Easy mask-mold fabrication for combined nanoimprint and photolithography

Helmut Schiff,^{a)} Christian Spreu,^{b)} Arne Schleunitz,^{c)} and Jens Gobrecht^{d)}

Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Anna Klukowska,^{e)} Freimut Reuther,^{f)} and Gabi Gruetzner^{g)}

Micro Resist Technology GmbH, Koepenicker Str. 325, 12555 Berlin, Germany

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Hybrid transparent working stamps with both a surface relief and absorbing mask pattern were fabricated by replicating nanostructures in an Ormstamp film on prepatterned glass substrates. By using a combined nanoimprint and photolithography process, self-aligned mixed patterns of nano- and microstructures can be generated within one single resist layer. In this article the authors present a simple process based on the organic-inorganic hybrid polymer Ormstamp by replication on prepatterned Borofloat substrates. Using these working stamps, grating arrays with 35 nm half pitch were replicated in thermoplastic UV-curable resist. The method is easy to employ for generating mesas with nanostructures on top or the backfilling with microstructures in thermal nanoimprint lithography applications. © 2009 American Vacuum Society. [DOI: 10.1116/1.3250260]

I. INTRODUCTION

Combined nanoimprint and photolithography (CNP) has been developed¹ as a self-aligned mix and match process to generate mixed patterns of nano- and microstructures within one imprint cycle in a single resist layer. CNP also produces three-step profiles and resist structures without residual layer.^{2–4} This is done by using a hybrid semitransparent mask mold, which consists of a transparent stamp with both a surface relief and an absorbing mask pattern. In a first step thermal nanoimprint lithography (T-NIL) is used to generate a thickness profile in resist by squeeze flow and capillary filling.⁵ After mold filling and before detachment of the stamp, the (negative) resist is locally exposed through the stamp areas not covered by the mask absorber, demolded, and the non-cross-linked resist selectively removed by wet development. Many photoresists exhibit thermoplastic behavior and can therefore be used for such a mix and match process.

Depending on the location of the absorption pattern (typically Al or Cr on the stamp protrusions or in the stamp recessions), different types or structures can be generated (see Fig. 1). However, the silane based antisticking layer (ASL) does not covalently bind to metal layers and therefore damage is possible due to resist adhesion on the metal, particularly if the metalized area is large.⁶ It would therefore be desirable to define the absorption pattern independently from the shape and the properties of the surface relief. One solution is to coat a thin transparent layer with the stamp relief on top of a substrate with a patterned metal layer (see Fig. 1). Appropriate layers with suitable mechanical and chemical properties can be applied via plasma-enhanced chemical-

vapor deposition of SiO₂ or Si₃N₄ and patterned by standard lithography and etching processes. In this article we present a simple process based on the replication of thin layer on top of the absorber pattern on a flat substrate, Ormstamp[®] from Micro Resist Technology GmbH. It is a novel organic-inorganic hybrid polymer system which is now used for the fabrication of NIL working stamps.^{7–9} The UV-curable hybrid polymer offers, besides high transparency, high thermal stability, and can therefore be used for UV-NIL and T-NIL, as well as for combined processes (e.g., CNP, or more general TUV-NIL). Because of the high silicon content, the stamp surface can be permanently coated with silane based ASL layers, which is a large asset in contrast to the polymer stamps used until now. In contrast to the standard process described in Refs. 7 and 10 the glass substrates were prepatterned with a thin Cr absorber pattern.

II. EXPERIMENT

The microstructured absorption layer was generated by standard UV photolithography in a SÜSS MA-6 mask aligner and dry etching of up to 100 nm thick Cr using Cl₂/CO₂ plasma on a 0.7 mm thick Borofloat[®] 33 substrate from Schott AG. After spin coating with a 100 nm thick Ormoprime[®] 08 adhesion layer (from Micro Resist Technology GmbH), the relief was generated in a thick transparent hybrid polymer layer (see Fig. 2). The thickness can be chosen from a few microns up to 100 μm and more. The latter is important if large mesa structures have to be replicated. For this a macroscopic drop of Ormstamp precursor was dispensed on the Borofloat substrate and the transparent stamp original placed on it. Then it was gently pressed at 300 N in a Jenoptik HEX03 NIL machine, until the viscous polymer was spread to a film, while the air was squeezed out from the gap between glass and stamp. Thus a moderate thickness of Ormstamp can be generated, which in our case is chosen between 20 and 50 μm. For more precise thickness definition, spacers with defined thickness can be applied between stamp and substrate. The replicated relief was cured

^{a)}Electronic mail: helmut.schift@psi.ch

^{b)}Electronic mail: christian.spreu@psi.ch

^{c)}Electronic mail: arne.schleunitz@psi.ch

^{d)}Electronic mail: jens.gobrecht@psi.ch

^{e)}Electronic mail: a.klukowska@microresist.de

^{f)}Electronic mail: f.reuther@microresist.de

^{g)}Electronic mail: g.gruetzner@microresist.de

FIG. 1. (Color online) [(a)–(d)] Schematic of CNP processes using different mask-mold designs, depending on the location of the absorber pattern [dark lines in the stamp in process step a to c in cases (1)–(3)]: (1) on top of stamp protrusions, (2) in recessed stamp areas, and (3) below the surface relief (in both cases two dark lines on the right and left side). Steps (a) and (b) show imprint, (c) exposure through the semitransparent mask-mold, and (d) after development.

by narrow band flood exposure (10 nm at 365 nm, with maximum optical intensity $I=2.8$ mW/cm²) either through the stamp or the substrate, depending on the transparency of the stamp and the presence of absorber patterns. To avoid template fouling by silicon containing residues and preserve the tone of the original relief (zeroth generation master), a two-step process was applied, i.e., a first generation replica was generated by hot embossing into a 0.25 mm thick polycarbonate foil before the replicated pattern was copied into the hybrid polymer (second generation replica). Alternatively, first generation replica stamps made from Ormstamp and coated with ASL can be used.

After demolding, the film was hardened in a postexposure bake at 130 °C for 30 min. An ASL coating (F₁₃-TCS) is applied from the gas phase in vacuum at room temperature.⁶ To activate silanol groups for covalent binding of silanes, a short oxygen plasma flash was used. In our standard procedure, the plasma is applied for 1 or 2 min at 20 W. Here we needed to reduce this time to a minimum, and 30 s proved to be sufficient to avoid any kind of deterioration of the stamp surface due to the organic component of the hybrid material.¹⁰

As original stamp we used a 100 mm wafer covered with a regular array with 4 μm sized, 250 nm deep square pillars with a 10 μm pitch. The absorber pattern consisted of mac-

FIG. 2. (Color online) Process route for fabrication of hybrid daughter stamp: [(a)–(c)] Fabrication of first generation intermediate stamp by thermal imprint from silicon master (zeroth generation) into polycarbonate foil. [(d)–(f)] Replication into second generation Ormstamp daughter stamp by (d) casting a droplet of Ormstamp onto glass carrier, (e) squeezing and UV-exposure, and (f) demolding.

roscopic apertures with 0.40×0.40 mm². For these first experiments, no alignment of the absorption pattern with respect to the surface relief was needed.

The Ormstamp replica was used as a working stamp for combined thermal and UV-NIL with large apertures in the absorber patterns. For patterning by CNP we used two different resists. Initial test were made with the UV-sensitive, thermoplastic resist mr-NIL 6000.3 from Micro Resist Technology GmbH. In experiments described in Ref. 10, it was demonstrated that 35 nm structures can be replicated by TUV-NIL. The 300 nm thick layer with a T_g of 40 °C was imprinted at an imprint time of $t_{\text{imprint}}=20$ min using a temperature $T_{\text{imprint}}=110$ °C at the bottom and room temperature (20 °C) at the top, and a maximum force of $F=5$ kN (equivalent to $p=6.4$ bars). After molding was complete, the exposure of the negative resist through the locally transparent mask mold is performed (dose 600 mJ/cm²), i.e., only the exposed areas are cross-linked while the others can still be dissolved in standard propylene glycol methyl ether acetate (PGMEA) developer. A developing time of 2 min was sufficient. Alternatively to thin mr-NIL 6000.3 resists, thick layers of SU-8 (a resist with properties similar to mr-NIL 6000.3) from Microchem Corp. were used for the generation of mesa structures.¹¹ The glass transition temperature of non-cross-linked SU-8 has been measured to be 64 °C.¹ Here, a 30 μm thick layer was spin coated on a dehydrated Si wafer and prebaked for 5 min at 65 °C plus 15 min at 95 °C, imprinted at for 15 min at $T_{\text{imprint}}=100$ °C and $F=5$ kN, exposed using a 50 mJ/cm² dose and postbaked in the press for 5 min. For development, PGMEA was used for 3 min.

III. RESULTS

In our current TUV-NIL setup, a Cr thickness of 100 nm was suitable for blocking light from the shadowed areas. Both mr-NIL 6000.3 and SU-8 showed forming of mesa structures. Exposure through the 0.40×0.40 mm² square apertures of the mask results in elevated resist areas of 0.42×0.42 mm² with a micropattern on top of it (see Fig. 3), either with a residual layer of 200 nm or as 30 μm high mesas. Using only a thin (20 nm) Cr absorber led to residual exposure and cross-linking in masked areas. Interestingly, here some of the fully exposed areas are not entirely filled, in contrast with the shadowed areas surrounding them. It seems that during imprint of the 2×2 μm² orthogonal square array (4 μm pitch) the stamp does not exert a high enough pressure for complete filling. With a Cr thickness of 100 nm, good mesas with steep slopes were achieved in 30 μm thick SU-8. First measurements show that these slopes are inclined by about 20° with respect to vertical sidewalls. By using smaller apertures, mesas of around 80 μm were formed after development, which evidently is not the limit of the process (see Fig. 4). At the border of the imprinted mesa plateau, structures are slowly fading out over a 10 μm distance.

IV. DISCUSSION

The manufacturing of hybrid semitransparent mask molds works without any major differences to standard hybrid mold

FIG. 3. SEM micrographs of a mesa structure in SU-8 with imprinted surface relief (a) and (b) magnification. The $420 \times 420 \mu\text{m}^2$ large, $30 \mu\text{m}$ high mesa results from exposure from a $400 \times 400 \mu\text{m}^2$ wide aperture in the hybrid NIL stamp during a UV-NIL process and after development in PGMEA.

fabrication. By using ASL, the demolding can be performed without defects due to ripping, etc. In contrast to the flood exposure used for the fabrication of the daughter stamps, a faithful 1:1 shadow projection with proximity exposure through an absorber pattern is limited due to the chosen setup (see case 3 in Fig. 1). Two reasons are responsible for a partial exposure of the shadowed areas and consequently a nonperfect transfer of the mask pattern in the resist (see Fig. 5): (a) Fresnel diffraction due to the finite residual thickness of the Ormostamp layer on top of the absorber. (b) Diffuse exposure due to noncollimated illumination by multiple

FIG. 4. SEM micrograph of a mesa structure in SU-8 with imprinted surface relief. The $80 \times 80 \mu\text{m}^2$, $30 \mu\text{m}$ high mesa exhibits results from exposure through an aperture of an alignment mark and demonstrates the ability to generate small mesas in SU-8 with a noncollimated illumination.

FIG. 5. (Color online) Two reasons are responsible for a partial exposure of the shadowed areas and consequently a nonperfect transfer of the mask pattern in the resist: (left side) Fresnel diffraction due to the finite residual thickness of the Ormostamp layer on top of the absorber; (right side) diffuse exposure due to noncollimated illumination by multiple (point) light emitting diode sources.

(point) light emitting diode (LED) sources. Our Jenoptik HEX03 UV-module consists of circular arrays of 23 UV-LEDs, located 10 mm behind a 10 mm thick matted quartz plate. According to its directivity characteristics, relevant irradiation is emitted from each LED into a cone of approximately 60° . Due to the matted quartz window, this angle is further enhanced.

Thus at least a structure widening in the order of the residual thickness of the Ormostamp layer was expected. In case of the SU-8 mesas only $10 \mu\text{m}$ measured at the top. First measurements show that these slopes are much steeper than the 30° given by the half angle of the cone (i.e., about $10\text{--}20 \mu\text{m}$ widening at the foot of the mesa). It shows that the contrast of the resist is high enough to enable a relatively precise shaping of mesas. Measurements and imprint tests will show whether these mesas are entirely flat on the top and whether the slopes are dependent on the location on the wafer.

V. CONCLUSION

The fabrication process for an Ormostamp mask-mold daughter stamp has been established. In contrast to process (2) in Fig. 1, the concept of hybrid layered stamps is easier to apply and even adds more functionality to a stamp, e.g., masking structures can be applied both in recessed and in protruding relief areas. This can be further enhanced by integrating sensing devices and heaters onto the glass surface. However, alignment issues may be more critical due to the relatively large Ormostamp thickness. While the Ormoprime adhesion seems to work properly on Cr absorber patterns, the main challenge is to generate a homogeneous residual thickness below $10 \mu\text{m}$. Further experiments have to show whether the $10 \mu\text{m}$ widening of the mesa area in contrast to the apertures can be reduced by this, as well as the fading of structures at the borders. After all, this method is an easy way to fabricate three-step profiles with mixed patterns in photoresists. A large asset of the technology is that an entire wafer with a regular pattern can be imprinted into the surface of a homogeneous layer of material, which enables to achieve good equilibration of pressure and mold filling, and three-dimensional structures are generated after imprint is

completed. The method is easy to employ for backfilling of large nonpatterned areas with microstructures in thermal NIL applications. Such stamps are needed for achieving low imprint times and homogeneous residual layers. As next steps, we plan to fabricate hybrid molds with Ormostamp mesas from these resist structures. This would be beneficial for stamps used for thermal step and repeat NIL with a minimum of structures loss, or for transparent microfluidic channels with integrated nanostructures.

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¹K. Pfeiffer, M. Fink, G. Gruetzner, H. Schulz, and H. Scheer, *Microelectron. Eng.* **57–58**, 381 (2001).

²X. Cheng and L. J. Guo, *Microelectron. Eng.* **3–4**, 277 (2004).

³X. Cheng and L. J. Guo, *Microelectron. Eng.* **3–4**, 288 (2004).

⁴M. B. Christiansen, M. Schøler, and Anders Kristensen, *Opt. Express* **15**, 3931 (2007).

⁵H. Schiff, *J. Vac. Sci. Technol. B* **26**, 458 (2008).

⁶H. Schiff, S. Saxer, S. Park, C. Padeste, U. Piesles, and J. Gobrecht, *Nanotechnology* **16**, S171 (2005).

⁷A. Klukowska, M. Vogler, A. Kolander, F. Reuther, G. Gruetzner, M. Muehlberger, I. Bergmair, and R. Schoeftner, *Proc. SPIE* **6792**, 67920J (2008).

⁸A. Klukowska, A. Kolander, I. Bergmair, M. Mühlberger, H. Leichtfried, F. Reuther, G. Grützner, and R. Schöftner, *Microelectron. Eng.* **86**, 697 (2009).

⁹See www.microresist.com.

¹⁰H. Schiff *et al.*, "Transparent hybrid polymer stamp copies with sub-50-nm resolution for thermal and UV-nanoimprint lithography," *J. Vac. Sci. Technol. B* (to be published).

¹¹See www.microchem.com.