MR-NIL210FC_XP – A VERY PROMISING RESIST FOR EMPLOYMENT OF SCIL TECHNOLOGY IN HIGH VOLUME INDUSTRIAL APPLICATIONS

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In this work, the performance of the recently developed imprint resist mr-NIL210FC_XP for UV-enhanced substrate conformal imprint lithography (UV-SCIL) from SUSS is evaluated. One major benefit of the material for UV-SCIL is a strongly reduced diffusion behavior of mr-NIL210FC_XP into the PDMS-based SCIL stamps compared to other organic resists. This results in an increased stamp lifetime. A complete imprint process was developed, showing a full wafer pattern transfer while addressing some of the major requirements for production processes, like resist storage time, pattern transfer fidelity and reproducibility, as well as stamp lifetime. The imprinted structures of 50 consecutive imprint processes (including successful automated separation) were found to be highly reproducible, showing height variations well below +/- 2.5 % within individually measured areas. Further tests showed that storage times of at least one week can be applied without any noticeable effect on the imprint result. In order to complete the process chain, the imprinted microstructures were successfully etched into silicon showing homogeneously etched structures.

Nanoimprint lithography (NIL) has been established as a very versatile parallel patterning technique for the fabrication of various functional nanosized features in scientific and industrial devices, e.g. wire grid polarizers, diffractive optical elements, or photonic structures [1, 2]. Over the course of the last years, particularly soft NIL techniques using flexible polydimethylsiloxane (PDMS) stamp materials gained much attention due to their great advantages compared to hard and rigid stamps typically employed in conventional NIL processes [3]. Specifically, soft NIL is very much predestinated for a full wafer patterning of large wafers in one single imprint step [4]. The flexibility of the SCIL stamp leads to a surface conformal imprint ensuring much less sensitivity to particle induced imprint defects because they can be easily overprinted and offers the potential for a patterning of non-planar and other arbitrarily shaped substrate surfaces.
However, the great majority of the currently used soft NIL resist materials suffer from a limited compatibility to PDMS based stamps as resist components like monomers reveal a pronounced propensity to permeate into the PDMS matrix of the stamp. As a consequence of this permeability, the crosslinking of resist components diffused into the PDMS matrix, will result e.g. in the formation of an interpenetrating polymer network at the interface between stamp and resist after several imprints, so that significant tear-off imprint defects during the stamp separation step are very likely to occur. Even before tear-off defects arise, the polymer matrix leads to higher adhesion forces, which can hinder an automated separation. In both cases, the phenomenon significantly reduces the lifetime of a PDMS stamp and thus limits also its utility in a high volume production process. This limitation is particularly relevant when a SCIL working stamp is used for several subsequent imprinting steps, as it would be an essential requirement for an efficient integration of this technology into industrial manufacturing processes [5]. Accordingly, there is a high demand for new soft NIL resists featuring a significantly improved PDMS-stamp compatibility.
In order to address this demand, **micro resist technology GmbH** has developed a new organic photo-curable resist for soft NIL, called mr-NIL210FC_XP. This new NIL resist is a further development of the previously launched mr-NIL210. The mr-NIL210FC_XP formulation contains additional compounds able to effectively suppress the influence of oxygen during the curing reaction, and therefore the cross-linking of the resist components proceeds typically very fast. Hence, imprints can be conducted very readily by applying relatively low illumination intensities in the range of only 10-15 mW cm^{-2} compared to approx. 40 mW cm^{-2} of the predecessor mr-NIL210. Practically, this feature becomes in particular very relevant for the imprinting of resist films with thicknesses significantly below one micrometer, where the impact of the oxygen towards the curing reaction is intrinsically much more pronounced than for thicker films. However, all other resist parameters of mr-NIL210FC_XP are very comparable to those of mr-NIL210 like the outstanding film forming and adhesion characteristics, enabling an extended storage time of spin-coated films over several days without

revealing any negative effects on the film quality. And as the mr-NIL210FC_XP contains only components that feature a very low tendency to permeate into the PDMS matrix of the stamp, imprint defects like adhesion or cohesion failures are very unlikely and adhesion forces are generally reduced, leading thus to a largely prolonged stamp life-time.

The current article details the results of the collaboration project between **Fraunhofer IISB, micro resist technology GmbH,** and **SUSS MicroTec** to fully qualify the new mr-NIL210FC_XP resist within the UV-enhanced substrate conformal imprint lithography (UV-SCIL) from SUSS. The aim was to define and characterize a complete imprint process for an exemplary application, namely etch mask structures usable for patterned sapphire substrate (PSS) fabrication.

For the qualification of the novel UV-NIL resist, all important parameters connected to imprinting were analyzed and partially optimized, like curing time or long-term stability of the uncured resist film, pattern transfer quality, residual layer analysis and stamp lifetime. To define the lifetime of a stamp there exist two different criteria: Firstly, it can be described by the number of imprints before significant stamp degradation would affect feature transfer. It has been previously demonstrated that PDMS stamps could, depending on different parameters, sustain up to several hundred imprints before showing damaging [6]. Secondly, and more pertinently to industrial processes, the definition of stamp lifetime refers to the reached number of automated separations between stamp and imprint before tear-off defects start arising from the imprint process. This latter definition is employed in the current article because automated separation is an essential process step within the applied UV-SCIL technology. Therefore, 50 consecutive imprints were performed with two different stamps without any observable change in separation behavior. Finally, etching experiments were performed to define the etching behavior of this material during reactive ion etching (RIE) into silicon.

SCIL PRINCIPLE AND EQUIPMENT SETUP

Substrate Conformal Imprint Lithography (SCIL) is a NIL technique developed within a collaboration between Philips Research and SUSS MicroTec. It bridges the gap between UV-NIL using rigid stamps for best structure transfer fidelity and soft stamps for imprinting larger substrates with a single imprint step. SUSS mask aligners can be upgraded with SCIL technology, enhancing the aligner's capability by supporting nanoimprint of features with critical dimensions below 50 nm on areas with a diameter of up to 200 mm.

The core blocks of the SCIL principle are (a) the stamp and (b) the imprint procedure. The SCIL stamp is composed of several flexible layers of different blends of PDMS glued to a thin glass carrier. The in-plane stiffness (i.e. the stiffness against lateral distortions) of the thin glass carrier (AF-32, Schott) and the high-modulus X-PDMS (Philips Innovation Services) material of the structured layer minimize lateral distortions during stamp preparation (shrinkage) and imprinting (expansion). The out-of-plane flexibility of the glass carrier and the elasticity of the soft PDMS buffer layer (Sylgard 184) allow the stamp to adapt to the unevenness of the substrate. In addition, the soft PDMS buffer layer provides tolerances to particles between stamp and imprinted substrate.

In order to achieve conformal contact over a large area at low imprint pressure, the SCIL technology *(link)* uses a process of sequentially bringing stamp and wafer into contact with each other. This sequential contact mechanism prevents from trapping air pockets in between the stamp and the substrate and ensures that the stamp follows the (possibly) uneven topography of the whole substrate surface. For the current project the SCIL tooling was used in combination with a SUSS MA/BA8 Gen4 *Pro* mask aligner.

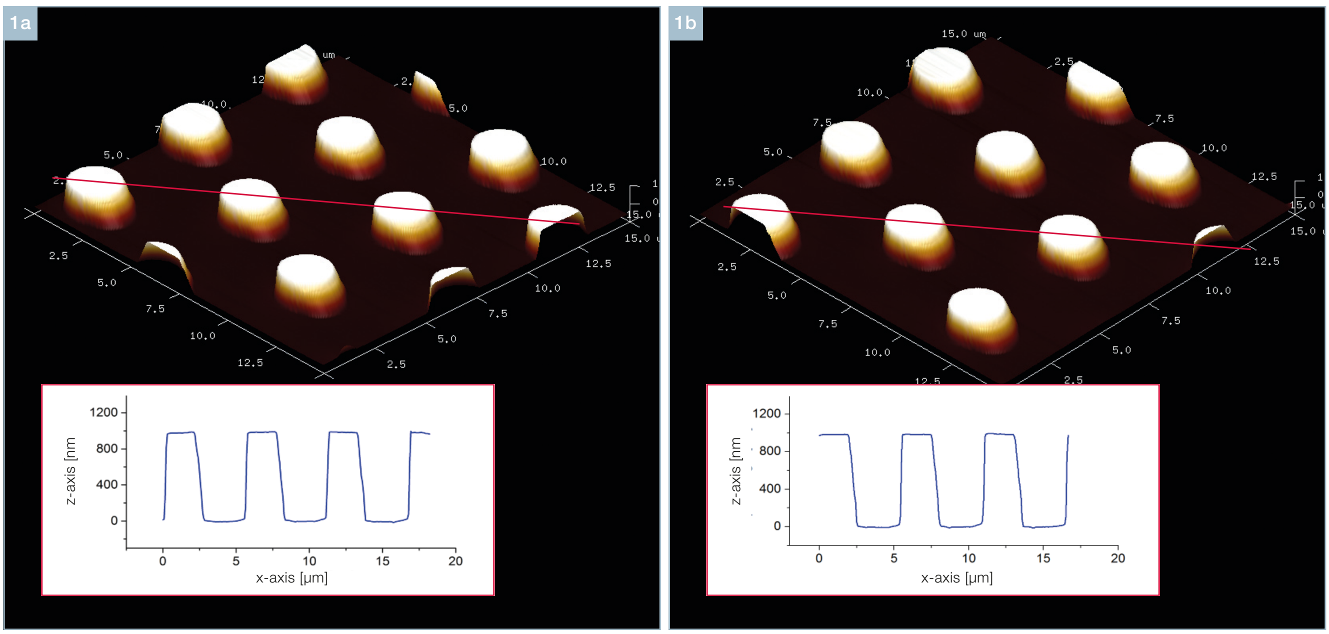

Figure 1 Images of AFM height measurements of imprinted pillar structures in mr-NIL210FC_XP located (a) between two vacuum groves and (b) below a vacuum grove (imprint parameters are given in the text)

STAMP MASTER DESIGN AND PREPARATION

The master chosen for the present work was a 150 mm Si wafer containing periodic pillar structures, produced by Fraunhofer IISB via a standard optical lithography process. The dimensions of the pillar structures were the following: pitch 5.6 µm; pillar diameter 2.2 µm. The silicon master showed inhomogeneous etching depths (i.e., pillar heights) ranging from approximately 940 nm to 990 nm (5 % variation over the average pillar height of 965 nm). Since the SCIL working stamp is a one-to-one copy of the master it also showed the same height distribution, which has to be considered when comparing different positions within one imprint or between different imprints. Two identical tri-layered SCIL stamps were produced, one for process demonstration, the second for results validation.

OPTIMIZATION OF PROCESS PARAMETERS AND EVALUATION OF EASE OF RESIST APPLICABILITY

Four imprints were performed using three different exposure times: 30, 60, and 180 seconds. For the setup of this project it was found that after 60 s the structures were fully cured, so that no material re-flow would occur after stamp separation leading to height differences in the imprinted pillars over the whole substrate area (for example, due to the the vacuum groves of the stamp holder [8], as shown in Figure 1, measured by atomic force microscopy (AFM). The average structure height between two vacuum grooves (Figure 1a) was evaluated to be 989 nm +/- 1.4 % and underneath a vacuum groove (Figure 1b) to be 986 nm +/- 1.6 %.

For the investigation of the resist workability over time three wafers were coated with mr-NIL210FC_XP and afterwards soft-baked for 2 min at 90° C. Different storage times before the

Time lag between initial wafer coating and imprint	Simulation of different fabrication procedures	Average pillar height (nm)
10 min	Alignment	959 +/- 2.5 %
1 day	Full-cassette processing	964 +/- 1.3 %
7 days	Shipment between facilities	958 +/- 1.3 %

Table 1 Average AFM height measurement data of mr-NIL210FC_XP pillars imprinted at different times after initial wafer coating

imprinting of the coated wafers were applied, to cover and simulate possible cases that can occur in a production environment: The first imprint was performed 10 min after the soft-bake (typical time to perform fully manual alignment), the second imprint 24 hours after the soft-bake (typical time to coat and process a complete cassette of wafers), and the third imprint after 7 days storage time (e.g. for the case that the coated cassette of wafers would be transferred between different facilities or other unexpected production uncertainties). During that time, the wafers were stored in a not-sealed wafer box in cleanroom environment. No difference in resist film quality was observed and, more importantly, also the imprint performance was not affected, even 7 days after the wafers had been initially coated. The resist film remained uniform without any noticeable degradation, material reflow or agglomeration effects. Further on, the quality of the imprinted substrates was within the master specification, as monitored by AFM measurements and summarized in Table 1.

Due to this outstanding film characteristic of the newly developed mr-NIL210FC_XP resist, prepared films facilitate industrial processes as they can be stored after spin-coating over several hours and days.

EVALUATION OF THE IMPRINTING PERFORMANCE OF MR-NIL210FX_XP FOR UV-SCIL

Another main part of the project was to investigate the quality of the structure transfer from the SCIL working stamp to mr-NIL210FC_XP imprint resist. Therefore, five imprints with identical parameters applying the described SCIL working stamp with microsized hole structures were performed on 100 mm Si substrates and for each of them five different positions were analyzed, by scanning electron microscopy (SEM) as well as atomic force microscopy (AFM). Figure 2 shows the high level of uniformity from one of the example cases.

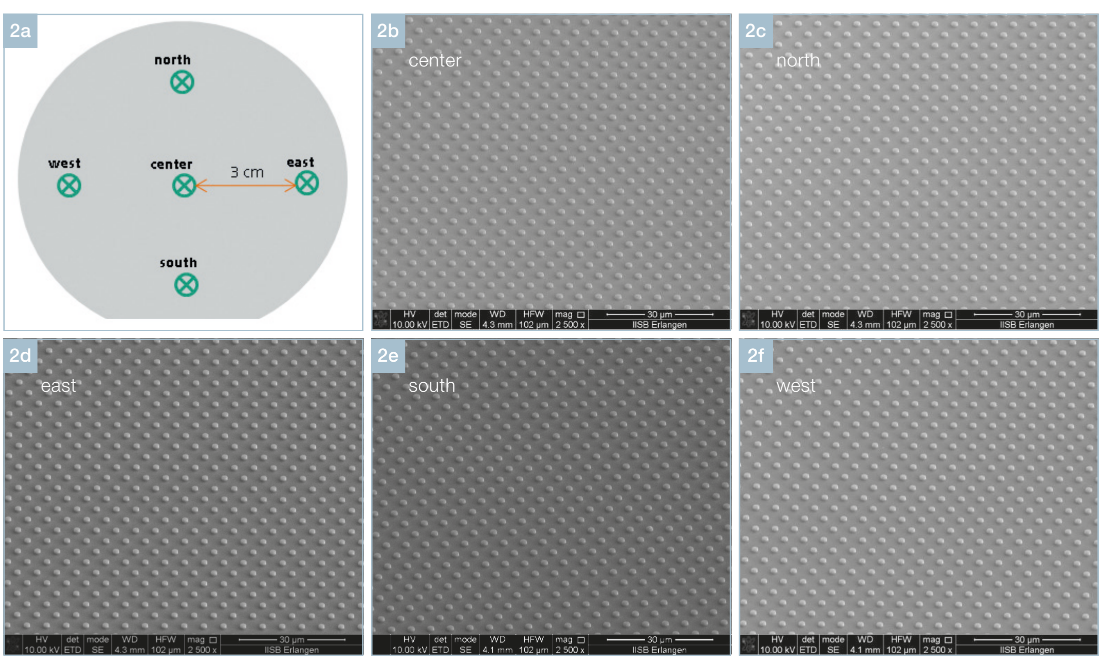

Figure 2 Ilustration of inspected positions for each wafer (a) and corresponding SEM images of imprinted structures at defined positions taken from the first wafer (b-f). Images are tilted by an angle of 52°

The SEM-images show fully transferred and defect-free qualitative results of the imprinted pillars for every investigated wafer at all inspected positions. AFM measurement results confirm the impression of the SEM images with quantitative data. The structure height does not change systematically for all investigated wafers and positions, laying within the master specifications.

Since a residual layer (RL) value significantly smaller than the feature height is important for further process steps such as etching, RL analysis was performed using SEM investigations at five different positions (see Figure 3). To optimize the final RL thickness, several resist thicknesses have been analyzed via modulating the spin coating recipe and then performing an imprint to measure the resulting RL. By varying the spin speed between 6000 rpm and 6500 rpm, the resist thicknesses (of the soft-baked but not yet UV-cured resist before imprinting) ranged from 170 nm to 180 nm. During the imprint step, the SCIL stamp features will be filled with resist by capillary forces. Within this work, given the height of the master pillars, a RL thickness below 100 nm was targeted and all substrates coated with the spin speeds as mentioned above achieved this requirement. The dependence between the coated layer thickness and the spin speed also showed the potential to achieve even smaller residual layer thicknesses, as the measured RL values decreased within the investigated samples from about 90 nm - 100 nm down to about 50 nm - 60 nm.

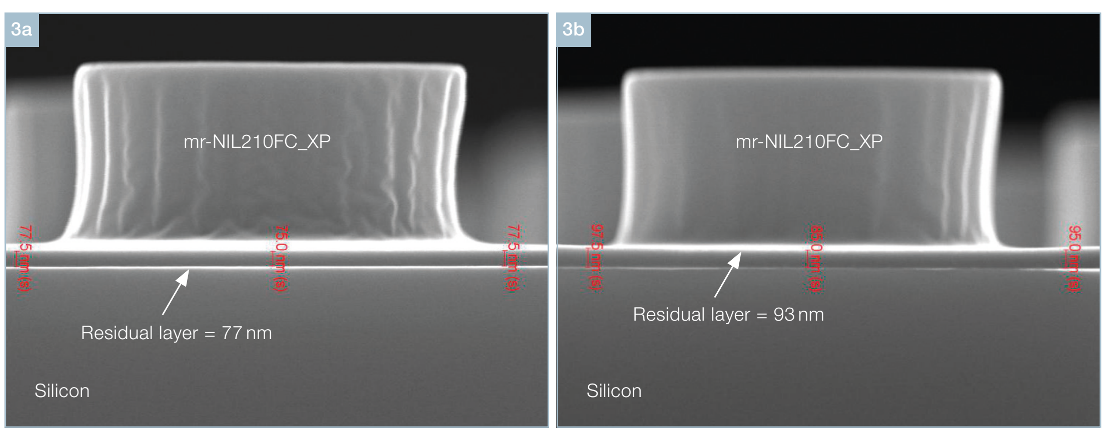

Figure 3 SEM-images of micro pillars imprinted in mr-NIL210FC_XP. The observed pillar sidewall roughness and shrinkage are considered to derive from the applied 10 kV acceleration voltage during SEM imaging; the left image had a longer observation time than the right one

INVESTIGATION OF AVERAGE STAMP LIFETIME

As aforementioned for standard SCIL stamps the critical aspect regarding stamp lifetime is typically the automated separation. In order to show the capability of mr-NIL210FC_XP regarding stamp lifetime, 50 consecutive imprints were performed with a first stamp and validated by repeating the tests with a second stamp. In both cases, at least 50 imprints were performed successfully with automated separation, and they all showed a high pattern transfer fidelity. To prove the latter, the first, the twenty-fifth and the fiftieth imprint were analyzed and compared to each other.

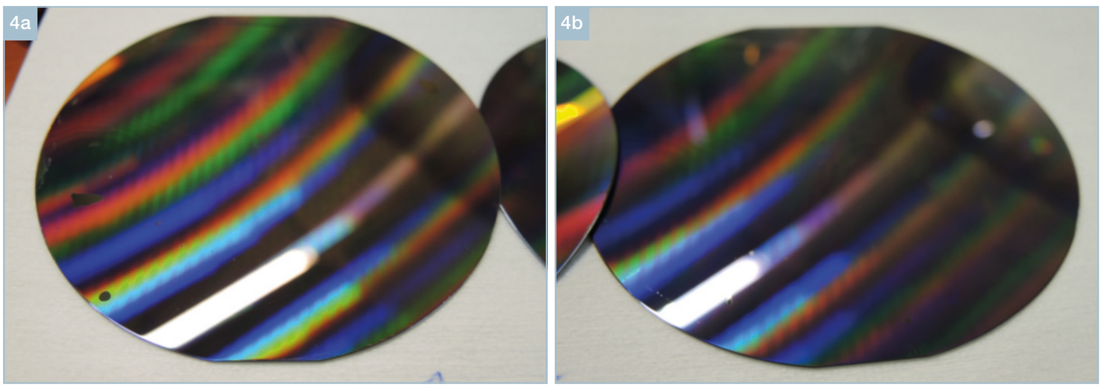

Figure 4 *Photographs of imprint results showing the 1st (a) and the 50th (b) imprint into mr-NIL210FC_XP consecutively processed using one single SCIL stamp*

From the analysis of the results from those imprints, it was clear that more imprints could have still been successfully carried out but an extended stamp lifetime qualification was out of the scope of the present project, and it is planned for follow-up experiments. Figure 4 shows pictures of two imprinted wafers out of the 50 consecutive imprints. The automatic separation of the stamp from the fiftieth imprinted wafer (see Figure 4b) was as easy as for the first one (see Figure 4a). All SCIL specific process parameters (e.g., chuck vacuum) remained unchanged over the course of the imprint study. No yellowing or turbidity or other detrimental effects, as already shown elsewhere with different process conditions [7], were observable on the stamp after the imprints, indicating an extremely low migration of by-products from the curing process from the resist into the PDMS materials. SEM investigations (not shown here) as well as AFM measurements revealed no changes of the dimensions of imprinted patterns (Figure 5).

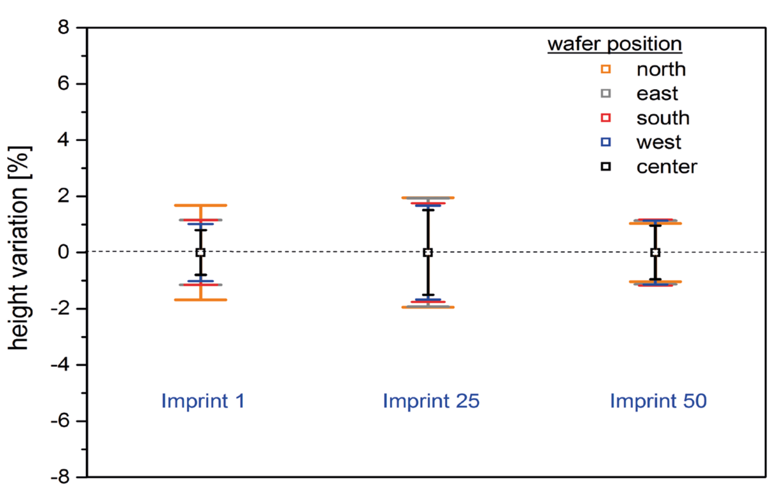

Figure 5 *Average pillar height variation of investigated wafers for lifetime evaluation tests from three different imprints, determined with AFM. The height variation is well below 2 % of the absolute value for each individual imprint (one measurement position covered an area of 15 µm by 15 µm). The total values between different positions are ranging from 890 nm to 950 nm (3 % variation over the average pillar height of 920 nm) with no observable trend with increasing imprint number. These results correspond well to the inhomogeneous etching depth of the master wafer. The small reduction in total height compared to the master of below 4 % can be explained by a common material shrinkage*

ETCHING RESULTS USING HBR RIE PROCESS

As in previous investigations, HBr was chosen for etching of the silicon substrate and Ar-sputtering was employed for removal of the residual layer [8]. All experiments were performed using a Plasmalab 100 system from Oxford Instruments Prior to HBr etching evaluation with mr-NIL210FC_XP, the removal of the residual layer was optimized. Therefore, three samples were treated with 50 sccm Ar at 125 W RF and 800 W ICP power at a chamber pressure of 10 mTorr. The process time was varied between 30 sec, 45 sec, 60 sec and 90 sec. Judging from optical microscope images, the residual layer was apparently removed after 45 sec. Samples were inspected with AFM and SEM to gain depth values of the pillars for each etching experiment.

From standard photolithography applications it is already known that a conducted hard-bake of the patterns before the dry etching for pattern transfer is able to further increase the etching stability of a resist. In order to demonstrate the usability of this approach for UV-NIL, we have performed etching experiments with and without such a hard-bake. After the performed hard-bake of the imprinted structures, no pattern reflow of the pillars was observed, which is a necessary requirement for such an approach. The silicon substrate was structured using 50 sccm HBr at 125 W RF and 800 W ICP power at a chamber pressure of 15 mTorr. Etching experiments without a previously performed hard-bake showed etching rates for mr-NIL210FC_XP of about 90 nm / min. For those samples where an additional hard-bake (100° C, 1 min) was applied the etching rate was below 72 nm / min, leading to an etch selectivity compared to silicon of 1.04 using this particular dry etching recipe applied in our investigations. Etching tests were performed with 2 min and 4 min process time to evaluate the etching rate. A long term etching process (lasting 10 min) resulted in 620 nm deep etched pillar structures with still some remaining resist on top of the pillars. This shows that even higher pillars can be etched using this recipe for longer etching time. The SEM images in Figure 6 show the corresponding etching results. They demonstrate very vertical side walls of the transferred pillars into Si, displaying the excellent usability of the applied UV-NIL resist for RIE etching.

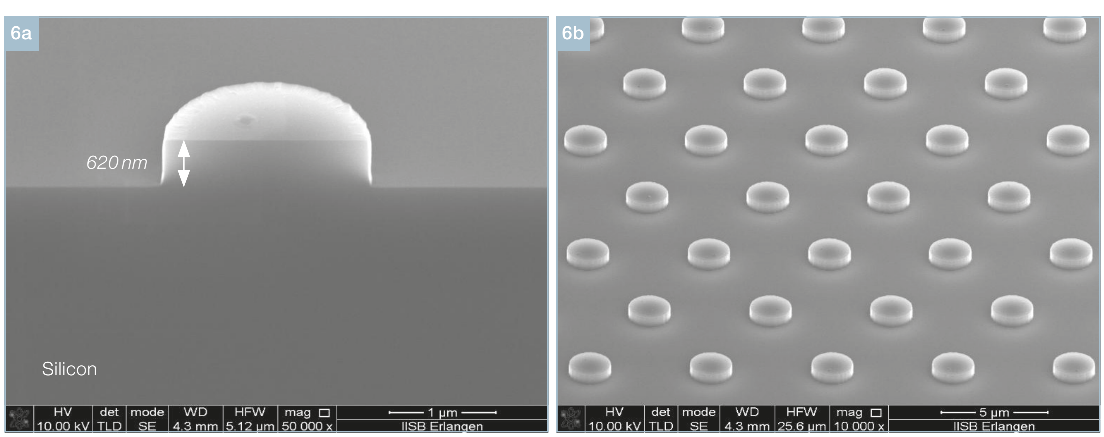

Figure 6 *SEM images after RL removal with Ar sputtering and 10 min HBr etching into silicon. The samples underwent a hard-bake step before etching as discussed above. The left image shows the cross-section of a pillar, where the focal plane is located at the front most part of the feature, to highlight the sharpness of the pillar edges. The roundness of the background portion of the pillar is caused solely by the optical defect from the defocusing. On the right side, an overview to demonstrate the homogeneously etched pillars. Etching depth was 620 nm*

CONCLUSION

A good chemical match between the nanoimprint material and the PDMS stamp is key to enhance stamp lifetime, and, thus, a door opener towards high volume industrial employment of the SCIL technology. The in-depth investigations conducted in the frame of the present work indicate and thus promote the applicability of the UV-SCIL technology in industrial manufacturing processes enabled by the excellent match between the newly developed UV-NIL resist mr-NIL210FC_XP and this particular imprint technology. This success is based on newly implemented resist features, namely excellent film forming and film storage properties, a high imprint fidelity, a fast cross-linking of the resist material due to a very low oxygen sensitivity of the curing reaction when using PDMS stamps, and an excellent pattern transfer fidelity into substrate materials exemplarily shown for silicon and HBr as etch gas in a RIE dry-etch process. Especially of interest for a UV-SCIL application, no influence of the inhomogeneous UV-intensity due to the vacuum groves was found using this UV-resist. Moreover, in the frame of an imprint study with the mr-NIL210FC_XP we could verify that at least 50 consecutive imprints can be conducted with one single SCIL stamp without revealing any indication of a decrease of the imprint quality, indicating that the stamps could have been further employed for many more imprints; an extended stamp lifetime qualification was out of the scope of the present project, and it is planned for follow-up experiments. This highlights that the combination of the UV-SCIL technology with this resist is very suitable for high-volume fabrication processes.

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