Flexible Replication Technique for High-Aspect-Ratio Nanostructures

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A flexible, nondestructive, and cost-effective replication technique for nanostructures is presented. The advantages of the process are: 1) it allows for tailoring structural parameters of the replica (e.g., line width) nearly independent of the structural geometry of the master; 2) it allows for replication of high-aspect-ratio structures also in polymer materials from solution (especially noncurable polymers) such as polystyrene and polymethylmethacrylate; 3) it includes an easy separation process, thus preserving the master for repeated use. Linear grating replicas with line widths ranging from 88 to 300 nm are obtained using a single nanostructured master. Nanofibers and complex nanopatterned replicas are achievable. The presented technique and its flexibility show that atomic layer deposition is a unique tool for the preparation of high-efficiency polarizer diffractive optics, photonics, electronics, and catalysts.

1. Introduction

The demand for high-aspect-ratio nanopatterns is rapidly increasing, as nanostructures often show highly interesting properties, mostly in strong contrast to the corresponding bulk materials.[1–11] However, the fabrication of large-area ordered nanostructured materials is often difficult, time-consuming, and expensive. Replication techniques present a relatively inexpensive way towards mass production.[12–19] However, replication of high-aspect-ratio nanostructures is still challenging.[12,13] The master template is often rapidly altered or even destroyed during the replication process. Additionally, each target replica requires its own master depending on the desired characteristics of the final product. Individual designs require trial and test steps to optimize many parameters of the production process involving several techniques such as lithography and various etching technologies. Although highly developed, interference lithography or e-beam lithography and etching processes still pose limitations concerning the achievable nanostructure sizes, aspect ratios, and nanostructure profiles.[6,7] To name other encountered difficulties, the choice of the materials used for the replica (and the master) is highly restricted by their physical and chemical properties. These properties additionally restrict the achievable parameters of the nanostructures.

Atomic layer deposition (ALD) is a rapidly evolving coating technology and several template-assisted nanostructuring applications of ALD have recently been reported.[20–35] In those approaches, the negative replicas consist of metal oxides deposited by ALD whereby the templates were destroyed after the ALD process. Various template materials were used in these studies such as polymers,[20–23] biomaterials,[24–31] proteins,[24] egg shell membranes,[25] fly eyes,[26] butterfly wings,[27,28] or porous anodic alumina membranes.[32–35] Metal/oxide/cellulose composites[30,31] with photocatalytic properties have been reported with the template embedded in the end product. Although for some applications it is not essential to produce highly-ordered nanostructures and some of the above mentioned templates are low-cost materials, a

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nondestructive replication technology taking advantage of the ALD capability to atomically control the thickness would be of great interest and has been explored in this study.

Specifically diffractive optical elements such as polarizer gratings would highly benefit from a cost-effective replication of high-aspect-ratio nanostructures. High-efficiency and high-polarization-extinction-ratio (PER) polarizer optics are difficult to produce because tight production tolerances must be met. A PER element is essentially a binary grating with a high lateral periodicity and a very large aspect ratio. To get high polarization efficiency (extinction coefficient), the structural parameters (especially line width) have to guarantee tolerances in the nanometer scale. These tolerances will be discussed based on rigorous coupled wave analysis (RCWA) calculations. Furthermore, there is a need for high-volume optics showing "moth eye structures" made of soluble polymers such as polymethylmethacrylate (PMMA) or polystyrene (PS).

In this paper we present an attractive replication technique assisted by ALD. This procedure can be characterized as an extremely gentle replication strategy. The master is coated by a conformal ALD film that serves as a sacrificial layer. The thickness of this layer can be easily tuned with the number of applied ALD cycles in subnanometer precision.[36–38] A polymer solution is applied onto this individual mould, and the sacrificial layer is selectively removed in acidic or basic solutions with the release of the polymer replica. Since the lateral size of the nanostructure of the replicas can be easily diversified by the ALD film thickness, we refer to this technique as flexible replication (FlexRep). Although motivated by optical applications of nanostructured materials,[39–42] this replication process may find relevance in the development of nanofluidics,[43] biosensors,[44] antimicrobial,[45] or hydrophobic surfaces,[12,13] biodegradable products,[46] organic solar cells,[47] catalysts,[48,49] mechanical and electrical nanodevices,[50–52] etc. through further functionalizing the polymer replica by coatings and/or doping.

2. Results and Discussion

2.1. Structural Tolerances for High-Efficiency Optics

The necessity to replicate nanostructures very precisely is discussed on the example of a PER element. Typical PER elements show a periodicity in the range below 600 nm depending on the useful wavelength. The aspect ratio of such binary structures is in the range of 1:4 to 1:14. In the following we want to assess the tolerances that will be allowed to guarantee a high extinction coefficient. The allowed tolerances are directly related to the production and replication processes. Therefore we used the RCWA method to calculate the tolerance of the line width onto the transmittance diffraction efficiency and the polarization extinction ratio. For this purpose we selected a linear grating with a period (p) of 450 nm, a height (h) of 1000 nm, and a refractive index of 1.55. The ridge width (w) of the grating has been varied from 60 to 360 nm with a step size of 10 nm. The aspect ratio ranges from 1:16.7 to 2.7. Light passing such gratings will be diffracted with polarization sensitivity. For specific grating parameters, the transverse-electric (TE) polarization propagates on the –1 diffraction order with high efficiency, while the transverse-magnetic (TM) polarization is suppressed (see **Figure 1**) in the –1 order. Figure 1b shows the color-coded TE polarized diffraction efficiency above 80% (black below 80%), while Figure 1c depicts the PER (TE/TM intensity on the –1 order) as a function of w. For clarity, Figure 1d presents selected PER data for 70 and 90 nm ridge widths. Dielectric polarizer optics with PER values above 1000 can be produced only for a narrow wavelength range. Hence a polarizer for monochromatic light at 633 nm has very low PER efficiency at 583 nm, although the diffraction efficiency for the useful polarization is above 80%. The line width of the linear grating will determine the effectiveness of the polarizer (see Figure 1d).

The RCWA calculations presented in Figure 1 visualize the rigorous production tolerances for the ridge width of dielectric polarizer optics, and the need for high-aspect-ratio optics to increase the PER. High-aspect-ratio dielectric polarizer optics may also become important to improve the contrast in fluorescence microscopy. Whereas low-aspect-ratio gratings such as holographic gratings can be easily replicated with high quality and are widely applied in optics, the replication of high-aspect-ratio optics is often hampered by the collapse of the nanostructures.

Other optical applications may include moth eye nanostructures. The effective refractive index has to be adjusted by a precise subwavelength periodic structure to diminish reflectance and increase the transmittance efficiency. Until now it has been difficult to produce "moth eye nanostructures" for anti-reflection on PS or PMMA optics. The high-throughput production of fine nanostructures in these polymers is not possible, although nanopatterning of UV curable polymers is common. Severe difficulties are also encountered in the replication of nanostructures in PS or PMMA polymers.[12,13] In this study we focus on an ALD-assisted replication and test its versatility to produce high-aspect-ratio nanostructures with tunable lateral size. The technique has been also applied to complex nano- and micropatterns.

2.2. Linear Grating Replicas with Tunable Line Width

The replication technique is outlined in **Figure 2**. First, the master is coated with conformal Al_2O_3 films by atomic layer deposition. The deposition cycle was repeated 250–1800 times and allowed for tunable film thicknesses of the sacrificial layer. The resulting sample was spin-coated with 8–40% polystyrene (PS) and polymethylmethacrylate (PMMA) solutions in CH_2Cl_2, and the sacrificial layer removed in 10–20% H_3PO_4 solution. The polymer replica is mechanically stable and can be re-detached from the substrate with a drop of distilled water, despite of its thickness being only 2–5 µm. Thick polymer bases may be applied to obtain free standing

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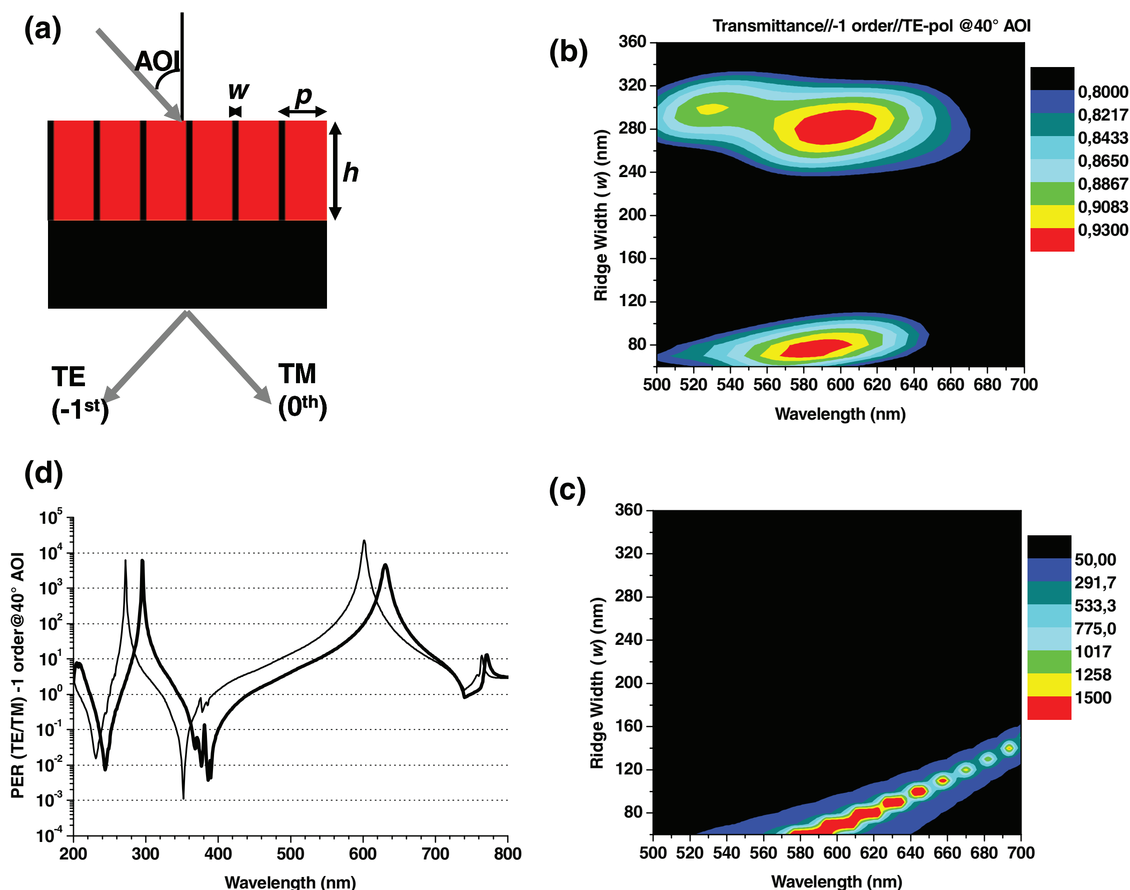

Figure 1. High-efficiency high-aspect-ratio polarizer diffractive optical elements. a) Grating and illumination parameters: period (p = 450 nm), height (h = 1000 nm), and ridge width (w) black variable from 60 to 360 nm; AOI = angle of incidence. b) Diffraction efficiency of the grating as a function of ridge width. Transmittance values below 80% are depicted black. c) Polarization extinction ratio (TE/TM) for the −1 diffraction order. PER values below 50 are depicted black. d) Selected PER data presented for clarity.

replicas with good mechanical stability and elasticity for easy handling even on curved surfaces.

Figure 3 depicts various linear grating polymer replicas with ridge widths w of 293, 148, and 88 nm, respectively. The same master has been reused for all replicas, after rinsing with CH_2Cl_2 and drying. The linear quartz grating master used in this study has a period p of 450 nm, ridge width w of ca. 110 nm (filling factor F: ca. 0.25), and a height h of ca. 1.1 µm. The period of the replicas is identical to the period of the master. The height of the master grating could also be retained in the replicas, providing gratings with high aspect ratios (w/h) of ca. 1:3, 1:7, and 1:12, respectively. To obtain such a large variation of the replica grating width, the template was coated with 250, 1500, and 1800 cycles of Al_2O_3. Hence, by varying the number of the ALD cycles, one can easily tune the ridge width of the replica, making FlexRep a versatile replication technique.

High stability of the polymer grating replicas has been observed over large areas. The template grating has a 7×7 mm^2 dimension. The grating replica with 88 nm width tended to adhere at the edge and break regions, and locally two adjacent grids were merged. Lower magnification SEM images (**Figure 4**) show that far from the edge, this polymer grating is free of defects. Noteworthy, FlexRep achieved a replica grating in a stable polymer with a ridge width smaller than the width of the quartz master structure.

Another interesting feature is the fact that some polymer replicas show some air inclusions formed during drying of the spin-coated polymer solution (see Figure 3). Hence, at these inclusion points the grating width is smaller with the replica still being stable. Finally, one should note that the height of the grating structure can exceed the thickness of the polymer base supporting the nanopattern (middle panel Figure 3). The total thickness of this replica is ca. 2 µm with a base being only 900 nm. These effects depend on the parameters of the spin-coating process filling the trenches[1] and will be further optimized. These replicas may serve as ultra-thin, flexible nanostructured surfaces.

The master did not considerably degrade during the replication process, since FlexRep does not apply mechanical forces to the template as imprint techniques do. Possible remains of the ALD coating or the polymer on the master can be completely removed after each replication process without alteration of its parameters. Organic solvents (CH_2Cl_2) used

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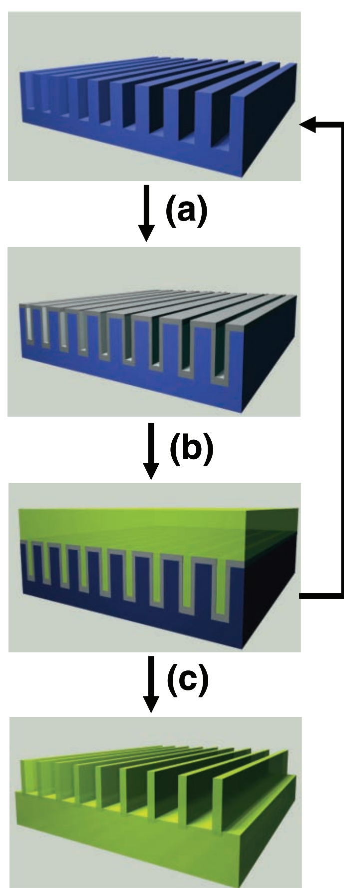

Figure 2. Schematics of the flexible replication process: a) coating a sacrificial layer (grey) onto a template by ALD (here Al_2O_3), b) spin-coating a polymer film, c) selectively removing the sacrificial layer (here wet-chemical etching). Steps a–c can be repeated with discretionary thickness of the ALD layer to adjust the line width of the replica.

to remove polymer remains, and H_3PO_4 to etch the Al_2O_3 sacrificial layer do not attack silicon or silica templates.

Currently, it is time consuming to produce deep linear gratings with very large or very low filling factors and with well defined profiles, since many parameters must be optimized for each target sample. The presented replication procedure overcomes this problem. The replica shown in Figure 3 (top panels) has a filling factor of ca. 0.7, and the spacing between the columns is ca. 150 nm. The replica with a very low filling factor depicted in Figure 3 (bottom panel) has a spacing of ca. 360 nm.

The limiting time factor for a large scale application of the ALD-assisted replication procedure is the wet-chemical etching step. The lateral diffusion of the etching solution between the master and the replica depends on the temperature, the thickness of the sacrificial layer, and the aspect ratio of the nanostructures (effective surface). The etching solution must diffuse and react with the sacrificial layer, and the by-products will diffuse into the bulk solution. The very thin ALD layer of ca. 25 nm produced by 250 cycles required higher temperature (60 versus 40 °C) and longer time (~48 versus ~8 h) for parting the replica from the template. Optimization and systematic characterization of the diffusion and etching process will be carried out to analyze the influence of the ALD layer thickness, aspect ratio, and solution temperature and pH values. These are technical aspects necessary for large scale application of FlexRep.

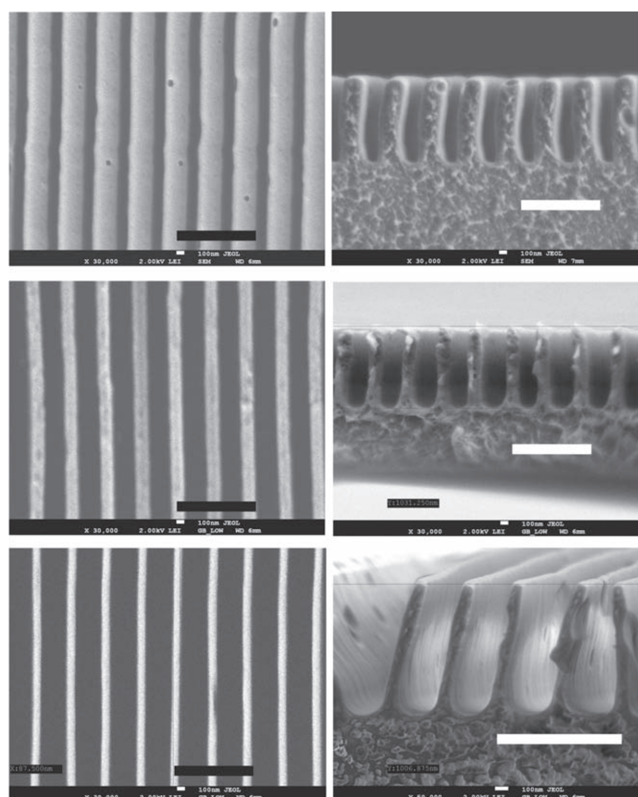

Figure 3. PS replicas with diverse line widths. SEM images of linear PS gratings replicated from a single quartz template with a period of 450 nm, width of ca. 110 nm, and length of ca. 1000 nm in top view (left column) and cross section view (right column). Reusing the template after each replication, the grating was coated by (top) 250, (middle) 1500, and (bottom) 1800 cycles Al_2O_3 and produced replica gratings of 293, 148, and 88 nm width, respectively. Scale bars 1000 nm.

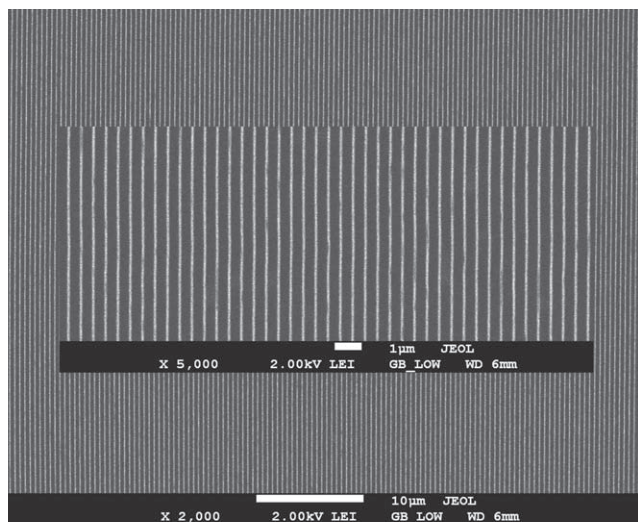

Figure 4. Large-area SEM images of the linear PS grating (width 88 nm). Although distorted at the break edge, the structures have high quality over a large area. Scale bar: 10 µm, and for inset 1 µm.

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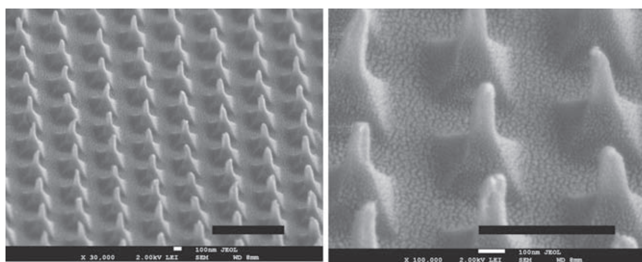

Figure 5. SEM images of a nanopyramid-nanofiber polystyrene replica with a period of 450 nm, a length of ca. 600 nm, and a width of fiber ca. 80 nm (sample after Au sputtering with ca. 10 nm). Scale bars 1000 and 500 nm, respectively.

2.3. Nanofibers and Superimposed Nano- and Microstructures

The versatility of this ALD-assisted replication consists also in the ability to copy superimposed nano- and microstructures. Two types of Si-wafer templates with pits produced by standard HF-etching were used. One template was pre-patterned with inverted pyramids (depth ca. 250 nm, hexagonal arrangement with a period of 450 nm). The second template was pre-patterned with a 500 nm period also in hexagonal arrangement. The etched templates were coated with Al_2O_3 (500 ALD-cycles). The obtained replicas are presented in **Figure 5** and **6**, respectively. In Figure 5 the pyramid base can be clearly identified, with a nanofiber on top of the pyramid. The total height of the nanostructure is ca. 600 nm. The ordered nanofibers shown in Figure 6 have a height of ca. 1000 nm and a diameter of ca. 120 nm (at the middle).

Figure 7 presents the microchannel replica of an e-beam written template. The SEM image (Figure 7a) shows columns with a width of ca. 400 nm and ca. 200 nm height serving as a master template. The SEM and the optical micrographs of the master (Figure 7b, at 50× magnification) have been recorded after the replication procedure. The templated material is an

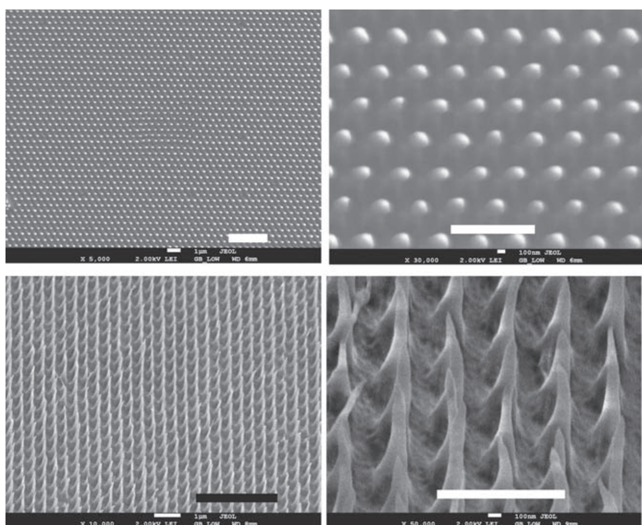

Figure 6. SEM images of nanofiber polystyrene replica with a period of 500 nm, a length of ca. 1000 nm, and a diameter of ca. 120 nm. Scale bars 3 µm (left images) and 1000 nm (right images), respectively.

Figure 7. Replication of complex structures. a) SEM and b) optical micrograph (50×) of the master nanopattern showing ca. 400 nm width columns. c) Optical micrograph of the polymer replica with microchannels in a mirror image of the master. d) Flipped image of the replica presented for clarity. e) Corresponding SEM image of the replica. Scale bars: a) 10 µm (left) and 500 nm (right); e) 1 µm.

inverse copy of the template structure. Hence, the microchannels (towards air) are a mirror image of the written master (Figure 7c). The optical image has been vertically flipped for clarity (Figure 7d) corresponding to a sample with the microchannels facing a substrate. Bonding a substrate[43] to the replica would produce closed channels with application potential in nanofluidics. For sensing applications, it would be of interest to combine nanostructures and such microstructure channels, with the nanostructure adequate for optical detection. The positive results from the replication of the pyramid combined with a nanofiber on top of it, demonstrate the feasibility of FlexRep to cost effectively produce lab-on-chip devices.

The replication of thermoplastics (such as polystyrene) usually suffers from plastic deformation or breakage because of the forces applied to detach and extract the polymer replica from the master.[1,12,13] Specialty polymers overcome such drawbacks by reduced adhesion or by shrinkage after cross-linking during a thermal or photo-induced curing process. Silanization may be also applied to minimize adhesion between the pore walls and the polymer.[13] Stable nanofibers with 120 nm diameters and height above 1000 nm could be obtained with specialty polymers by such a procedure. However, these additional treatments are also time consuming, require expensive equipment, and most importantly limit the choice of the polymer material.

The FlexRep technique presented here has been easily applied to PS and PMMA, and can be transferred to various polymers since most of them are resistant to diluted acidic solutions. A reasonable selection of sacrificial materials and spin-coated polymers enables the production of a large variety of structured polymers or even metal oxides. Promising new strategies include coating the sacrificial layer (here Al_2O_3) with inert oxides or metals such as SiO_2, TiO_2, Ir, etc. and providing/bonding a support substrate by rapid coating technologies. Rapid developments in molecular layer deposition (MLD) capable to deposit organic material in the ALD

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manner[53] would provide an organic sacrificial layer. This layer could be alternatively removed by pyrolysis, or organic solvents.

The resulting structures benefit from the precision of the ALD process, which enables tuning of the replicated features on a sub-nanometer scale. Further benefits are the scalability as ALD processes can easily be applied to large substrates and numerous samples in one single run. The polymer replicas may, similarly to PDMS replicas, serve as a second master, for subsequent replication with a hard material, adding even more structural flexibility to the structures. The resulting replicas are desired for many applications, including optics, nanofluidics, as biocompatible substrates or (super) hydrophobic surfaces. Colloidal metals, quantum dots, and organic functional materials may be embedded into the polymeric material to further diversify the application field of the replication process.

3. Conclusion

In summary, the presented strategy overcomes the destruction of nanostructured templates upon replication involving a wet-chemical etching step. Primarily, the FlexRep technique allows for precisely tunable structural parameters of the replicas compared to the master. Linear gratings down to 88 nm width and above 1 µm height, well-ordered nanofibers, and complex nanopatterns could be replicated. The present replication has a broad application potential in various fields where highly ordered nanostructured materials are needed. The flexibility of tuning the lateral parameters of the replica compared to the master template is especially advantageous. The removal of the replica from the master does not require the application of mechanical forces, thus increased lifetime of the master can be achieved.

4. Experimental Section

The Beneq TFS200 ALD equipment has been used for thin film deposition. An ALD cycle, consists of alternating TMA ($Al(CH_3)_3$, Strem Chemicals) (250 ms pulse, 2 s purge) and H_2O (250 ms pulse, 2 s purge) under N_2 (200/200 sccm flow rate). The resulting sample was spin-coated with 8–40% PS and PMMA (Polymer Source Inc.) solutions in CH_2Cl_2 (Merck KGaA), and subsequently dipped into a 10–20% H_3PO_4 (Merck KGaA) solution at ca. 40 to 60 °C overnight or 48 h. After complete removal of the Al_2O_3 sacrificial layer, the polymer replica detached from the template and floated on the surface of the liquid. Finally, the replica was lifted onto a substrate (Si wafer, quartz) and dried under normal conditions.

The removal of the sacrificial layer has been initially tested on Si-wafer flat surfaces. In this case the spin-coated polymer detached after ca.1 h in acidic solution at room temperature, while the high-aspect-ratio samples required considerably longer time. The diffusion of the reaction solution between the master and the replica additionally depends onto the ALD film thickness.

SEM images were obtained from a JEOL JSM 7500F electron microscope at 2 kV accelerating voltage, under gentle-beam condition. Top view images of the linear gratings could be obtained without Au sputtering. Au sputtering was applied for lateral image analysis. All nanofibers were Au-coated for the SEM.

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