Video Article

Nanomoulding of Functional Materials, a Versatile Complementary Pattern Replication Method to Nanoimprinting

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URL: <http://www.jove.com/video/50177>

DOI: [doi:10.3791/50177](https://doi.org/10.3791/50177)

Keywords: Materials Science, Issue 71, Nanotechnology, Mechanical Engineering, Electrical Engineering, Computer Sciences, Physics, dielectrics (electronic application), light emitting diodes (LED), lithography (circuit fabrication), nanodevices (electronic), optoelectronics (applications), photoelectric devices, semiconductor devices, solar cells (electrical design), Surface patterning, nanoimprinting, nanomoulding, transfer moulding, functional materials, transparent conductive oxides, microengineering, photovoltaics

Date Published: 1/23/2013

Citation: Battaglia, C., Söderström, K., Escarré, J., Haug, F.J., Despeisse, M., Ballif, C. Nanomoulding of Functional Materials, a Versatile Complementary Pattern Replication Method to Nanoimprinting. *J. Vis. Exp.* (71), e50177, doi:10.3791/50177 (2013).

Abstract

We describe a nanomoulding technique which allows low-cost nanoscale patterning of functional materials, materials stacks and full devices. Nanomoulding combined with layer transfer enables the replication of arbitrary surface patterns from a master structure onto the functional material. Nanomoulding can be performed on any nanoimprinting setup and can be applied to a wide range of materials and deposition processes. In particular we demonstrate the fabrication of patterned transparent zinc oxide electrodes for light trapping applications in solar cells.

Video Link

The video component of this article can be found at <http://www.jove.com/video/50177/>

Introduction

Nanopatterning has gained tremendous importance in many fields of nanotechnology and applied sciences. Pattern generation is the first step and may be accomplished by top-down approaches such as electron-beam lithography or bottom-up approaches based on self-assembly methods such as nanosphere lithography or block copolymer lithography¹. As important as pattern generation is pattern replication. Besides photolithography, nanoimprinting (**Figure 1**) has emerged as a promising alternative in particular suitable for high-throughput large-area nanoscale patterning at low cost²⁻⁴. While photolithography requires a patterned mask, nanoimprinting relies on a prefabricated master structure. Pattern transfer from the master is commonly performed into a thermoplastic or a UV- or thermally curable polymer. However there are many cases, where it is desirable to transfer the pattern directly onto a functional material.

Here we describe a replication method based on nanomoulding and layer transfer (**Figure 2**) which we recently introduced in Ref.⁵ to transfer nanoscale patterns onto functional zinc oxide electrodes. Our nanomoulding method can be easily implemented if a nanoimprinting setup is available. Nanomoulding offers the potential to be generalized to many other functional materials, materials stacks and even complete devices, provided that the mould material is chosen such that it is compatible with the material deposition process(es). As an example we present here nanomoulding of transparent conductive zinc oxide (ZnO) electrodes deposited by chemical vapor deposition (CVD) which find their application to enhance light trapping in solar cells⁵.

Protocol

1. Mould Fabrication

We use our home-built nanoimprinting setup for the fabrication of the negative mould following Ref.⁶, but any alternative nanoimprinting setup will work fine. Alternatively a functionalized polydimethylsiloxane (PDMS) mould might also work.

1. Fabricate or buy a suitable master carrying the nanoscale pattern to be transferred. In principle, any master suitable for nanoimprinting will do the job. We use a textured ZnO layer on a glass sheet (Schott, AF32 eco, 41 mm x 41 mm x 0.5 mm) deposited as described in 3.1 as a master structure to illustrate the method.
2. Apply an anti-adhesion layer on the master structure as described in 2.
3. Clean a polyethylene naphthalate (PEN) sheet (Goodfellow, 82 mm x 41 mm x 0.125 mm) in an ultrasonic acetone bath for 2 min followed by an ultrasonic isopropanol bath for 2 more min. Rinse once more with isopropanol and blow dry with nitrogen.

4. Deposit a sputtered Cr adhesion layer (5-10 nm) on the PEN sheet.
5. Spin-coat the UV-curable resin (Microresist,Ormocer, 1-2 ml) on the PEN sheet at 5,000 rpm to get a uniform coverage.
6. Perform a prebake for 5 min on a hot plate at 80 °C to evaporate the solvent, improve film uniformity and adhesion to the PEN sheet.
7. Use your nanoimprinting setup to stamp the master pattern into the UV-curable resin. Although not mandatory, we perform stamping under vacuum to prevent bubble inclusions by applying a homogenous pressure of 1 bar onto a flexible silicone membrane. In our setup, the silicone membrane separates the vacuum chamber into two sub-compartments. Pressure is generated by venting the upper compartment, while the lower compartment remains under vacuum. Venting pushes the flexible membrane towards the bottom initiating the stamping.
8. Expose the resin to UV light to provoke the cross-linking reaction of the resin. We apply a moderate light intensity of 1.4 mW/cm² at a wavelength of 365 nm provided by several LEDs. Exposure time through the PEN sheet is typically 15-20 min.
9. Carefully demould by manually peeling the mould off the master structure.
10. As the resin may undergo slight shrinkage during the deposition of the functional material, which may lead to spontaneous peeling, we perform a mild thermal post bake at 150 °C during 6-8 hr in an oven with ambient atmosphere before further processing.

2. Anti-adhesion Layer

For successful demoulding, the anti-adhesion layer must be adapted to the materials and the pattern roughness. Generally rough patterns require low sticking coefficients. Low sticking coefficients on smooth patterns may lead to peeling of the functional material from the mould. High sticking coefficients on rough patterns may result in peeling of the resin from the PEN sheet during mould fabrication as the adherence of the resin to the master is stronger.

1. Coat the mould (or master) with a sputtered chromium layer (5-10 nm) to promote the adhesion of the anti-adhesion agent. For smooth patterns we drop this step. In some cases the chromium layer may prevent the anti-adhesion agent to etch the master structure.
2. Apply a small drop of anti-adhesion agent (Sigma-Aldrich, (1H, 1H, 2H, 2H-Perfluorooctyl)-trichlorosilane) on a glass slide. Put the glass slide together with the mould into a vacuum chamber and pump down. The anti-adhesion agent will evaporate and deposit as a molecular monolayer on the mould.
3. Anchor the anti-adhesion agent via annealing during 1-2 hr at 80 °C.

3. Material Deposition

We demonstrate here three deposition techniques suitable for material deposition to illustrate the versatility of nanomoulding. Other deposition techniques might also be applied. The third example describes the fabrication of a complete thin-film silicon solar cell.

1. Chemical vapor deposition (CVD) of zinc oxide: Put the mould onto the heating plate of the CVD reactor heated to 180 °C. Use a metal frame to avoid bending of the PEN mould during ZnO deposition. Close the reactor, pump down and allow thermalization. Admit the precursor gases (H₂O and (C₂H₅)₂Zn). In addition we dose small amounts of B₂H₆ for doping. The ZnO layer thickness is proportional to the deposition time. We use ZnO layer thicknesses of typically 1-5 µm. Details on typical depositions parameters may be found in Ref. ⁷
2. Physical vapor deposition (PVD)/sputtering of silver: Put the mould into the PVD system. Close the system and pump down. Admit argon process gas. Turn on the DC generator. The Ag layer thickness is again proportional to deposition time. We use Ag layer thicknesses of typically 1 µm. Typical deposition parameters are an argon pressure of 5.5x10⁻³ mbar and a setup specific DC power of 250 W yielding a deposition rate of approximately 45 nm/sec.
3. Plasma-enhanced chemical vapor deposition (PE-CVD): Deposit ZnO as in 3.1). Put the mold into the PE-CVD reactor heated to 200 °C. Close the reactor, pump down and allow thermalization. Admit the precursor gases (SiH₄ and H₂). In addition we dose small amounts of B(CH₃)₃ and PH₃ to achieve p- and n-type doping respectively. To increase the open-circuit voltage of the solar cells, we also use small amounts of CH₄ and CO₂ for the doped layers. After deposition of the p-i-n amorphous silicon solar cell stack, we deposit a ZnO backcontact as described in 3.1.
4. Avoid excessive bending of the mould, as bending might cause peeling of the deposited layer.

4. Layer Transfer

We use glass slides (Schott AF32 eco, 41 mm x 41 mm x 0.5 mm) as final substrate. But other substrates, including metal foils or polymer sheets, could be used alternatively.

1. Clean glass slides with acetone and isopropanol and blow dry with nitrogen.
2. Spin-coat UV-curable resin (Microresist,Ormocer, 1-2 ml) on the glass slide at 5,000 rpm.
3. Use your nanoimprinting setup to anchor the mould carrying the deposited layers onto the final substrate. As for stamping, we perform anchoring under vacuum by applying a homogenous pressure of 1 bar.
4. Expose the resin to UV light to provoke the cross-linking reaction. We apply a moderate intensity of 1.4 mW/cm² at a wavelength of 365 nm provided by several LEDs. Exposure time through the glass slide is only 1-3 min due to the higher UV transmission of glass compared to PEN.
5. Demould by manually peeling the mould off the glass slide.

5. Sample Characterization

1. Use your favorite morphological, electrical or optical technique to characterize the nanomoulded samples. Here we characterize our nanomoulded samples using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Representative Results

Figure 3 summarizes some illustrative examples of nanomoulded structures. A ZnO master structure grown by CVD on glass is shown in (a). The corresponding nanomoulded ZnO replica is shown in (d). Comparison of the local height (g) and angle (j) histograms extracted from AFM images reveal the high fidelity of the nanomoulding process. Analogous results are shown for a one-dimensional grating fabricated by interference lithography (b,e,h,k) and anodically textured aluminum (c,f,i,l).

Figure 1. Standard nanoimprinting process consisting of negative stamp fabrication (a-d) and the nanoimprinting process (e-h).

Figure 2. Nanomoulding process consisting of negative mould fabrication (a-d), deposition of the functional material (e), anchoring to the final substrate (f-g). Note that the nanomoulding process conceptually resembles the nanoimprinting process in **Figure 1** except for the additional material deposition step (e).

Figure 3. Representative results obtained by nanomoulding: SEM images with AFM images in the inset of three master test structures for nanomoulding: ZnO grown by CVD (a), grating fabricated by interference lithography (b), dimple array obtained by anodic oxidation of aluminum (c). The corresponding nanomoulded ZnO replicas are shown in (d-f). Fidelity analysis comparing the local height (g-i) and angle (j-l) histograms of master and replica structures (black continuous lines represent the masters, dashed red lines the replicas). The scale bar in **Figure 3a** is also valid for **Figure 3b-f** including all AFM insets.

Discussion

Nanomoulding allows the transfer of nanopatterns on arbitrary functional materials. Comparison of the individual processing steps in **Figure 1** and **2** reveals the close relationship between nanomoulding and nanoimprinting. The major difference between nanomoulding and nanoimprinting is the additional material deposition step in **Figure 2e**. The remaining process flow is identical. Nanomoulding can therefore be performed on any available nanoimprinting setup.

Provided that a compatible mould material and anti-adhesion agent is selected, material deposition can be carried out using various methods such as the family of chemical and physical vapor deposition techniques, thermal evaporation, but also solution-based deposition approaches. Correspondingly wide is the range of materials that can be nanomoulded. While nanoimprinting is performed into a deformable polymer, nanomoulding can also be applied to hard brittle materials such as ZnO. In addition, while common nanoimprinting resins are insulating, conducting materials can be patterned.

For deposition techniques reaching elevated temperatures, the PEN sheet used as mould support can be replaced by a high performance polyimide sheet (such as DuPont's Kapton PV9202 which supports temperatures up to 500 °C). High temperature nanoimprinting resins have also been developed withstanding temperatures up to 600 °C¹².

A major advantage of our nanomoulding technique is that the material can be deposited onto the mould as a solid film. Compared to sol-gel based imprinting or moulding^{8,9} techniques, where the precursors to a functional material are diluted in a solvent, our nanomoulding approach avoids typical problems associated with solvent evaporation, curing and calcination such as shrinkage and the formation of pores, bubbles and cracks.

After material deposition, the flexible mould must be handled carefully to prevent crack formation or local peeling of the material. The PEN sheet thickness may be adjusted to avoid accidental bending of the mould beyond the critical radius of curvature for crack formation. However, a certain mould flexibility is required for the demoulding process.

ZnO deposited by CVD in this study leads to a high fidelity replication of the master pattern. **Figure 3a** presents a SEM image of an as-grown ZnO master texture. The corresponding nanomoulded replica is shown in **Figure 3d**. Height and angle histograms extracted from the AFM images for the master and replica ZnO structure shown in **Figure 3g** and **j** respectively almost coincide and confirm the high fidelity. The angle histogram, which is much more sensitive to subtle morphological changes than the height histogram, exhibits a slight shift towards lower angles for the replica. This trend is also observed for the other two test structures and represents a slight smoothing of the features. However, even very fine details such as fine genuine crystal dislocation lines along the facets of the ZnO pyramids are reproduced with high accuracy and give a rough idea of the resolution capability of our nanomoulding technique. Fine modulations along the rims of the line grating in **Figure 3b** are also visible in the replica **Figure 3e**. While the dominant morphological features are nicely reproduced for the dimple pattern, only the onset of the sharp tips occurring at domain boundaries in **Figure 3c** are replicated in **Figure 3f**. Pattern fidelity and resolution both depend on the deposited

material. Preliminary tests with nanomoulded silver films, deposited by sputtering, reproduced the dominant morphological features, but lead to a much lower fidelity and resolution.

The achievable aspect ratio depends on the deposition technique. CVD of ZnO allows easily for aspect ratios up to unity. For aspect ratios above unity, a depletion of precursor gases in the valleys of the structure will lead to a faster growth rate on top resulting eventually in shadowing and possibly the inclusion of cavities in the structure. These cavities risk compromising the mechanical integrity of the film and potentially lead to breaking of the film during demoulding. These problems could be avoided using water-soluble moulds as recently in Ref. 10 in the context of transfer moulding.

As mentioned in the introduction, nanomoulding can also be used to pattern composite layer stacks and full devices. In Ref. 11 we combined the deposition of ZnO by CVD with the deposition of a full thin-film silicon solar cell by PE-CVD and transferred the complete solar cell on its final substrate.

Disclosures

No conflicts of interest declared.

Acknowledgements

The authors thank M. Leboeuf for assistance with the AFM, W. Lee for the anodically textured aluminum master and the Swiss Federal Energy Office and the Swiss National Science Foundation for funding. A part of this work was carried out in the framework of the FP7 project "Fast Track" funded by the EC under grant agreement no 283501.

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