Innovative and Tailor-made Resist and Working Stamp Materials for Advancing NIL-based Production Technology

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As a new manufacturing technique based on replication of surface topographies, nanoimprint lithography makes specific demands on materials used as resists for pattern transfer, as molds during replication or as functional materials for permanent application. Thus, highly specialized polymer solutions play a key role for the innovations in nanoimprint-related production technology where a high-throughput and low-cost nanolithography step is performed. In this contribution, recent material innovations at micro resist technology GmbH are reviewed with focus on OrmoStamp® as versatile working stamp material with superior mold properties and its unique applicability to various nanoimprint processes. It is shown by the example of multidimensional nanofluidic devices how tailor-made materials facilitate mass production of innovative applications using nanoimprint lithography.

Keywords: nanoimprint lithography, hybrid polymer, functional material, anti-adhesive property, release force, polymeric working stamp, nanofluidics

1. Introduction

Nanoimprint lithography (NIL) is a promising candidate for high throughput and low-cost nanofabrication processes covering a variety of applications such as nanophotonic devices, bit-patterned media, light emitting diodes (LED), but also (bio)sensors and lab-on-chip devices. While NIL-based nanofabrication is currently in transition from a R&D motivated background to a real industrial production environment, the general acceptance and applicability of NIL is closely linked to the availability of suitable material systems. Specific demands originate from the variety of possible applications as well as the fact, that NIL is a contact-based technology, where an exact replication of a stamp surface topography is generated via molding. This applies for standard thermal and UV-based NIL (T-NIL and UV-NIL) processes as well as advanced step-and-repeat (S&R) or roll-to-roll methods (R2R).

There are three major needs for innovative materials in NIL: resists used for pattern transfer, master replica to replace the stamp original and functional materials for permanent application. While only the first case makes specific demands on pattern transfer (e.g. etch selectivity), in all three cases tailored mechanical, thermal and/or surface-related properties enhance reliability and throughput in production. Furthermore, stamp lifetime, fast processing times and attractive cost structures have to be considered as well as specific pattern functionality such as optical absorption. Besides this, NIL materials have to fulfill a range of requirements to ensure the adaptability to individual equipment and should enable process chain integration for applications from R&D environments to large-scale industrial production.

In this work, we review on recent innovations of NIL materials provided by micro resist technology GmbH and show their applications in a technological context. We highlight a polymeric mold material and present its suitability by means of selected technology implementations. NIL-based mass production capabilities will be described by an exemplary nanofluidic application with ultra-high resolution features.

2. Materials

2.1 Working stamps

The success of NIL is based on the fact that high resolution stamp originals can be fabricated in silicon and quartz using standard silicon micro and nano manufacturing equipment. However, it becomes a key aspect for the setup of new
processes, surface enlargement or real mass production, to have access to reliable, low-priced and easy-to-manufacture working stamps when replacing the valuable master. While NIL has the inherent capability to fabricate master copies by imprint and pattern transfer [1], polymeric master copies generated by simple molding process have several advantages: it provides an exact surface topography with replicated 3D features and shapes, it allows to generate transparent stamps from non-transparent silicon masters, it enables the fabrication of negative and positive surface topographies by multiple copying, and it facilitates the generation of specific mold shapes and combinations of properties by hybrid approaches which were not attainable so far. An additional general benefit of using polymeric working stamps is the possibility to integrate anti-sticking properties in the polymer system in order to effectively lower the release forces. However, the polymer system applied for working stamps should still offer resolution and hardness parameters similar to silicon and quartz.

This can be accomplished by using a material which offers the advantages of both silicon and polymers, such as inorganic-organic hybrid polymers. According to the requirements of NIL, the UV-curable OrmoStamp® was developed [2] for the purpose of simple and cost-effective stamp copy manufacture [3]. It can be used for both thermal and UV-NIL and therefore is ideally suited to replace silicon and quartz molds. It also provides an alternative to electroplated Nickel molds, which are used as flexible metal shims in R2R processes.

OrmoStamp® is based on sol-gel condensation of organically modified silicic-acid precursors, where nano-scaled oligomers with inorganic backbones are synthesized which can be cross-linked by a free-radical reaction. A diligent formulation (i.e. adding various functional additives and a photo-initiator) creates a viscous and solvent-free oligomer solution which can be easily processed by standard UV exposure setups. For the purpose of polymeric stamp manufacture the hybrid polymer cross-links to a multi-dimensional network by UV light.

The OrmoStamp® formulation can be cast or spin-coated on a glass substrate (coated with adhesion promoter, e.g. OrmoPrime®08) as it is depicted in Fig. 1. A nanopatterned master stamp with an adequate anti-sticking layer (ASL) [4] is brought into contact with the viscous OrmoStamp® film. By gently pressing the stack, the OrmoStamp® fills the pattern cavities and spreads laterally while the air is displaced in the closing gap between master and glass substrate. When no additional force is applied, the final layer thickness is solely determined by the amount of OrmoStamp® previously dispensed on the substrate. The stack is finally exposed by UV light (e.g. broadband, 365 nm or 405 nm) through the transparent glass plate. Subsequently, the hardened material adhering to the glass backbone can be easily released from the master in a de-molding step. For receiving the original pattern polarity, this first generation replica can be copied again within a second replication step [3]. An exemplary OrmoStamp® working stamp with accurate replication of a 200 nm wide line grating is depicted in Fig. 2. The overall resolution capabilities were shown to be in the sub-10 nm regime [5].

Once the OrmoStamp® working stamp is manufactured, it shows superior properties (as are summarized in Table 1). On the one hand, the presence of inorganic domains in the network leads to high chemical and thermal stability as well as high optical transparency for UV and visible light (see Fig. 3) allowing the generation of transparent
working stamps for UV-NIL. Unlike perfluorinated-polyether (PFPE) based stamp materials, this is combined with superb mechanical stability. This facilitates the replication of nanoscaled patterns also with critical high aspect ratios of five and higher [6]. Furthermore, the risk to deform or even to damage the polymeric nanopattern during imprint is significantly reduced, which is of utmost importance for the stamp lifetime in NIL-based nanofabrication. The high thermal stability also allows the use in thermal NIL with imprint temperatures of up to 180 °C. On the other hand, the organic moieties of the network contribute to UV patternability and to sufficient bulk flexibility. As a result, OrmoStamp® shows enhanced imprint characteristics due to the possibility to compensate mechanical stress (e.g. during pattern de-molding) and due to the reduced risk of mold breakage. This is complemented by a sufficient long stamp lifetime, i.e. molds can be used for 100’s of replicas before any mechanical degradation sets in. Thus, all-purpose polymeric working stamps can be manufactured from OrmoStamp® for both, UV-based and thermal NIL processes, as will be demonstrated in the subsequent chapters.

Table 1. Bulk properties of OrmoStamp® after UV-curing and hardbake.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparency (&gt; 90%)</td>
<td>λ ≥ 320 nm</td>
</tr>
<tr>
<td>Thermal imprint temperature</td>
<td>up to 180 °C</td>
</tr>
<tr>
<td>CTE (20 – 100 °C)</td>
<td>105 ppm K⁻¹</td>
</tr>
<tr>
<td>Hardness</td>
<td>36 ± 1 MPa</td>
</tr>
<tr>
<td>Volume shrinkage</td>
<td>~ 6 %</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>650 MPa</td>
</tr>
</tbody>
</table>

A unique feature of OrmoStamp® is the possibility to achieve a durable bonding with standard silane-based ASL coatings (e.g. F13-TCS) [4] due to the high silicon content and defined surface chemistry. This is important for the replication of high-resolution and high-aspect ratio nanopattern, where reduced de-molding forces are required for minimizing the imprint defecitivity. However, a limited lifetime or/and repetitive application of ASL coatings are unfavorable for industrial application. Therefore, the OrmoStamp® formulation was improved by incorporation of fine-tuned fluoro components similar to the successful implementation in thermoplastic NIL resists [7]. On the one hand, the enhanced anti-adhesive properties simplify the replication of master originals with dense nanopattern on large-area [8] or where ASL coatings are not applicable. On the other hand, improved yield is possible due to the intrinsic release-properties which indirectly prolong the overall lifetime of the ASL applied to the surface even when the coating slightly wears during repetitive imprints.

2.2 Resist materials

A variety of commercial resist materials has been introduced [9,10] covering the diverse technical requirements from thermal and UV-based NIL as well as from wafer-scale, S&R and R2R replication methods. Since there is an increasing demand to enhance the lifetime of stamps and to reduce de-molding defects (i.e. deformation of critical structures), the optimal reduction of release forces is accomplished by enhancement of anti-adhesive properties of stamp coatings combined with modified resist materials. Lower release forces in the resist also increase the lifetime of the ASL coating on working stamps and eventually allow replication with uncoated stamps.

For thermal NIL processes, the well-established nanoimprint polymers mr-I 7000E and mr-I 8000E were modified with fluoro-surfactants [7]. The types and the concentrations of these additives were carefully tuned since their chemical nature was found to have a large impact not only on the release force reduction but also on the substrate adhesion and the internal cohesion of the polymer. Besides the materials’ capability to lower the surface energy, non-toxicity and environmental aspects [11] were considered.

The modified resists have been evaluated by thermal S&R NIL at VTT Finland on a SET NPS300 machine using mesa-type working stamps with a contact surface of 4x4 mm². The in-situ measurement of release forces during the de-
molding step revealed a 40% reduction of the release forces [7]. Both modified NIL resists are now commercially available as mr-I 7000R and mr-I 8000R. These kind of enhanced NIL resists enable large-area full-field 300 mm wafer scale replication by thermal NIL. The built-in anti-adhesive properties allow to easily separate the imprinted resist from the stamp with low defect rate due to the minimized release forces. An example is given in Fig. 4 where a 3D silicon mold [12] is imprinted into 300 mm thick resist film using fully-automated NIL system EVG560. When working with the enhanced resist materials, defect-free replication at minimized total cycle time of 3 min was demonstrated by imprinting at 150 °C and a pressure of 850 kPa. The 300 mm wafer imprint with sub-100 nm resolution can be calculated to an equivalent patterning throughput of 4 cm² s⁻¹.

For UV-based NIL processes the implementation of PFPE components in spin-on UV-curable NIL resists (denoted as XNIL) led to lower release forces while ensuring high substrate adhesion [13]. It was found that these novel XNIL formulations show full pattern fidelity and low release forces at sub-100 nm resolution with various stamp materials without the use of any ASL (e.g. Si, Ni, or OrmoStamp®). The achieved resolution could be determined to be below 20 nm regime. Furthermore, ink-jet dispensing for high throughput industrial production was accomplished including superb wetting and adhesion on polymeric substrates for roll-to-roll processing [14].

3. Process chain integration

As mentioned in the previous section, OrmoStamp® is much more than a polymer material for low-cost alternatives to stamp originals. It is a key factor for industrial production chains by the integration of specialized mold shapes and material combinations in different replication techniques, which have not been attainable so far by other lithography means. Particularly demanding is the integration of mesas with a height of few tens of micrometers for S&R processes [15] or hybrid layered flexible molds for R2R systems [16], which are examples of scale-up processes often obligatory when working with industry-relevant large-area replication. Moreover, the ability to use of OrmoStamp® on metal inserts (i.e. steel) for injection molding prototyping have been confirmed [17]. Furthermore, the clever combination of advanced resist and working stamp materials allows the reliable replication of complex 3D pattern – e.g. as needed to generate light guiding patterns [18,19]. The SEM micrographs in Fig. 5 illustrate a process chain, which addresses all three types of NIL material (i.e. resist, mold and final application). A mixed 3D structure with binary and blazed grating elements is generated by grey-scale electron-beam lithography on NIL pre-patterned PMMA resist [20] and replicated into OrmoStamp® showing the inverse pattern polarity using UV-NIL process. The OrmoStamp® is then used to repeatedly copy the 3D pattern by T-NIL into a non-polar thermoplastic resist mr-T85, which can be used as permanent optical pattern in light-guide devices.

4. Application example

The described combination of tailor-made NIL materials are crucial for realizing specific high-end applications. A recent example is the reproducible manufacture of multilevel and multidimensional fluidic devices for single molecule biosensing [21], made on 100 mm wafer level in a parallel way. Here, the easy process handling combined with the excellent resolution capability of OrmoStamp® was employed to generate a transparent working stamp from a complex 3D patterned silicon master. This way, planar and 3D microfluidic structures (i.e. tapered inlets minimizing the typical entropic barrier between micro- and nanochannels [22,23]) together with numerous 30 nm wide and 30 nm deep nanochannels were simultaneously copied with sufficient pattern fidelity by the standard UV replication. Detailed views of the OrmoStamp® working stamp with fluidic features – showing inverse pattern polarity – are depicted in Fig. 6 a-c.
The OrmoStamp® working stamp is subsequently used to fabricate the working devices, by a second direct UV-NIL step. The material used for patterning the all-transparent polymeric device is the inorganic-organic hybrid polymer OrmoComp®. This manufacturing process is very convenient, since the complex multilevel and multidimensional fluidic circuitry is defined in a single step, without the need of subsequent patter transfer or post-processing. Thus, the pattern reproducibility especially for the critical sub-50 nm dimensions is greatly improved. In addition, since the parallel manufacture of multiple devices takes place on wafer-scale, effective fabrication time is reduced and the costs are kept low.

![OrmoStamp® working stamp for multi-dimensional fluidic devices, showing microchannels, 3D inlets and nanochannels in negative polarity (a-c). Verification of the fluidic performance of the sealed devices after replication into OrmoComp® (d). (scale bar: 50 µm)](image)

The functionality of the sealed devices has been verified by fluorescent microscopy, as shown in Fig. 6 d. Here, water with a fluorescent dye flows along a microchannel by capillarity, enters and flows along the 30 nm x 30 nm nanochannel thanks to the precisely fabricated 3D inlets— and finally fills the microchannel at the opposite side. This example concludes the high throughput and low-cost nanofabrication capabilities of NIL and demonstrates the importance of innovative material solutions, i.e. easy-to-use NIL polymers.

**5. Conclusion**

The material developments by *micro resist technology* GmbH have resulted in enhanced resist formulations with built-in release properties for increasing yield and reliability in NIL-based manufacturing. Additionally, mass production with low cost of ownership (i.e. direct and indirect costs of a product) is facilitated by the tailor-made working stamps material OrmoStamp® which provides superior properties compared to standard mold polymers. The ability to easily multiply the number of OrmoStamp® molds enables high throughput NIL manufacturing by parallel imprinting of multiple substrates. Furthermore, flexible molds tackle the technically challenging
situation to pattern non-planar substrates in industry-relevant applications such as LED or photovoltaics manufacturing were rigid stamps do not allow the conformal replication of nanostructures on a given topography. Here, a significant advantage of NIL over conventional lithography methods, which typically are not applicable to non-planar substrates due to the characteristic depth of focus, is pronounced.

In summary, the possibility to tailor-made polymer systems, e.g. in terms of its optical properties, mechanical flexibility as well as the incorporation of fluorinated chemicals for enhanced release properties, makes materials play a key role for current process chain integration in NIL-related production technology. The presented innovations in this contribution address resists for pattern transfer, hybrid polymers for working stamps and materials for permanent application. This way, it is illustrated by different examples how complex the portfolio of innovative NIL materials has to be for advancing NIL-based production technology.

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