

Replication of sub-100 nm structures using h- and s-PDMS composite stamps

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Abstract

Soft-UV-NIL as replication technique was used to replicate sub-100 nm structures. The aim of this work is the stamp production and the replication of structures with dimensions smaller than 100 nm in a simple manner. Composite stamps composed of two layers, a thin hard PDMS (h-PDMS) layer supported by a thick soft PDMS (s-PDMS) layer are compared to common s-PDMS stamps regarding the resolution by using a Siemens star (star burst pattern) as test structure. The master is fabricated by Electron Beam Lithography (EBL) in a 140 nm thick PMMA resist layer. The stamp is molded directly from the structured resist, without any additional anti sticking treatment. Therefore the resist thickness determines the aspect ratio, which is 1.5 at the resolution limit. The replication is done in a UV-curing cycloaliphatic epoxy material. The employed test structure provides good comparability, the resolution limit at a glance, and it integrates a smooth transition from micro- to nanostructures. Therefore it is a capable structure to characterize the UV-NIL.

Introduction

Soft lithography and UV-NIL is an important technology to replicate nanostructures in a simple and fast kind of way. This field has attracted the increasing interest of scientists all over the world. There it is possible to functionalize surfaces for many applications regarding e.g. wetting or reflection properties [1]. In this work a Siemens star is used as test structure to evaluate the capabilities of the soft UV-NIL and to compare composite stamps with common s-PDMS stamps. Besides PDMS, also PFPE or siliconized silsesquioxane acrylate as flexible stamp materials could be used with a resolution down to sub-20nm [2] [3]. The advantage of PDMS as stamp material is the simple processing. Adding a second layer of h-PDMS is a convenient way to improve the resolution limit and to reduce deformation effects compared to s-PDMS [4]. Therefore the soft UV-NIL using composite stamps could be useful for the replication of photonic crystals in the visible range (with structure sizes below 100nm).

Fabrication Process

Starting with the production of the master a 4" silicon wafer as substrate is spin-coated with resist 2200 PMMA A2 (MicroChem Corp.) for EBL. Then a pre-bake is carried out for 3 min at 180°C on a hotplate. The writing of the master structures is performed using a 100 kV Electron Beam Lithography System (EBPG 5000+, Vistec) with a dose of 750 $\mu\text{C}/\text{cm}^2$. The following developing step is done by rinsing the master for 30s in AR 600-56 developer (ALLRESIST GmbH), then for 3s in AR 600-60 stopper (ALLRESIST GmbH) and again for 10s in a new bath of AR 600-60. Finally the master is dried by nitrogen blow-off.

Like shown in Fig. 1, the stamp production for a composite stamp is carried out by spin-coating the h-PDMS mixture directly onto the master. No additional anti sticking treatment of the master was needed. The h-PDMS is obtained by mixing step by step 3.4g of a vinylsiloxane prepolymer (CAS 67762-94-1, ABCR GmbH) with 0.016g of platinum-divinyltetramethyldisiloxane as catalyst (CAS 68478-92-2, ABCR GmbH), 0.1g of 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (CAS 68478-92-2, Sigma-Aldrich Corp.) as modulator and 1g of a hydrosiloxane prepolymer (CAS 68037-59-2, ABCR GmbH) [5] [6]. For 3 min the coated master is degassed in a vacuum oven. Then, under vacuum the oven is heated up and within 5 minutes a final temperature of 70°C is reached. When the second layer of s-PDMS is added the h-PDMS is in a partially cured state. The s-PDMS, Elastosil RT 601 (Wacker Chemie AG) is mixed and degassed according to the manufacturer's specification [7]. Then it is poured onto the h-PDMS layer (depicted in Fig. 2). Determined by the s-PDMS's surface tension and its viscosity, the thickness of this layer reaches 4 mm. After 30 minutes at 70°C the curing is finished. The obtained composite stamp can be peeled off easily.

For comparison purposes the common stamp is produced by pouring the s-PDMS Elastosil RT 601 onto the master. Previous mixing and degassing is done like described before. This PDMS is especially suitable as a stamp material for UV applications because of its relatively low absorption of light at a wavelength of 365 nm. To obtain a good cavity filling, the s-PDMS is degassed again for 5 minutes after pouring. Afterwards, the curing is done like described before. With a final thickness of about 4mm the stamp purveys a good manageability.

In a next step the stamps are replicated by UV-NIL. As replication material 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CAS 2386-87-0, Sigma-Aldrich Corp.) mixed with 3 wt% triarylsulfonium hexafluorophosphate salts (CAS 109037-77-6, Sigma-Aldrich Corp.) as photo-initiator are used. This bis-cycloaliphatic epoxy is spin-coated onto a silicon wafer as substrate obtaining a 5 µm thick layer. For the replication step the stamp is laid down onto the epoxy by hand with tweezers, making contact from one side to the other without entrapping air. Due to the low viscosity of the epoxy layer, the liquid fills the cavities of the PDMS stamp. This epoxide system is curing by cationic polymerization. By exposure of UV-light of 365 nm through the stamp the epoxy cures. With an intensity of 1 mW/cm², the dose is 600 mJ/cm². After curing the stamp is peeled off slowly by hand (the result is depicted in Fig. 3).

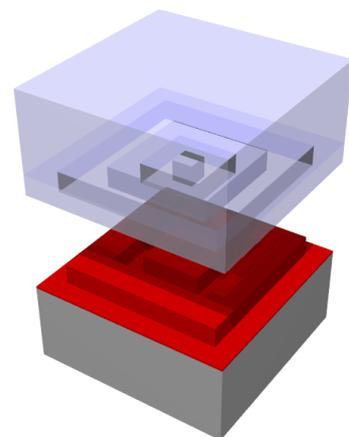
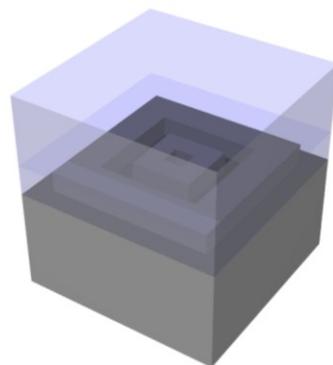
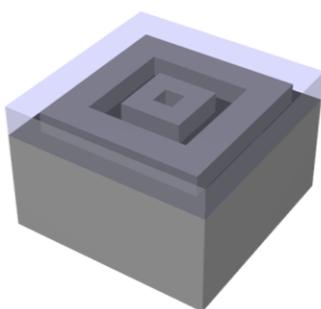


Fig. 1 Composite stamp production: thin, spin-coated layer of h-PDMS on master structure

Fig. 2 Composite stamp production: second layer of s-PDMS added on the h-PDMS

Fig. 3 Transferred pattern replicated by UV-NIL using a composite stamp

Results

SEM analysis is used for evaluation of the replication fidelity. Therefore, master and replication are coated with a thin conductivity layer of gold. The dimensions of interest are the diameter of the area in the Siemens star's center that differs from the design (called 'inner diameter' in the following) and the width of one spoke at the inner diameter. The depicted master is analyzed after the stamp molding steps. For the two employed Siemens star structures the outer diameters are 40 and 80 μm , with 36 and 96 equally-sized spokes, respectively, shown in Fig. 4 & Fig. 5. The inner diameter of a Siemens star defines the resolution limit for this method as depicted: in Fig. 6 & Fig. 7 for the master; in Fig. 8 & Fig. 9 for the replication done with the composite stamp; and in Fig. 10 & Fig. 11 for the replication done with s-PDMS stamp. As shown in the figures, the resolution could be improved by a factor of 3 using composite stamps. With a structure height of 140 nm and a minimum spoke width of 90 nm an aspect ratio of about 1.5 was achieved.

Due to the master fabrication process, the design of the test structures needs to be optimized regarding the Siemens star's center. As a consequence of the surface tension between the spokes and the developer liquid, three or more spokes each adhere together when drying the surface after development. Furthermore, the Siemens star's center is over exposed due to the limited resolution of the EBL step.

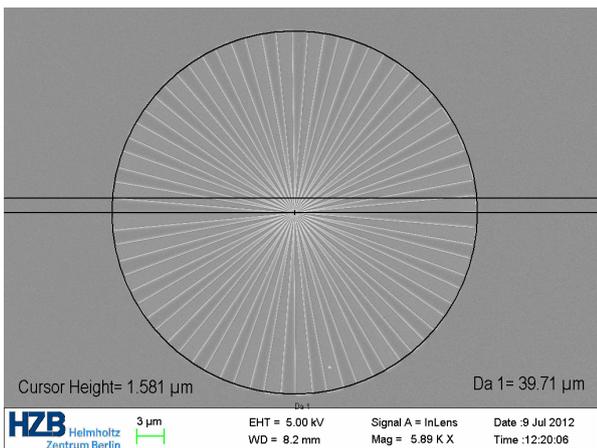


Fig. 4 SEM image: Overview of the master; 40 μm diameter; 1.6 μm spoke width (cursor height)

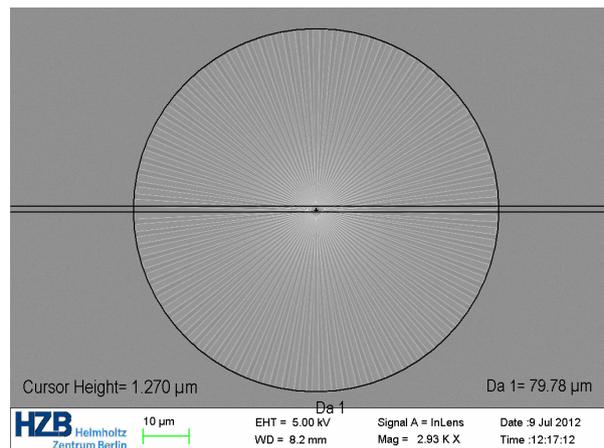


Fig. 5 SEM image: Overview of the master; 80 μm diameter; 1.3 μm spoke width (cursor height)

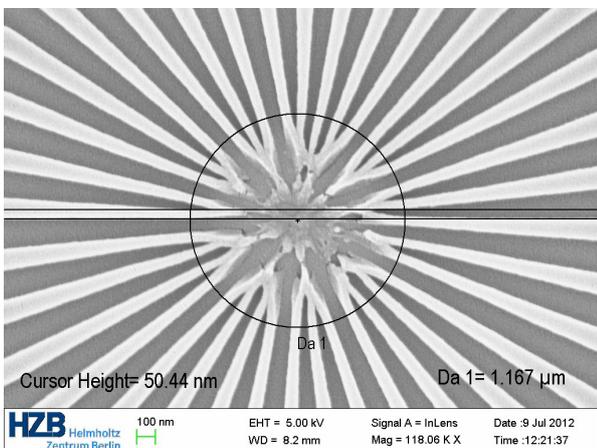


Fig. 6 SEM image: Detail of Fig. 4; 1.2 μm diameter; 1.6 μm spoke width (cursor height)

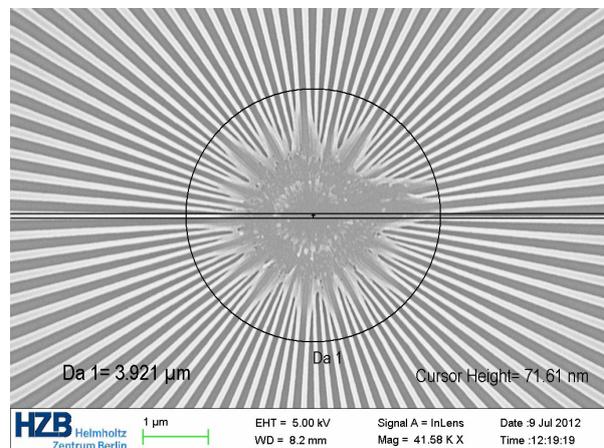


Fig. 7 SEM image: Detail of Fig. 5; 1.2 μm diameter; 1.6 μm spoke width (cursor height)

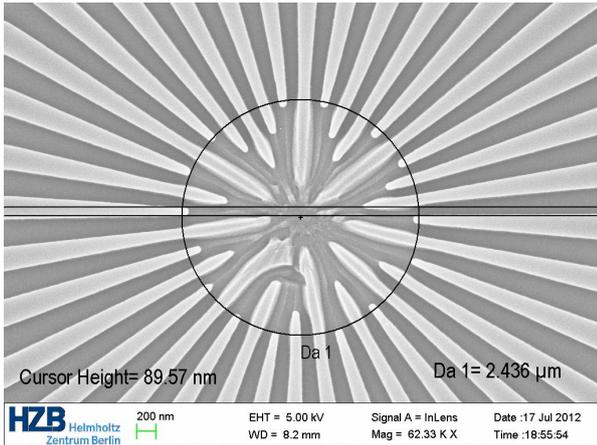


Fig. 8 SEM image: Replication of Fig. 6 made with composite stamp. 2.44 μm diameter; 90nm spoke width (cursor height)

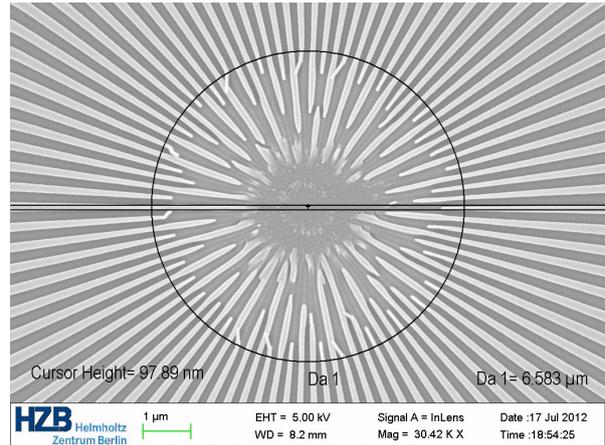


Fig. 9 SEM image: Replication of Fig. 7 made with composite stamp. 6.58 μm diameter; 98nm spoke width (cursor height)

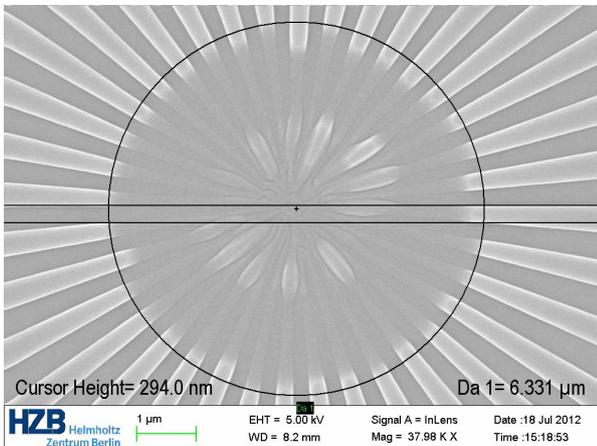


Fig. 10 SEM image: Replication of Fig. 6 made with s-PDMS stamp. 6.33 μm diameter; 294nm spoke width (cursor height)

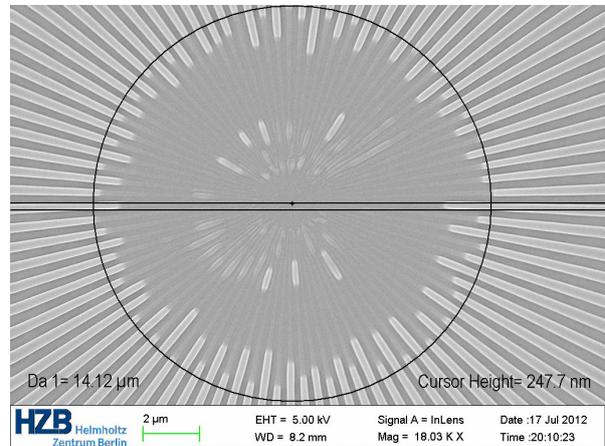


Fig. 11 SEM image: Replication of Fig. 7 made with s-PDMS stamp. 14.1 μm diameter; 248nm spoke width (cursor height)

Conclusion

The presented method is used to fabricate high aspect ratio nanostructures on plane surfaces. The master structure for the production of the stamp was obtained using EBL. The UV-NIL process allowed us to replicate these structures with high accuracy from a PMMA master in an epoxy material by means of a PDMS stamp. As shown in the figures the resolution could be improved by a factor of 3 using composite stamps. A capable structure to characterize PDMS as stamp materials for UV-NIL is the Siemens star, as it provides a good comparability, the resolution limit at a glance, and it integrates micro- and nanostructures. These results show that the soft UV-NIL using composite stamps has a high potential for the replication of photonic crystals in the visible range (with structure sizes below 100nm), which we are planning to implement in the near future.

Acknowledgements

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