SUBSTRATE CONFORMAL IMPRINT LITHOGRAPHY OF FUNCTIONAL MATERIALS – REVIEW OF A BFS-PROJECT

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1. INTRODUCTION

Substrate conformal imprint lithography (SCIL) is an innovative full wafer scale nanoimprint technology[1]. This sub-micrometer patterning method uses flexible PDMS stamps for the structure transfer. Originally, SCIL technology was developed for the transfer of structures into sol gel materials which hardened via diffusion of solvents into the PDMS stamp material. The work of Ji et al.[2] showed the extension of SCIL to UV-enhanced SCIL (UV-SCIL). With this new option, UV curable materials can be used as resists for the SCIL-method.

For the further development of this powerful technology, SUSS MicroTec and the Fraunhofer Institute for Integrated Systems and Device Technology (IISB) initiated the project "Substrate Conformal Imprint Lithography of Functional Materials" (SILFUMA) which was funded by the "Bayerische Forschungsstiftung" (AZ-864-09). As associated partners, DELO Industrial Adhesives and micro resist technologies substantially supported and strengthened the project. SILFUMA was divided into three main work packages. Purpose of the first work package was the evaluation of purely organic resists for UV-SCIL. Common resists for SCIL or UV-SCIL contain inorganic chemistry[2,3]. This fact limits their suitability for dry etching processes. Furthermore, all common resists for SCIL or UV-SCIL need long curing times (3min – 15min)[2,3]. The advantage of purely organic materials used as etching masks is that they are well suited for standard dry etching processes. As shown, another advantage of UV polymers for UV-SCIL is the significant reduction of curing time compared to commonly used resists. So, using UV curing polymers shortens the overall SCIL process time essentially.

The Second part of the project is aimed at simplified stamp manufacturing. The molding of the fragile PDMS stamps from master structures is a process with several complicated steps and needs an experienced operator. Even then, however, many stamp rejections are produced because most process steps can cause defects on the stamp. For an industrial application of SCIL, however, it is necessary to have a rather simple manufacturing process for the PDMS stamps which produce reproducible stamps without any defects. This in turn, requires practical manufacturing tools.

The objective of the third work package was the development of a functional resist material and the evaluation of a UV-SCIL process for such a material. A common structure transfer process uses a structured resist layer as etching mask for an etch process which transfers the structure into a substrate. With a functional resist material, however, the etch process step can be saved and a functional element can be produced directly by UV-SCIL. Therefore, the functional resist material already needs to have the properties necessary for the functional element (e.g. electrical conductivity, permittivity or refractive index). For this purpose, different kinds of nanoparticles (which should provide the functionality) were mixed with polymer matrix materials and the resulting functional resists were evaluated with regard to imprintability and functionality.

2. UV-SCIL WITH ORGANIC UV POLYMERS

For industrial applications, the long curing times of common resists for UV-SCIL[2,3] limit the possible throughput and their inorganic components restrict their suitability for dry etching processes. Using purely organic UV polymers with fast curing times would shorten the overall SCIL process time essentially, and thus enable much higher throughput. In addition, these polymers have the advantage that they are well suited for standard dry etching processes in semiconductor technology. Also, many well-known processes from classical photo lithography with organic photo resists suit for further processing of substrates.

UV-SCIL EMULATION ON NPS 300

For first investigations on promising UV-curing polymers for UV-SCIL, the UV-SCIL process was emulated on a NPS 300 nanoimprint stepper. This emulation of the UV-SCIL process was necessary to be able to test many different polymers without spin coating them and in order to save costs for PDMS stamps. For that, stamp pieces with a size of 1cm^2 were prepared out of the wafer size PDMS stamps. With these small PDMS stamp pieces, imprints into several different manually dispensed UV-curing polymers were performed. The interaction between UV-curing polymers, silicon substrates, and PDMS were analyzed to assess well suitable polymers for UV-SCIL.

The results of those experiments are summarized in Table 1. They show that most of the investigated materials are not suitable for UV-SCIL. For example, some materials have a very strong adhesion to the PDMS stamp after the UV-curing. Other materials could not cure during the contact with the PDMS stamp because of oxygen inhibition[4]: Oxygen diffused from the atmosphere into the PDMS material inhibits the curing of most acrylate based polymers. Only two of the evaluated polymers exhibited suitable properties for UV-SCIL, i.e., mr-UVCur06 and DELO Katiobond OM VE 110707 (highlighted in Table 1). Thus, in the following all required process steps for their use as UV-SCIL resists were developed only for these two polymers.

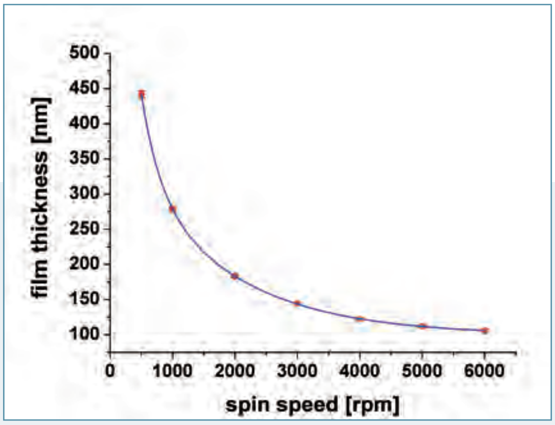

Figure 1. Spin speed curve for Katiobond OM VE 110707 diluted with 83wt% cyclopentanone

SPIN COATING

The deposition of the two most promising polymers (i.e. Katiobond OM VE 110707 and mr-UVCur06) on 100mm silicon wafers was realized by spin coating on the wafer. A manual coating system was used for the material deposition. For mr-UVCur06, a well-known coating process from micro resist technologies was used[5] and for Katiobond OM VE 110707 the coating process was developed within this project. For this spin coating process, Katiobond OM VE 110707 was diluted with cyclopentanone. After that surface conditioning of the silicon substrates, spin coating parameters for a manual coating system, and post coating proces-

Name of tested UV-curing polymer	Polymer base	Imprint result
NOA 61; Norland Products	Acrylates	Weak substrate adhesion
NOA 84, Norland Products	Acrylates	Curing not possible
NOA 89, Norland Products	Acrylates	No substrate adhesion
mr-UVCur21SF, micro resist technologies	Acrylates	Curing not possible
mr-UVCur06, micro resist technologies	Acrylates	Homogeneous imprint
Photobond OM VE 512494, DELO Industrial Adhesives	Acrylates	Curing not possible
Photobond GB310, DELO Industrial Adhesives	Acrylates	Strong adhesion to PDMS stamps
Katiobond OM VE 110707, DELO Industrial Adhesives	Epoxides	Homogeneous imprint

Table 1. Tested UV-curing polymers for UV-SCIL with their polymer base and their imprint result with PDMS stamps

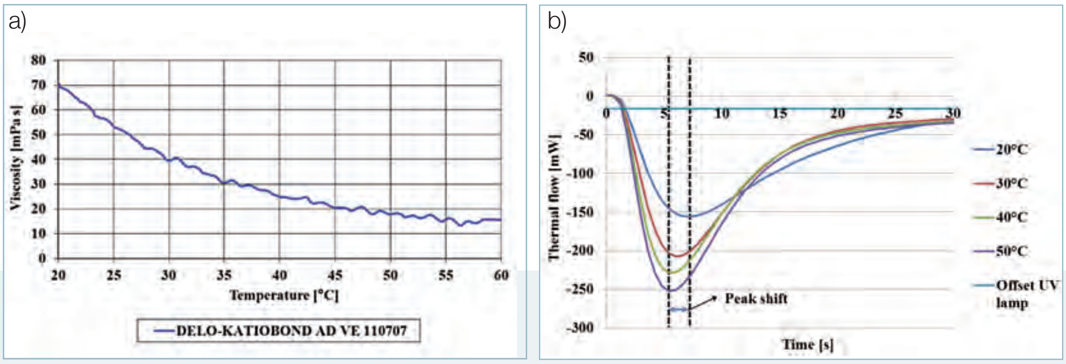

Figure 3. a) Viscosity of Katiobond OM VE 110707 at different temperatures and b) DSC measurement of the cross linking reaction

ses were evaluated. With the developed spin coating process for Katiobond OM VE 110707, film thicknesses from 50nm to 600nm with a standard deviation of 5nm can be achieved. Figure 1 shows a spin speed curve for Katiobond OM VE 110707 diluted with 83wt% cyclopentanone. The spin coating process for mr-UVCur06 uses mr-t 1070 from micro resist technologies as thinner[5]. With the process received from micro resist technologies, the film thicknesses of mr-UVcur06 can be adjusted homogeneously between 70nm and 500nm with a standard deviation of 5nm.

UV-SCIL IMPRINTING

The imprint processes were performed on a MA8/BA8 mask aligner with SCIL upgrade from SUSS MicroTec. The PDMS stamp used for these experiments contains a grating structure for resolution tests with feature sizes ranging from 100nm to 500nm. Figure 2a and Figure 2b show SEM cross section images of an imprinted line with mr-UVcur06 and with Katiobond OM VE 110707. Both imprints were performed with the same PDMS stamp. The comparison between Figure 2a) and Figure 2b) shows that the side walls of the line imprinted with Katiobond OM VE 110707 are much steeper than those of the line with mr-UVcur06.

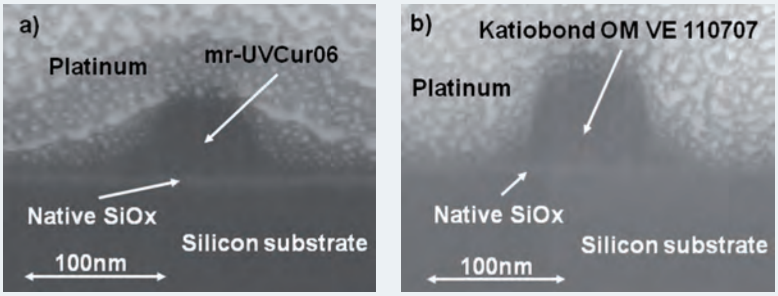

Figure 2a), b). SEM cross section images of an imprinted line with a) mr-UVCur06 and with b) Katiobond OM VE 110707, Platinum deposited for FIB cross sectioning

The exposure times were 17s for Katiobond OM VE 110707 and 3min for mrUVCur06. Compared to all commonly used resists the evaluated curing time for Katiobond OM VE 110707 is very short. The big difference between 17s for Katiobond OM VE 110707 and 3min for mrUVCur06 can be explained by oxygen inhibition of the polymerization of UV curing acrylates. The oxygen diffused in the porous PDMS stamp inhibits the polymerization reaction of the acrylate[4].

The curve of the viscosity measurement of Katiobond OM VE 110707 at different temperatures (Figure 3a) shows that the viscosity is reduced significantly at elevated temperatures compared to room temperature. The principle of UV-SCIL is based on capillary forces. These capillary forces increase with decreasing viscosity. Therefore, increased capillary forces accelerate the filling of structures in the PDMS stamp during the imprint process and, thus, the imprint speed can be increased. This faster imprint speed reduces the overall process time.

The differential scanning calorimetry (DSC) of the cross linking reaction of Katiobond OM VE 110707 at different temperatures indicates that the UV initiated reaction runs faster at elevated temperatures (Figure 3b). Therewith the exposure time at elevated temperatures can be shorter, which additionally reduces the overall process time. The imprint results with Katiobond OM VE110707 and the temperature dependent measurements led to the idea to further reduce the overall UV-SCIL process time by using an electrically heated chuck which then was designed

Chuck temperature	21°C (RT)	30°C	40°C
Exposure time	17 s	10 s	5 s
Imprint speed	3.5 mm/s	5 mm/s	8.3 mm/s
Delay before exposure	20 s	10 s	5 s
Delay after exposure	10 s	10 s	10 s
Separation speed	8.3 mm/s	8.3 mm/s	8.3 mm/s
Process gap	20 µm	20 µm	20 µm
Total process time for 180mm imprint area	**120.1 s**	**87.7 s**	**63.4 s**

Table 2: Evaluated UV-SCIL process times for Katiobond OM VE 110707 at different temperatures of the electrically heated chuck

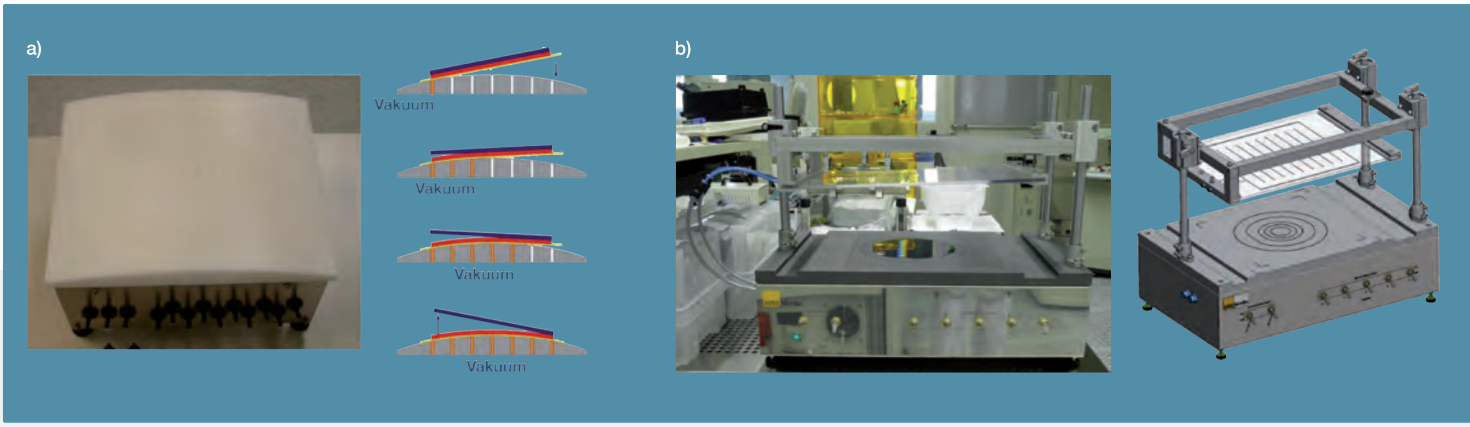

Figure 4a). Schematic drawing of the functionality of the first separation tool and b) pictures of the redesigned tool

by SUSS MicroTec within this project.

Table 2 compares the different UV-SCIL process times for Katiobond OM VE 110707 at different temperatures. It shows that if the temperature of the heated chuck is 40°C, the process time is half of the process time at room temperature because of a higher imprint speed and a shorter exposure time.

3. PDMS STAMP MANUFACTURING

In order to produce defect free PDMS stamps for an industrial application of SCIL it is necessary to have reliable and mature manufacturing tools and a stable manufacturing process. Within the project the tools were partly redesigned for improved usability. With these new tools a stable fabrication process could be achieved. The lifetime and the compatibility of the produced stamps with the Katiobond OM VE 110707 were finally tested with a new low cost method.

REPLICATION AND SEPARATION TOOL

Two different tools are used for the stamp manufacturing: the replication tool and the separation tool. With the replication tool the molding of the master structure is performed. The design of this tool was not changed within the project. Just a construction was added which allows dispensing the PDMS on the master wafer with strongly improved reproducibility.

The separation tool is required for the separation of the cured PDMS stamp with the glass carrier sheet from the master wafer. Figure 4a) shows a schematic drawing of the tool before the redesign. In principle it consisted out of a curved surface with vacuum grooves, where the bond out of PDMS stamp and master wafer was placed on top. By sequential switching of the vacuum grooves the wafer is separated from the stamp. The experimental work with this tool showed that the risk of breaking the stamp using this tool is rather high. Figure 4b) shows a picture of the newly designed separation tool. This tool consists out of a wafer chuck and an up and down movable flexible acrylic glass chuck above. The bond out of PDMS stamp and master wafer can be fixed between those two chucks, top side with PDMS stamp on the acrylic glass chuck and bottom side with the master wafer on the wafer chuck. By turning a screw the acrylic glass sheet can be bended round and the flexible PDMS stamp gets separated from the fixed stiff master wafer. With this new separation tool the risk of breaking stamps within this process step could be strongly reduced.

LIFETIME OF PDMS STAMPS

After the development of an optimized manufacturing process for PDMS stamps with the newly designed tools, the quality and the lifetime of the PDMS stamps were tested. Therefore, again the SCIL process was emulated on a NPS 300 nanoimprint stepper like described before in chapter 2. Here, the emulation was necessary to be able to perform many imprints (>1000) with one stamp in an automated cost effective way. Because of the small stamp size (1cm^2) more than 200 imprints could be performed on one 6inch substrate. The NPS 300 allows programming an automated process where all imprints on one substrate were performed without intervention of an operator. At the NPS 300, the stamp is separated at once from the hardened resist and not peeled off like in the normal UV-SCIL process. This means that there is a higher mechanical wear and the determined lifetime probably gives an underestimation of the lifetime of a real UV-SCIL stamp. The applied imprint resist for these experiments was Katiobond OM VE 110707.

Corresponding results are shown in Figure 5a), b) and c). The SEM pictures show structures in Katiobond OM VE 110707 transferred with the same PDMS stamp. After imprint no. 500

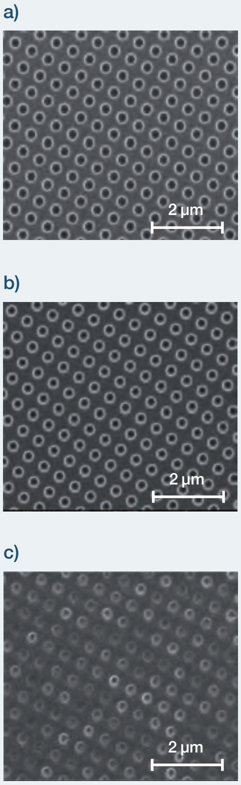

Figure 5. SEM pictures of imprinted patterns in Katiobond OM VE 110707 after a) 1st, b) 500th and c) 1000th imprint

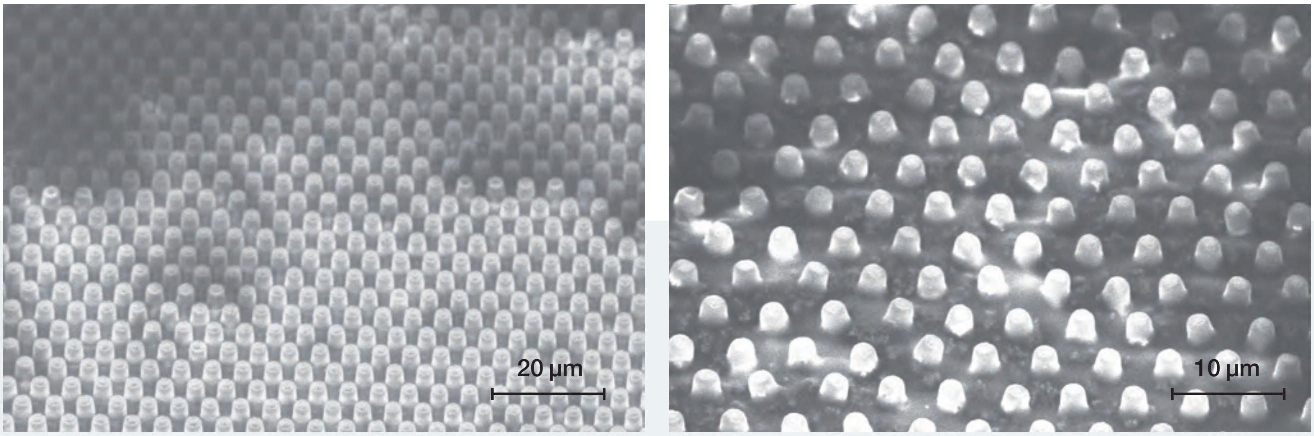

Figure 6. SEM pictures of pillar structures imprinted with UV-SCIL into a silver particle resist layer

(Figure 5b)), the structures are still well defined and no significant difference compared to the structures after the first imprint (Figure 5a)) can be detected. Compared to imprint no. 1, on the other hand, the structures after imprint no. 1000 (Figure 5c)) are weakly defined and diffuse. The PDMS stamp shows strong mechanical wear after 1000 imprints. In summary, these experiments show that minimum 500 imprints can be performed with the PDMS stamps for UV-SCIL.

4. FUNCTIONAL MATERIALS

For the design of functional resist materials for UV-SCIL different nanoparticles were mixed with UV polymers. Several different UV polymers served as matrix material for the nanoparticles. Two kinds of nanoparticles were investigated, silver particles and silicon dioxide particles. The silver particles were supposed to create a material with a certain electric conductivity. The functional resist composed out of silicon dioxide particles and a UV polymer could serve as a printable material for e.g. anti-reflection layers.

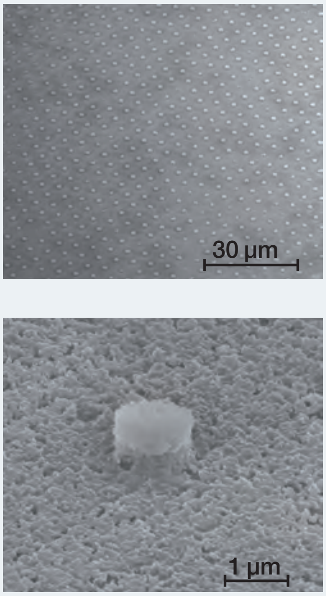

Figure 7. SEM pictures of pillar structures imprinted with UV-SCIL into a silicon dioxide particle resist layer

The first step for both materials was to disperse and to stabilize the particles in the polymer matrix. Therefore, many different dispersing methods were tested. Finally, the best results for both systems could be achieved with an ultrasonic finger. With this technique the application of energy into the particle-polymer-mixture was high enough to break agglomerated particles. The functional materials with homogenously dispersed nanoparticles are stable for some hours. The material deposition of both systems on different substrates was realized with developed spin coating processes.

FUNCTIONAL MATERIAL WITH SILVER PARTICLES

The specific resistance of the functional material was measured with the van der Pauw (vdP) method. Therefore, structures for vdP measurements were fabricated with nanoimprint lithography. After some post processing steps to remove the polymer matrix and to bake the particles together the measurements were performed. The lowest measured specific resistance was $1.8*10^{-5}\Omega$*cm. This value is in the same range as the specific resistance of commercially available silver inks treated with the same post process. In comparison, the specific resistance of bulk silver is $1.6*10^{-6}\Omega$*cm. As the size of the silver particles in the silver ink is of several micrometers, the inks cannot be used for the direct imprinting of functional elements in the micro- or even nanometer range. Figure 6 shows SEM pictures of pillar structures imprinted with UV-SCIL into a silver particle resist layer. The UV-SCIL process with the silver particle resist enables the transfer of structures in the µm range (<10µm). However, after the imprint, the PDMS stamps showed strong impurities. Residuals of the resist stuck on the PDMS surface of the stamp. Therewith, the stamps could only be used for one imprint with this material.

FUNCTIONAL MATERIAL WITH SILICON DIOXIDE PARTICLES

After testing different post processes for spin coated silicon dioxide particle containing resist layers SEM pictures showed that after an 1100°C annealing step the silicon dioxide particles form a compact layer. Annealing steps between 340°C and 900°C remove the polymer matrix and leave a porous fragile silicon dioxide layer. Figure 7 shows SEM pictures of pillar structures imprinted with UV-SCIL into a silicon dioxide particle resist layer. Compared to the process with the silver resist, only little impurities were observed on the stamp after imprinting. These impurities can be removed by rinsing the stamp with 1% HF solution. With such silicon dioxide resist antireflection layers on e.g. solar cells can be fabricated by UV-SCIL without further complicated etch process steps or material deposition.

5. CONCLUSION

The SILFUMA project introduced for the first time two kinds of fully organic polymers for UV-SCIL, Katiobond OM VE 110707 and mr-UVCur06. Using these polymers for UV-SCIL, the exposure time and thus, the overall process time can be reduced essentially compared to all commonly used resists. Especially with Katiobond OM VE 110707 and an electrically heated chuck, the exposure time was reduced down to 5s. Additionally, the fully organic polymers are well suited for standard dry etching processes in silicon technology. Many well-known processes from classical photo lithography can be used for further processing of substrates.

Within this project the manufacturing process for PMDS stamps was strongly simplified and matured by reconstructed replication and separation tools. The risk of breaking stamps was strongly reduced using the redesigned tools. With a developed process, defect free stamps can be manufactured that have a lifetime of more than 500 imprints.

First experiments with two different functional materials showed that the direct imprinting of functional elements is possible. A functional resist for UV-SCIL with silver nanoparticles dispersed in a polymer matrix enables the direct imprinting of conductive elements. With a functional resist containing silicon dioxide particles, the direct imprinting of e.g. an antireflection layer is possible by UV-SCIL. Therewith, these resists enable new applications for UV-SCIL.

Acknowledgments

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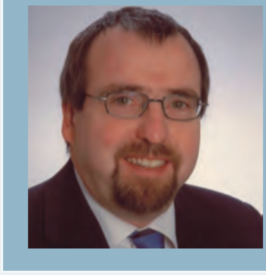
Robert Fader studied physics at the Friedrich-Alexander-University in Erlangen. After graduating in 2010, he continued doctoral research at the Fraunhofer Institute for Integrated Systems and Device Technology IISB in Erlangen in electrical engineering. Subject of his doctoral thesis is Substrate Conformal Imprint Lithography.

Holger Schmitt studied material science at the Friedrich-Alexander-University (FAU) in Erlangen. After graduating in 2004, he continued doctoral research at the "Chair of Electron Devices" at the FAU in Erlangen. He received his doctoral degree in 2008. The title of his doctoral thesis was "Investigation of the UV nanoimprint lithography as patterning technique for electron devices". Currently he is working for the BROSE Fahrzeugteile GmbH in Hallstadt.



Michael Hornung is Technical Marketing Manager at SUSS MicroTec Lithography based in Garching, Germany. During his career at SUSS MicroTec he passed further functions. So he was project manager in R&D responsible for the (nano) imprint technology and other new technologies for mask aligners. He also worked as application engineer for a while and leads the application group at SUSS MicroTec for two years. Before he joined SUSS MicroTec he was project manager at CERN in Geneva, Switzerland, working at the inner detector for the ATLAS project. Michael Hornung holds a Ph.D. degree in Natural Science from the University of Freiburg, Germany and an MBA from the University of Applied Science of Ludwigsburg, Germany.