 DOI: 10.1002/masy.201051044

Replication of Micro- and Nanostructures on Polymer Surfaces

Clemens Holzer,[*1] Jens Gobrecht,[2] Helmut Schift,[3] Harun Solak[4]*

Summary: Via geometrical micro- and nanostructures new functionalities like controlled wetting properties, biological adhesive / dehesive properties or surface patterns for guided self assembly can be added to polymer surfaces. This is especially interesting for medical or biotechnological applications, because there is no new approval process necessary. The whole process from producing the structures via EUV-interference lithography to the injection moulding will be shown. How far the limits for the smallness of these structures on polymers are already pushed forward show the results from our latest injection moulded samples. Grooves of 18 nm width - this means world record! - could be reproduced in an industrial process and in an economical very interesting high-volume production.

Keywords: EUV-interference lithography; high-volume production; injection moulding; micro- and nanostructures; polymers

Introduction

Geometrical micro- and nanostructures on polymer surfaces offer a broad range of new functionalities such as:

- Controlled hydrophilic or hydrophobic properties
- Easy to empty-properties
- Motheye antireflective effect
- Security features
- Controlled tribological properties
- Optical waveguide structures
- Biological dehesive or adhesive properties
- Surface patterns for guided self assembly

Most of these functionalities can be added to an existing properties profile, which opens the way to highly customer orientated products. A big advantage of structuring is that usually there is no need for a new and expensive approval procedure like it is with additives or with coatings. Thus especially for medical or biotechnological parts the structuring became extreme interesting, moreover because there are very economic production methods like hot-embossing or injection moulding for high volume production.

EUV Interference Lithography

The basic component for any structuring is the so called master. The quality of the master determines the quality of the structured product at the end of the process. There are different possibilities to structure a master, in the low micro or nano-range very often e-beam-lithography is used like at the Laboratory for Micro- and Nanotechnology LMN at the Paul Scherrer Institut PSI, Switzerland (Figure 1).

E-beam is a high resolution method, but it has some disadvantages:

- Extremely slow due to its serial writing nature

[1] Institute of Plastics Processing (IKV), University of Leoben, Franz-Josef-Str. 18, 8700 Leoben, Austria
E-mail: clemens.holzer@unileoben.ac.at
[2] Institute of Polymer-Nanotechnology (INKA), 5210 Windisch, Switzerland
[3] Paul Scherrer Institute, 5232 Villigen, Switzerland
[4] Eulitha AG, 5232 Villigen, Switzerland

Figure 1.
State of the art e-beam-system Vistec EBPG 5000+ at LMN / PSI (100kV).

- Jitter in nanostructure positions
- Proximity effects in closely neighboring features
- Defects in areas where two adjacent fields are stitched together

A break through in the production of high quality masters for replication in polymers was the development of the Extreme Ultraviolet-Interference Lithography (EUV-IL) technology. Still this technology is mostly used in the labaratory but there are already small high tech enterprises like Eulitha, Switzerland[1] which have made the transfer into industrial praxis.

In Figure 2 the principles of the EUV-IL is shown: the coherent extreme UV-light from the Swiss Light Source (SLS) is diffracted at the gratings of the mask and the so created interference pattern is projected on the resist coated substrate. Due to the frequency multiplication the interference pattern on the resist has twice the frequency (twice as small!) of the diffraction grating.

The advantages of the EUV-IL are:

- Relatively large field size - several square millimeters
- Larger patterns by step-and-repeat process possible
- Exposure time only a few seconds per field
- Higher throughput than e-beam lithography
- Higher quality
- Absence of defects
- Very good edge definition
- Uniformity of structures
- No charging of insulating substrates

For our masters we used the SLS at the PSI which enables with its wavelength of 13.4 nm theoretically structures down to 6.5 nm. With different gratings masks and multi beam interference not only simple figures like lines, spaces, dots or holes can be produced but also more complicated structures like rings or crosses.

The typical resists are PMMA or HSQ (hydrogen silsesquioxane). The resist itself is coated on a substrate and the structure of the resist is transferred via various etching methods in this substrate. Substrates like silicon, quartz or metals are used.

Figure 3 shows a four inch silicon-wafer with more than 500 repeated units (chips). The units itself contain line structures with different pitches (Figure 4).

Figure 5 shows silicon chips with different structures, different periods and different aspect ratios. The 11-nm-lines are current record for photon based printing!

Hot Embossing

Thermal Nanoimprint-Lithography (NIL) or Hot-Embossing Lithography (HEL) is a technique, where the die is pressed in the hot polymer surface.[2] Replication down in the low nanometer scale is possible. It is an extremely precise technique, high aspect ratios are possible and it can be done with a wide choice of materials. The biggest limitations are the restriction to planar surfaces and that it is a much slower process than injection moulding.

The hot embossing trials were done on a Hex03-machine from Jenoptik in a cleanroom. As polymer a 125 nm thick spin-coated PMMA layer on silicon substrates was used. The die / stamper was coated with

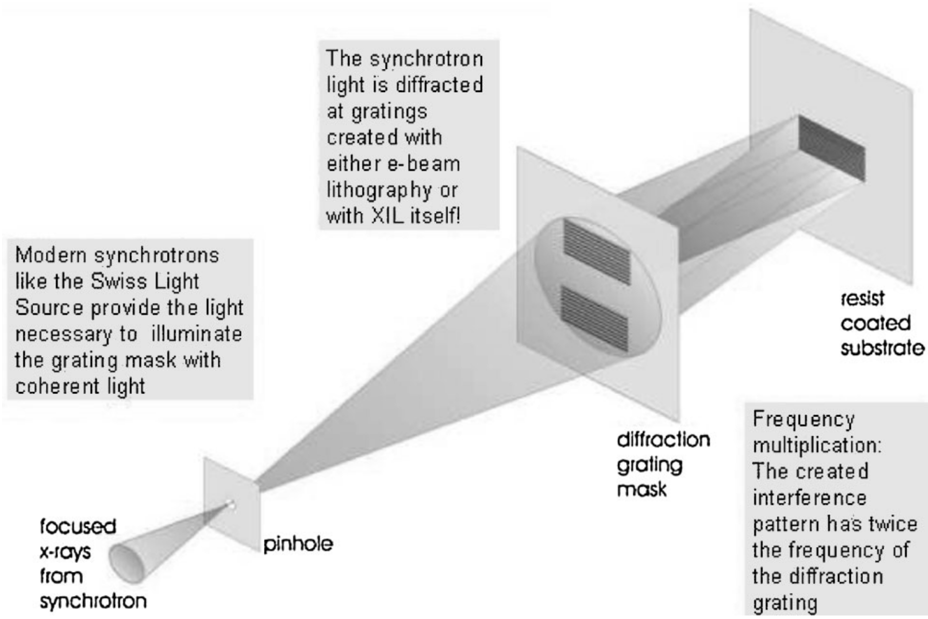

Figure 2.
Set-up for X-ray Interference Lithography.

a thin anti-sticking layer to improve the release.

Figure 6 shows photos of the filling phase.[3] Due to the pressure gradient at the border of the wafer, within a few mm different filling states can be observed.

In Figure 7 two SEM micrographs of hot embossed structures are shown: the wider one with a period of 300 nm and the narrower one with a 60 nm period.

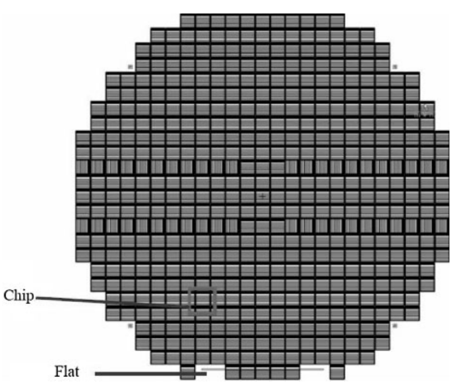

Figure 3.
4-inch silicon wafer with more than 500 repeated units.

Injection Moulding

Injection moulding is the most important technique for the production of polymer parts. It is a production method for high volume parts and usually cycle time is very short (within a few seconds). The significant difference to NIL is that the hot polymer is

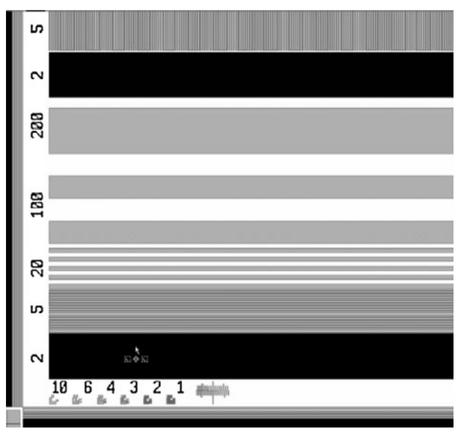

Figure 4.
Chip with different line-structures in the micrometer range.

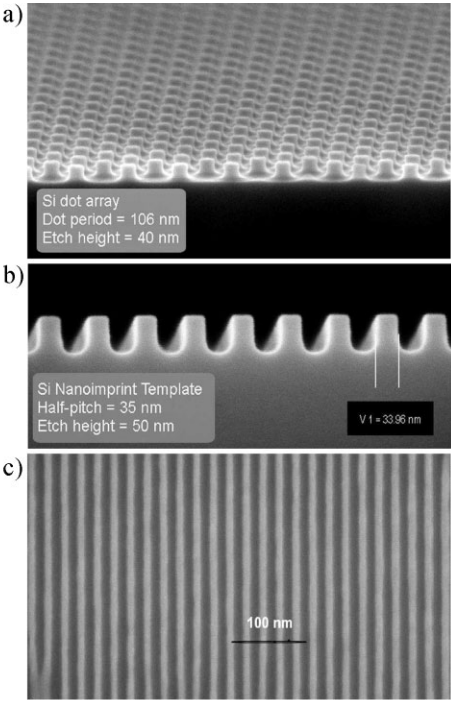

Figure 5.
Silicon chips with: a. dots with 106 nm period, b. 34 nm lines and c. 11 nm lines.

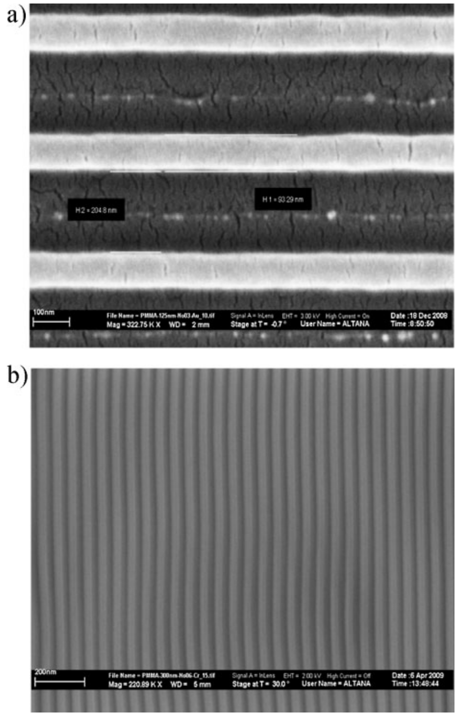

Figure 7.
SEM-graph of a hot embossed structure in PMMA: a. 300 nm period, b. 60 nm period.

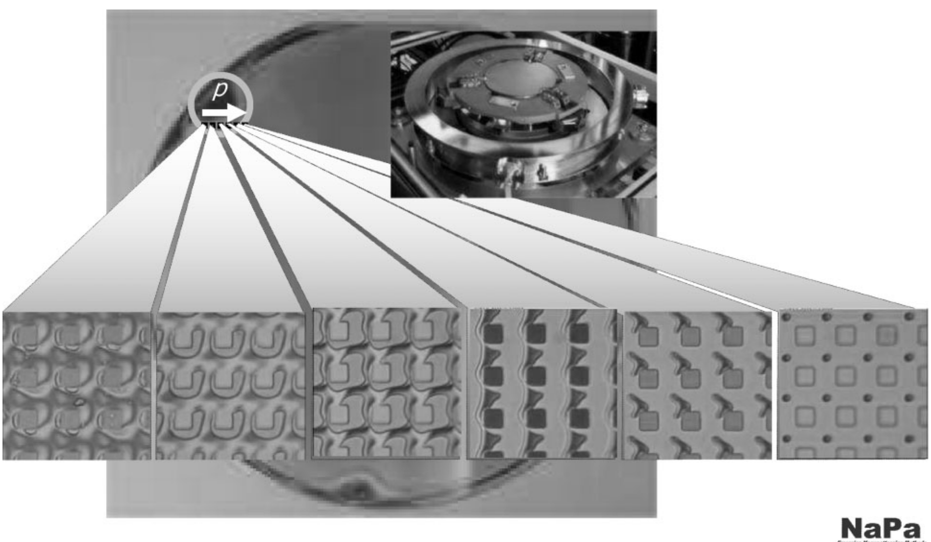

Figure 6.
Sequence of mold filling during the NIL.[3]

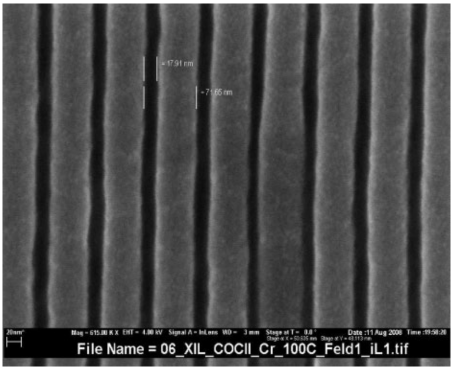

Figure 8.
Lines with a period of 18 nm injection moulded in COC.

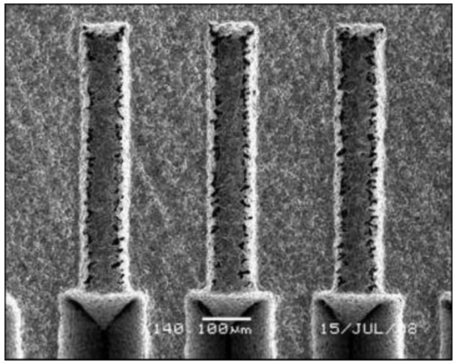

Figure 10.
Mould insert from steel micromachined by laser ablation.

injected into the mould thus giving a completely different filling of the die. The biggest disadvantage compared to NIL is a loss of precision in the replication.

By testing the limits of the injection moulding technique structures with a period of 18 nm were replicated with COC Figure 8!

Applications

Two applications will be shown here more in detail: the replacement of expensive silicon or metal parts and the functionalisation of polymersurfaces with nano-structures.

Figure 9 shows a microcantilever array like it is used in bioanalytics. To replace this silicon part with a polymer part a mould insert for injection moulding was micromachined by laser ablation with a 355 nm-laser (Figure 10).

For optimizing the injection mould and for the theoretically prove of the mould filling simulation with the software Moldflow was done. As a result of the filling study it can be seen in Figure 11 that not all cantilever are filled completely.

By optimizing the parameters on the injection moulding machine finally good parts with COC were produced (Figure 12). The dimensions of the bendable cantilever part are 500x100x30 micrometer. The bended cantilever on the left is due to inaccurate handling.

The polymer cantilevers offer – beside lower cost – a new range of stiffness for the

Figure 9.
Microcantilever array for bioanalytics (source: IBM Research).

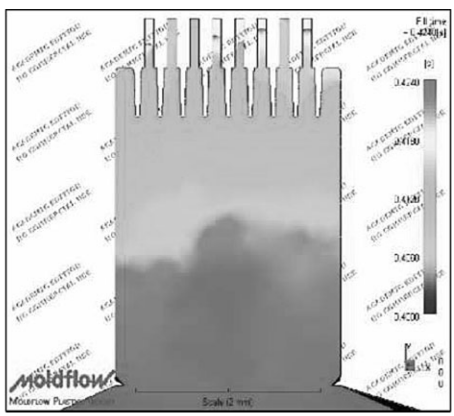

Figure 11.
Filling simulation with Moldflow.

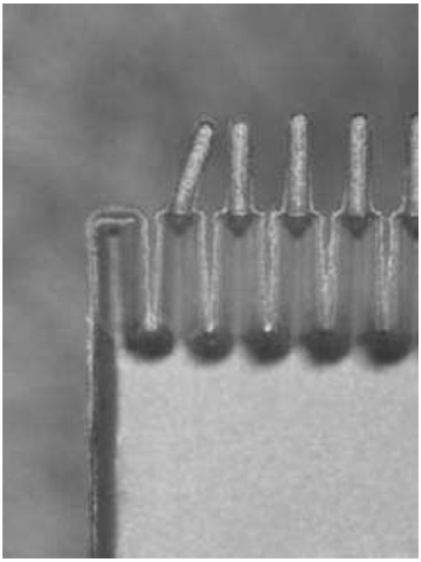

Figure 12.
Microcantilever injection moulded in COC.

analytics which make them very interesting also for new applications.

The second example is the hydrophobisation and hydrophilisation of polymer surfaces. With micro- and nanostructures of polymers wetting angles can be achieved in a very broad range: from smaller than 10 degrees (superhydrophilic) up to 170 degrees (superhydrophobic); depending on the polymer, liquid and structure.

This functionalisation of polymer parts is especially interesting for medical parts or food industry because the material remains unchanged and so no new and expensive approval process is necessary.

Figure 13 shows a SEM-micrograph of 100 nm-grooves in PP. With this grooves the wetting behavior of a medical part with medical liquids could be changed completely. The behavior shifted from hydrophilic to almost superhydropobic Figure 14!

A completely different effect was achieved by high aspect ration columns Figure 15.

The picture sequence in Figure 16 shows the complete disappearance of a drop of a bioanalytic test liquid that was positioned on the structured surface! For water this surface shows completely dewetting properties.

Beside the shown applications there are a many others, at most of them there is research carried out at the PSI as well[4]:

- Radiation grafting of polymers
- Surface patterns for guided self assembly
- Patterned magnetic media[5]
- Metal nanowires
- Structures for nanophotonic and plasmonic devices

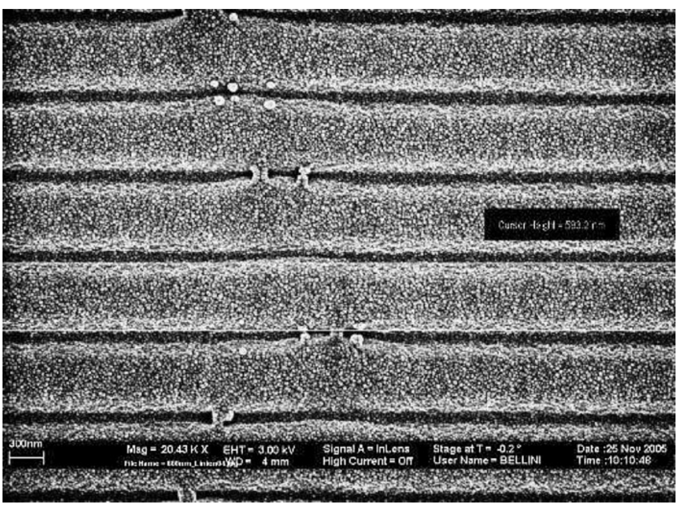

Figure 13.
Grooves with a width of 100 nm in PP.

	liquid 1	liquid 2
smooth surface	66°	70°
100 nm lines	120°	134°

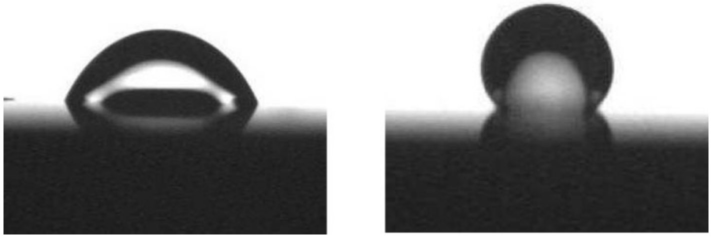

Figure 14.
Hydrophobisation by 100 nm lines in PP.

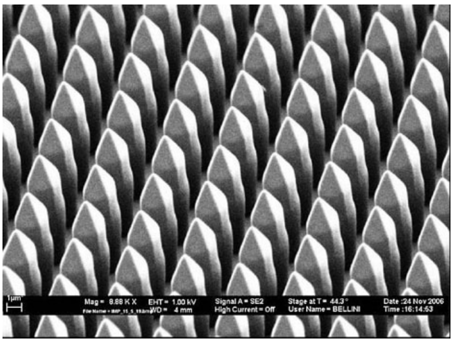

Figure 15.
High aspect ratio columns injection moulded in PP.

- Stamps for nanoimprint lithography
- Nanowire circuits
- 3D Crystal of GeQuantum Dots[6]
- Security features for product identification

Conclusion

E- beam and X-ray interference technologies with a resolution down to about 10 nm are well suited for production of dies / masters / moulds for polymer replication processes. NIL / hot embossing works well for "rapid prototyping" of precise planar micro- or nanostructures whereas micro- and nano-injection moulding is a high potential technology for high volume production in growing markets. The number of products with surface nanostructures that provide new functionalities is expected to increase dramatically.

The aim of our research will be:

- Develop the NIM process to series maturity
- Optimizing the replication fidelity

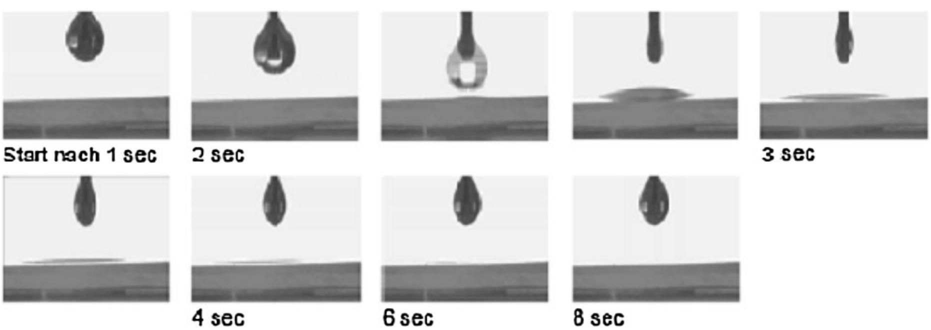

Figure 16.
High aspect ratio columns injection moulded in PP.

- Maintaining a short cycle time (= low production cost)
- Safeguarding a low wear of the precious master tool
- Find out the limits of the NIM technology

Acknowledgements: Part of the work reported here was performed at the Swiss Light Source, Paul Scherrer Institute – PSI and at the University of Applied Sciences Northwestern Switzerland – UASNW. We acknowledge contributions to this work by these students of the UASNW: M. Meier, S. Nedunkanal and B. Keusch.
Also Armin Stumpp of the UASNW is ackowledged for preparing the cantilever steel micromold.

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