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UV nanoimprint lithography with rigid polymer molds

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ABSTRACT

Transparent polymers are considered as alternative low-cost mold materials in UV nanoimprint lithography (UV-NIL). Here, we demonstrate a nanoimprint process with molds made of rigid polymers novel for this application. These polymer molds are found to show high performance in the patterning with UV-NIL. Sub-50 nm structures were fabricated with this process.

1. Introduction

Patterning of surfaces in the nanometer range is a key issue in both nanoscience and nanotechnology. Nanoimprint lithography (NIL) has been an emerging technology for future nanofabrication since it was introduced by Chou et al. [1]. NIL is considered to be an alternative to optical lithography (OL) and electron beam lithography (EBL), as it combines the advantages of high-resolution, low-costs and high throughput. Particularly, UV-based NIL (UV-NIL) [2] appears to be promising for the production of patterns in the sub-50 nm range due to the advantage of room temperature processing – in contrast to thermal NIL.

For UV-NIL a UV-transparent mold is required. Commonly, quartz or silica molds with nanoscale surface-relief features are fabricated by EBL and then used as the stamping tool. The processing of such dielectric materials by means of EBL appears to be difficult due to charging effects. Especially, fabrication of features smaller than 50 nm remains challenging and expensive. Since mold fabrication is considered to be the bottleneck in pushing UV-NIL towards a profitable industrial method, alternative approaches are highly sought. Potential substitute mold materials are UV-transparent polymer materials, which are formed from a patterned silicon master. Elastomers [3] as well as plastomers [4] have been successfully tested for UV-NIL with sub-100 nm resolution.

In this publication stiff plastomers were used as mold materials with mechanical properties more similar to quartz or silica than elastomers. The plastic molds were replicated from a master by hot embossing (Fig. 1a). The silicon master, fabricated by standard lithography, containing the desired pattern (i) and the appropriate thermoplastic material were pressed together at elevated temperature (ii). After cooling to room temperature, the molds were peeled off from the master (iii). For the NIL process (Fig. 1b) a substrate was coated with a UV-curable resist and the polymer mold was pressed into the resist (i). By exposure to UV light the liquid precursor crosslinked and formed a stable network (ii). The mold was removed, leaving a negative copy of its pattern in the cured resist (iii). The individual process steps are discussed below.

2. The master

First a master needs to be fabricated containing the negative copy of the desired mold pattern. The master pattern defines directly the pattern on the mold and determines the later imprint resolution. In this work EBL as the high-resolution patterning technique was chosen for master fabrication. Unlike the challenging fabrication of quartz or silica templates, processing of silicon by EBL is well-established and can be pushed to the sub-50 nm regime.

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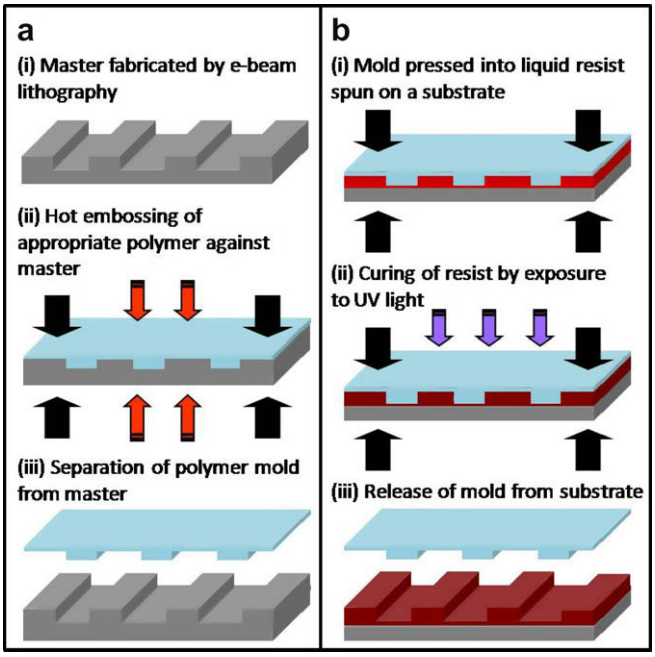

Fig. 1. Schematic process of (a) polymer mold fabrication from a master and (b) UV nanoimprint with the polymer mold.

Various silicon masters were fabricated by using positive as well as negative e-beam resist. PMMA (polymethylmethacrylate, AR-P series from Allresist) was used as positive resist. After development, the structures were transferred into a polysilicon layer on the substrate by reactive ion etching (RIE) with HBr. A silicon nitride layer underneath was used as etch stop. A detailed description of the process was given by Schwaab [5]. Thereby, 'positive masters' with cavities and protrusions of varying widths from 1 μm to sub-100 nm (Fig. 2a) were fabricated.

Using HSQ (hydrogene silsesquioxane) as negative resist and curing the HSQ structures after development, 'negative masters' with high-resolution (sub-50 nm) protrusions were achieved (Fig. 2b). The HSQ resist (FOX12, Dow Corning) was spincoated with 3000 rpm on a silicon substrate and baked at 90 °C for 40 min on a hotplate. The e-beam writing was done with a Leica EBPG 5000 Plus. After EBL the samples were developed and finally treated with oxygen plasma (0.8 mbar, 80 W, 5 min) [6] to oxidize the resist and obtain a structure close to silica. The results of the characterization of the masters by scanning electron microscopy (SEM) and atomic force microscopy (AFM) are listed in Tables 1–3.

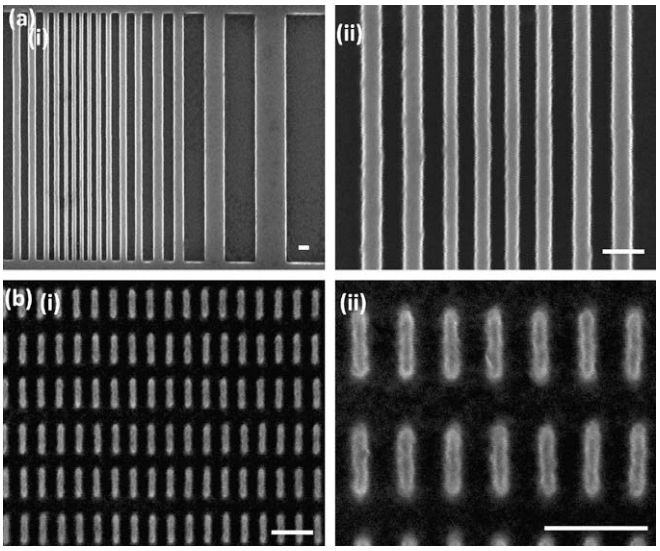

Fig. 2. SEM measurements of silicon masters: (a) PMMA-master with widths varying from 1 μm to sub-100 nm, (i) survey, (ii) zoom on smallest structures, (b) HSQ-master with sub-50 nm structures (i) survey, (ii) zoom; scale bars correspond to 200 nm.

3. The mold

Polymer materials are well-established as stamps in soft lithography techniques such as microcontact printing, replica molding or microtransfer molding [7]. A commonly used material in soft lithography is PDMS (polydimethylsiloxane), which is a soft elastomer. The Young's modulus, as a measure of the stiffness, of standard Sylgard 184 PDMS amounts to 1 MPa. With lower stiffness, the shape fidelity of polymer replicas is decreased [8] and the structural integrity of the mold patterns is jeopardized. Collapse or pairing may occur [5]. Therefore, we focused on materials with a significantly higher rigidity in order to combine advantages of molds made from inorganic materials and those made from soft polymers. These molds show structural integrity due to high stiffness as well as global flexibility to adapt to the surface morphology.

The plastomers Surlyn 1702 (DuPont) and Fluon ETFE (Asahi Glass Company) were used as mold materials in the scope of this work. Surlyn is an ethylene/methacrylic acid copolymer with a Young's modulus of ~190 MPa [9] and was recently found to be appropriate for creation of nanoscale features by Soft Lithography [5]. Fluon ETFE is an ethylene tetrafluoroethylene with an even higher rigidity (Young's modulus ~800 MPa [10]) and excellent anti-adhesion properties. Both polymers are commercially available commodities, which makes them low-cost materials.

The hot embossing process for the transfer of the pattern to the plastomer was done at temperatures above the glass transition temperature (T_g) of the polymers. Surlyn and Fluon were embossed at 120 °C, 4 bar for 5 min and at 250 °C, 7 bar for 5 min, respectively. The embossed Surlyn molds were investigated by SEM measurement after sputtering with a ~5 nm thick Pt layer (Fig. 3). Despite of the metal coating the SEM pictures of Surlyn molds were slightly distorted whereas imaging of Fluon molds was not possible at all.

All investigated pattern elements were replicated during the molding process. Even challenging structures like long, densely packed lines with aspect ratios of up to 1.6 did not show collapsing or pairing (Fig. 3a). The images were further analyzed with regard to feature width (w) and edge roughness (3σ) and compared to the results of the masters (Table 1). The structures were broadened on protruding patterns and narrowed on cavity patterns, which is reasonable due to the Pt-coating. The roughness of some lines was slightly increased, probably for the same reason.

Furthermore the molds were investigated by AFM. Measured structure heights and surface roughness (root mean square) are summarized in Table 3. Height values of the sub-50 nm molds were not accessible since it was impossible to reach the bottom

Table 1
Results of pattern accuracy of master, corresponding Surlyn mold and imprint with Surlyn mold; 1 μm to sub-100 nm pattern highlighted in bold.

	w (3σ)/nm					
Master	**94 (8)**	**75 (6)**	**66 (7)**	**75 (7)**	**94 (10)**	36 (10)
Mold	**114 (9)**	**98 (10)**	**88 (11)**	**98 (8)**	**114 (9)**	16 (10)
Imprint	**104 (17)**	**80 (17)**	**70 (19)**	**79 (19)**	**103 (19)**	33 (12)

Table 2
Results of pattern accuracy of master and corresponding imprint with Fluon mold; 1 μm to sub-100 nm pattern highlighted in bold.

	w (3σ)/nm					
Master	**138 (10)**	**92 (9)**	**67 (6)**	**93 (6)**	**139 (7)**	36 (10)
Imprint	**119 (14)**	**86 (12)**	**73 (14)**	**92 (12)**	**130 (11)**	41 (16)

Table 3
Summarized results of height (h) and roughness (r) measurements of masters, corresponding polymer molds, and imprints by AFM; 1 μm to sub-100 nm pattern highlighted in bold.

	h/nm		r/nm	
Master	**107 ± 3**	73 ± 4	**1.8**	1.1
Mold: Surlyn	**106 ± 6**	n/a	**1.8**	0.8
Mold: Fluon	**108 ± 2**	n/a	**2.1**	1.0
Imprint: Surlyn	**99 ± 2**	67 ± 2	**1.7**	0.9
Imprint: Fluon	**107 ± 2**	69 ± 3	**1.8**	1.1

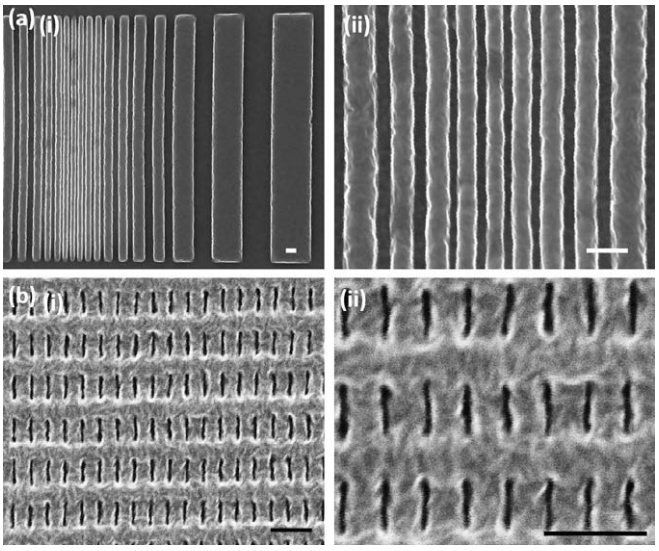

Fig. 3. SEM measurements of Surlyn molds: (a) Protrusion mold with widths varying from 1 μm to sub-100 nm, (i) survey, (ii) zoom on smallest structures, (b) cavity mold with sub-50 nm structures (i) survey, (ii) zoom; scale bars correspond to 200 nm.

of the small cavities even with super sharp AFM tips. The vertical dimensions of the mold features correspond well with those on the masters indicating that there is no shrinkage during the hot embossing process. Also, the roughness of the surface of mold and master are very similar.

4. The imprint

The nanoimprint process was carried out with the structured polymer films as molds. An air cushion press process (Nanonex NX2000) was used allowing a compensation of the mold's stiffness by adjusting the imprint pressure. The UV resists NXR-2010 (Nanonex Corp.) and mr-UVcur06 (micro resist technology GmbH) were imprinted at 38 bar with a UV exposure time of 4–5 min. Cavities and protrusions were imprinted by means of molds replicated from the PMMA-master. Large and small structures with widths ranging from 1 μm to sub-100 nm (Fig. 4a) were created simultaneously. Furthermore, protruding patterns down to ~30 nm in width, replicated from the HSQ-master, were fabricated (Fig. 4b).

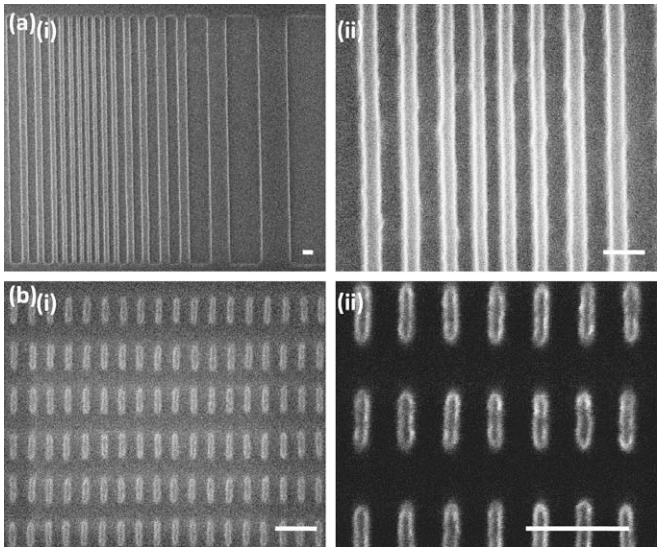

Fig. 4. SEM measurements of imprints with Surlyn molds in UV resist: (a) Cavity imprint with widths varying from 1 μm to sub-100 nm, (i) survey, (ii) zoom on smallest structures, (b) protrusion imprint with sub-50 nm structures, (i) survey, (ii) zoom; scale bars correspond to 200 nm.

Analyzing the SEM measurements of the imprint with Surlyn mold (Table 1) showed that the widths of the features agree well with the original pattern. Only minor line broadenings were observed for the cavity imprint (1 μm to sub-100 nm). The edge roughness of the structures increased in average by a factor of two. Probably, the lower imaging quality of the dielectric polymer resist contributes to this increase. The sub-50 nm features were replicated very reliably with Surlyn (Table 1, far right column). The same structures were also imprinted with Fluon molds (Table 2). The sub-50 nm features were resolved but showed slight increase in width and in edge roughness (Table 2, far right column). We found indications that imprinting of long, dense, and narrow lines seems to be critical with Fluon molds. However, imprinting of analogous but less dense protrusion structures worked successfully. The results are summarized in Table 2. Here the change of edge roughness was less significant. AFM measurements (Table 3) revealed that there was a height decrease for the imprints performed with Surlyn stamps. We assume that the Surlyn is slightly compressed by the high imprint pressure whereas this seems not to be the case for the more rigid Fluon.

The areas patterned in a single step attained up to 2.5 by 5 mm. During the manually performed separation of mold and substrate, the resist was not ripped off by the mold, although, neither of them was coated with an additional release agent. Therefore, the polymer molds are not contaminated and can be used many times for imprinting. Even single use of molds is economically feasible, due to the low-costs for the mold material. Replication of molds from one master can be done again and again.

5. Conclusions

It was shown that Surlyn and Fluon are applicable mold materials for a high-resolution patterning process. The process comprises of master fabrication, hot embossing of polymer mold and UV nanoimprint. High-resolution patterning with features smaller than 50 nm was demonstrated with good pattern fidelity.

Advantages and drawbacks for both of the mold materials were found. In comparison, the advantage of Surlyn is the lower embossing temperature and the ability to imprint all types of patterns

tested. On the other hand, Fluon molds showed no compression at high pressure.

We plan to use this patterning procedure for various bioelectronic applications, such as fabrication of biomolecular junctions and locally controlled cell growth.

References

[1] S.Y. Chou et al., Appl. Phys. Lett. 67 (1995) 3114–3116.
[2] M. Colburn et al., Proc. SPIE 3676 (1999) 379–389.
[3] N. Koo et al., Microelectron. Eng. 84 (2007) 904–908.
[4] D.Y. Khang et al., Langmuir 20 (2004) 2445–2448.
[5] D. Schwaab, Dissertation, Department of Physics, RWTH Aachen University, 2006.
[6] D. Lauvernier et al., Microelectron. Eng. 77 (2005) 210–216.
[7] Y. Xia et al., Annu. Rev. Mat. Sci. 28 (1998) 153–184.
[8] O.D. Gordan et al., Langmuir 24 (2008) 6636–6639.
[9] Datasheet Surlyn 1702, DuPont <http://www.dupont.com>.
[10] Datasheet Fluon ETFE, Asahi Glass Company <http://www.agc.co.jp>.