpatterned area (top part of the substrate). The detailed process is described in Haslinger et al.<sup>17</sup>. Figure 3b shows an atomic force microscope image of the moth-eye pattern. Figure 3c shows transmission measurements through a sample

patterned on both sides with two different materials. As can be seen, different materials show different performances, but both result in a significant increase in transmission. The reference transmission without coating and nanostructures is around 91.8%. The material with the better performance has a refractive index close to the one of the substrates. Depending on the imprint material, transmission values of up to 98.2% for a both side-imprinted lens could be achieved.

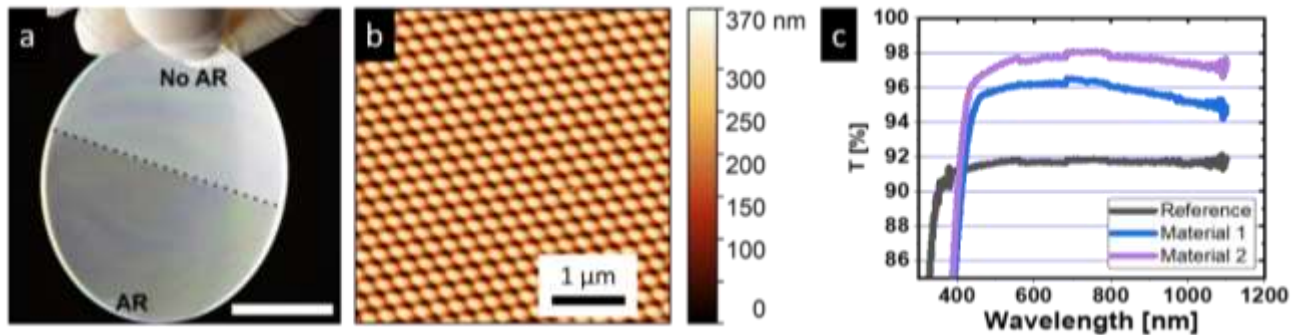


Figure 3 Photograph, AFM image and transmission measurement of an imprinted lens. a) The photograph shows a 70 mm diameter lens with one half-side imprinted with AR moth-eyes on front and back surface. Scale bar is 1.5cm. b) AFM image of imprinted moth-eyes. c) Transmission measurements of two samples with AR moth-eye structures imprinted with two different coatings.<sup>17</sup>

As demonstrated by the moth-eye structure, the apparent refractive index can not only be a function of the material, but also of the nanostructure. Another example found in nature are the structural colors found in many species, e.g., in butterflies (e.g. ref<sup>3</sup> and references therein). Figure 4 below gives another example where nanoimprinting into a functional material was used to realize a biomimetic structure inspired by the Morpho butterfly, which has metallic blue wings, resulting from a complex arrangement of nanostructure, providing a Bragg type of a reflector, which reflects the blue color into all directions<sup>29,30</sup>. The details on the imprinting process and master fabrication can be found in references<sup>5,31</sup>. This is an example where the requirements from the nanoimprint process side were especially high, since the removal of the stamp on the nanoimprint process is especially difficult for these undercut structures. A material was formulated to exhibit the right mechanical properties to allow this. Figure 4 shows from left to right first the master structure, which has a T-shaped cross section. The center image in figure 4 shows the stamp, which was fabricated from the master structure, without destroying it, and finally on the right the imprint is shown, exhibiting the same polarity as the master structure. It can be noted that also the slanted angle of the T cross bar has been faithfully replicated in the nanoimprinting process.

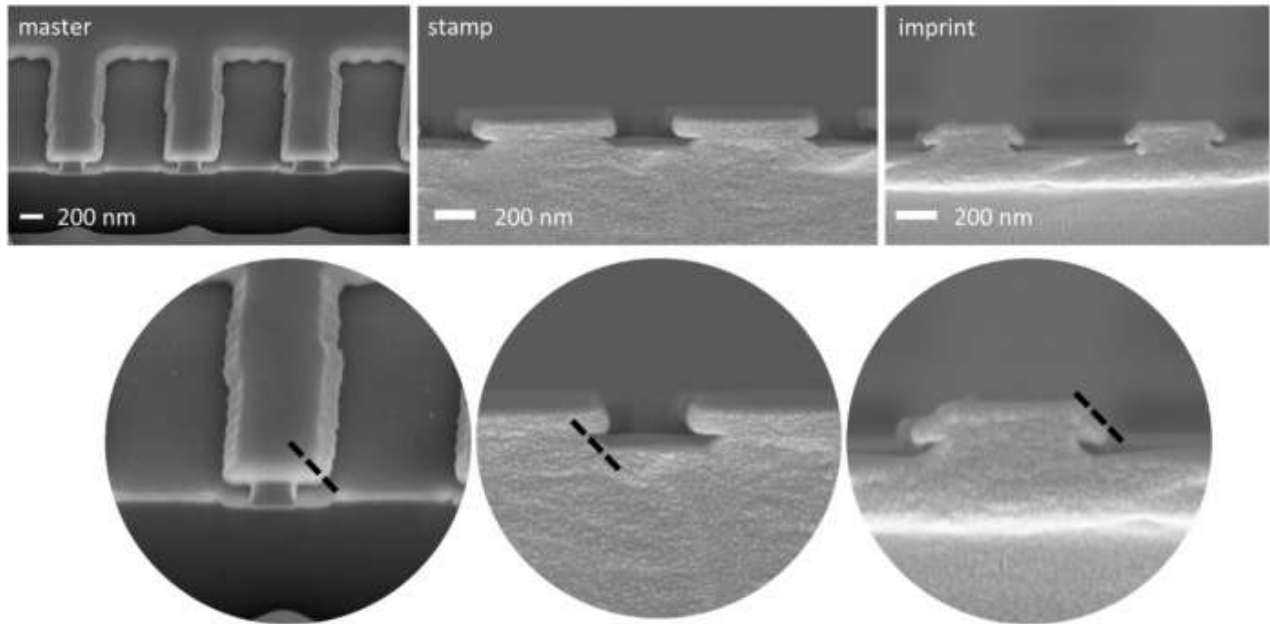


Figure 4 SEM cross-sectional images of the sample sequence from the master structure<sup>31</sup> (left) over the stamp in NILCure® JR5 (center) and the imprinted structures in NILCure® JR5 (right). The second row shows close-ups from the images in the upper row<sup>5</sup>

A final example relating to optics is a more traditional structure relating to microlens arrays. Figure 5a shows a master structure fabricated using two photon polymerization 3D printing. This master structure was fabricated at the Medical University of Vienna using a two photon polymerisation 3D printer (upnano, Vienna). The size of the patterned area is approx. 4x6 mm<sup>2</sup>. From this master a PDMS (Sylgard 184) copy was made and used in a step and repeat nanoimprint process in a self-built step and repeat nanoimprint tool (figure 5b) resulting in a sample as shown in figure 5c. It consists of 96 imprints and can either be a final product or can be used in a further step to fabricate a stamp for full area printing of the 96 optical elements in a single nanoimprint step, e.g. in a roll-to-plate nanoimprint process. For such optical elements there are often demanding requirements if they are to be used e.g. in automotive applications, which go much beyond just only the refractive index. The imprints in this case were fabricated using OrmoClear® (micro resist technology).

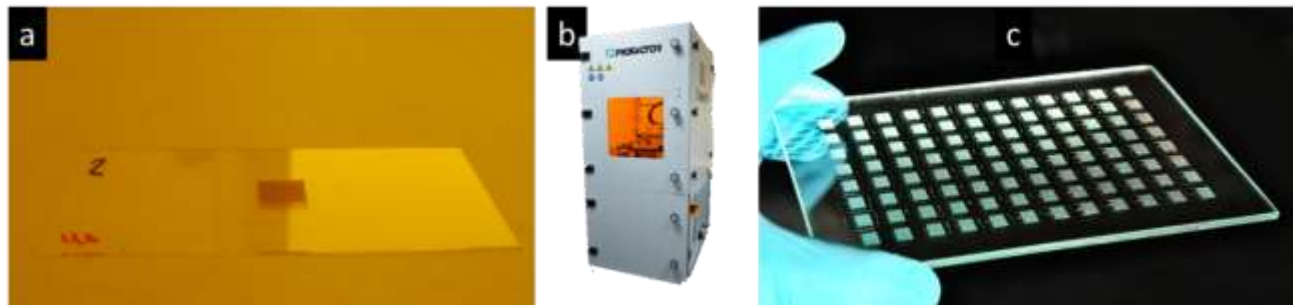


Figure 5 a) Photograph of the master structure on a 75x25mm<sup>2</sup> glass slide. b) self-built step and repeat nanoimprint tool for dedicated to microstructure replication. c) final imprinted structure of 12x8 imprints.

### 3.2 Life Sciences

For life science applications biocompatibility of the material is often one of the main requirements. OrmoComp® is one of the materials that is often used. The example given in figure 6 uses OrmoComp® as imprint material. Here, we were aiming at providing a substrate for the growth of cardiomyocyte fibers. Details on the background, the imprinting and the first cell growth results can be found elsewhere<sup>32</sup>. Here it should be noted that several criteria had to be met by the

imprinting material: i) biocompatibility, i.e. the cells have to survive, if placed on such a surface, ii) good imprinting properties (also for roll-to-plate nanoimprint processes) and iii) excellent optical properties for observation of the cells in optical inverted microscopes. Nanoimprinting provided a fast and cost-efficient way to fabricate the cell growth substrates on various substrates in different configurations<sup>32</sup>.

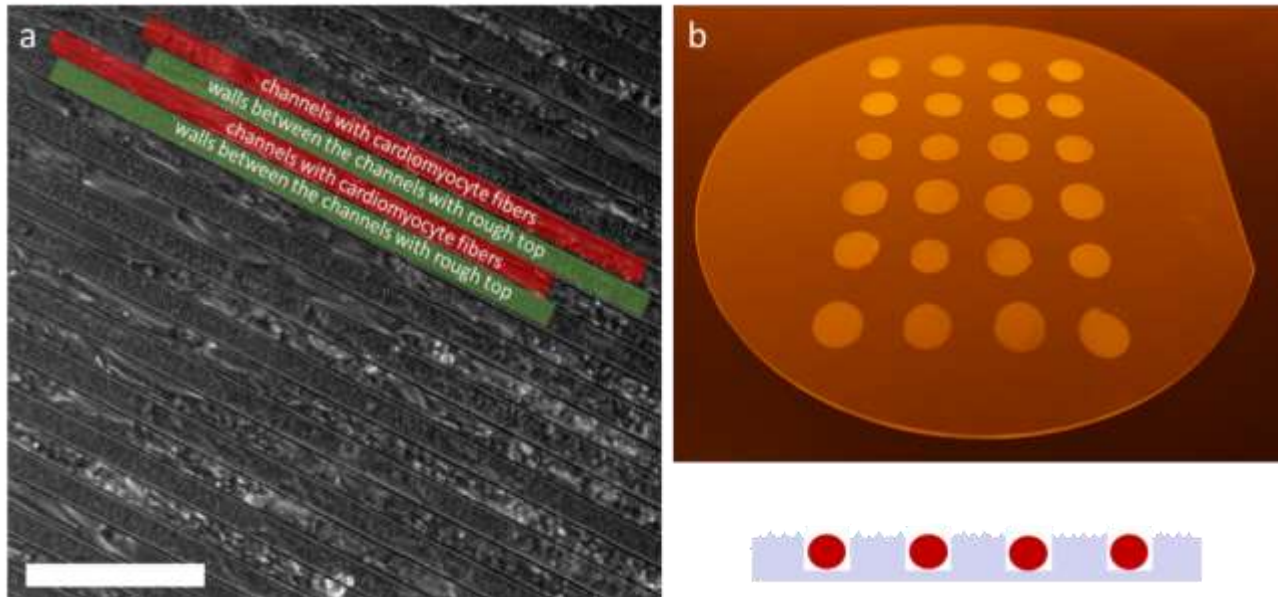


Figure 6 Cardiomyocytes forming fibers inside nanoimprinted channels: The cells tend to grow inside the channels between the walls. a: optical micrograph with some of the wall and channels areas highlighted. b: 24 imprints made on a 150 mm glass wafer to act as an intermediate large area master for printing plate fabrication for roll-to-plate nanoimprinting. The inset to the lower right sketches the arrangement of the cardiomyocyte fibers located inside the trenches.<sup>32</sup>

OrmoComp® was also used to nanoimprint the nanoneedles shown in figure 7. Here<sup>33</sup> it was the aim to mechanically improve the stability and electrically functionalize the nanoneedles by coating them after imprinting with first a layer of Au followed by SiN to provide electrical insulation. Figure 7a shows the imprinted needle. The master in this case was a nanoneedle fabricated by FEBID as detailed in reference<sup>33</sup>. Figure 7b shows the final functionalized needle. The top of the needle was opened to expose the underlying Au layer. In figure 7c the schematic cross section of the functionalized needle is shown. For this application the mechanical stability of the cured material was essential in addition to the imprint properties and the biocompatibility (there are potentially uncovered areas of the imprint material in contact with the cells).

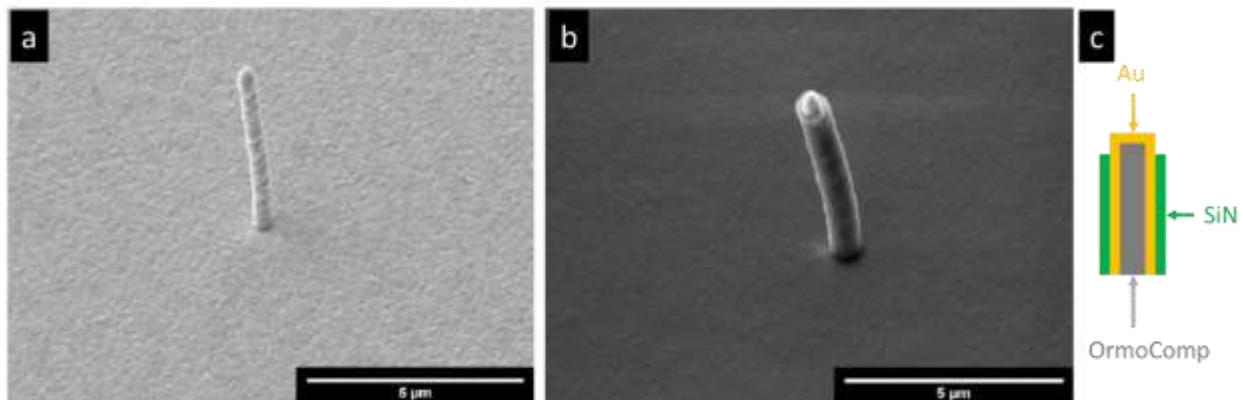


Figure 7 a: SEM image of a nanoimprinted nanoneedle. The imprint material is OrmoComp®. b: imprinted nanoneedle, coated with Au and SiN, after tip opening. c: schematic cross section of the functionalized needle in b.

Microneedles can be interesting for long term electrodes<sup>34</sup> (ecg eeg), trans dermal drug delivery or vaccination purposes<sup>35</sup>. Using nanoimprinting, it is also possible to replicate such structures. Figure 8 shows such examples. On the left in figure 8a a small array of microneedles is shown. The master was 3D printed and used for stamp fabrication. The imprint material was OrmoComp® in this case. The high replication fidelity of the nanoimprint process makes the fabrication of sharp microneedles feasible, which is beneficial in the application.<sup>35,36</sup>

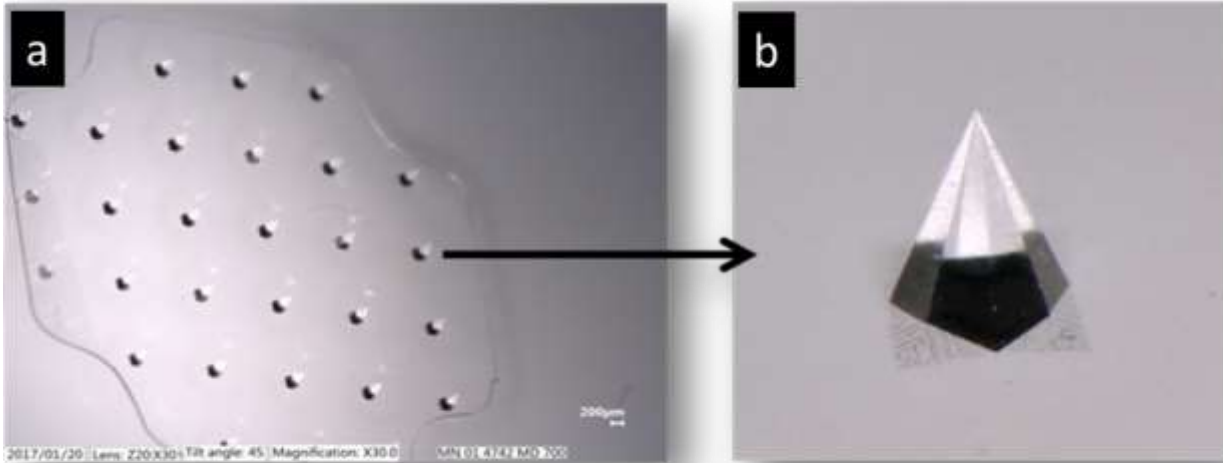


Figure 8 a: nanoimprinted microneedle array. The material is OrmoComp®. b: close-up of one of the microneedles of the array shown in a.

### 3.3 Other examples from literatures

Other applications where nanoimprinting was used to structure functional materials include organic photovoltaics<sup>37</sup>, a dual damascene process<sup>38</sup>, riblet structures for wind turbines<sup>13</sup>, anti-fouling structures for ships<sup>14</sup>, microfluidics<sup>39</sup>, waveguides<sup>40</sup>, and many more.

## 4. CONCLUSIONS AND OUTLOOK

The fact that nanoimprinting can directly pattern a wide range of functional materials enables a broad range of applications and makes nanoimprinting a very versatile micro- and nanofabrication technology. We showed examples from the fields of optics and life sciences. Using the right materials, nanoimprinting has the potential to be a sustainable, cost-efficient micro- and nanopatterning technology for a large number of applications. We therefore hope that many novel materials will become available in the future to support additive nanoimprint processes.

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