Transparent hybrid polymer stamp copies with sub-50-nm resolution for thermal and UV-nanoimprint lithography

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The organic-inorganic hybrid polymer Ormostamp was successfully used for the fabrication of inexpensive, transparent working stamps to be used in nanoimprint lithography. The stamps were produced from different masters by casting and UV exposure of a viscous precursor. The cured hybrid stamp with the replicated surface relief was imprinted into several thermoplastic materials with up to 180 °C imprint temperature. In this article the authors show the effect of the imprint temperature on the structural fidelity. By using combined thermal and UV-nanoimprint lithography at 110 °C imprint temperature, a resolution down to 35 nm is demonstrated. They also investigated deterioration effects due to plasma treatment to simulate the effect of multiple recoating steps.

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I. INTRODUCTION

In nanoimprint lithography (NIL) one of the critical issues is the fabrication of working stamps in sufficient quality and quantity. Stamp copying has not only become a means to enhance the lifetime of the original but also to reduce the risk of contamination and damage.¹ Recently a novel organic-inorganic hybrid polymer system was successfully used for the fabrication of NIL working stamps and commercialized under the name Ormostamp[®]. The UV-curable hybrid polymer offers, besides high transparency, high thermal stability, and can therefore be used for UV-NIL and thermal NIL (T-NIL), as well as for combined processes (TUV-NIL).^{2,3} Thus, transparent stamps can be fabricated by combining the structured surface layer in Ormostamp and a substrate with appropriate mechanical and optical properties.

Because of the high silicon content, the stamp surface can be permanently coated with fluorinated silane based anti-sticking layers (ASLs), which is a large asset in contrast to the polymer stamps used until now.⁴ To comply with the requirements for high resolution and structural fidelity, the oxygen plasma step needed for the surface activation prior to silane coating is considered as particularly crucial. The organic component in the cured hybrid material is susceptible to the oxygen treatment which may lead to deterioration of

surface hardness and loss of structural fidelity. We have now investigated the material in terms of different requirements. We have fabricated stamps with high resolution by using our large area, narrow band UV-NIL setup from different masters. We have coated it with a chemical vapor deposition based ASL coating process and varied plasma treating conditions to investigate the deterioration of small structures. We have made imprints in different materials under various process conditions. These investigations go further than those presented in Ref. 5 and aim to show the current limitation of the daughter stamp fabrication for thermal molding processes. Using this, we will be able to determine which processes are most suited for the use of these inexpensive daughter stamps.

II. EXPERIMENT

Ormostamp is a novel stamp material system based on an UV-curable inorganic-organic hybrid polymer with *i*-line characteristics. It can be spin coated or cast, depending on the thickness needed. With its high sensitivity around 365 nm, it can be exposed with the common broadband emission spectrum of Hg lamps in mask aligners, but also with narrow band UV-light emitting diode devices as implemented in our Jenoptik HEX UV-NIL module. Because exposure in UV-NIL is done through transparent stamps or substrates, a high UV-transmission is necessary both for the structured top layer as well as for the substrate. As has been shown in Ref. 2, the high UV transparency in Ormostamp is preserved after thermal treatment, i.e., 90% transparency at 350 nm of a 200 nm thick film after processing at 270 °C. Furthermore a thermal expansion coefficient adapted to silicon for thermal imprint processes is needed. Borofloat[®] 33, a borosilicate glass from Schott AG with excellent UV transparency and heat

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FIG. 1. (Color online) Process route for fabrication of hybrid daughter stamps and replication in thermoplastic material: [(a)–(c)] Fabrication of first generation daughter stamp from silicon master (zeroth generation), (d) optional copying of second generation daughter stamp, [(e)–(h)] combined thermal and UV-NIL in spin coated resist.

expansion adapted to silicon, shows the necessary qualities for TUV-NIL processes. As Pyrex[®] from Corning it is not only highly suitable for anodic bonding but also serves well as an inexpensive substitute for quartz substrates for the fabrication of hybrid stamps.

As a working stamp we generated a replica in Ormostamp, activated it in a short oxygen plasma step and coated it with ASL [Figs. 1(a)–1(c)]. Alternatively, if the tone of the original relief (zeroth generation master) needs to be preserved, a two-step process can be applied, i.e., a first generation intermediate replica can be generated by UV-NIL in Ormostamp or by hot embossing a polycarbonate foil before the replicated pattern is copied into the hybrid polymer (second generation replica) [Fig. 1(d)]. Prior to casting, the transparent glass substrate was cleaned in $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ (1:2) Caros etch for 10 min at 90 °C, rinsed in de-ionized water, dried with nitrogen, and activated in O_2 -plasma for 10 min. Afterward it was spin coated with a 100 nm thick film of adhesion promoter Ormoprime08 from Micro Resist Technology. The fabrication of the high resolution originals (masters) was done by extreme ultraviolet -interference lithography, as described in Ref. 6. Using this technique, periodic structures on relatively large areas can be generated with high resolution of down to 11 nm. They are now available from Eulitha GmbH. For our experiments we choose stamps with multiple $0.5 \times 1 \text{ mm}^2$ areas of period 76 nm, linewidth of 20 nm, and 47 nm depth made from direct hydrogen silsesquioxane (HSQ) pattern transfer into Si by reactive ion etching (RIE) (see Fig. 2). After dispensing of a defined quantity of the viscous Ormostamp precursor on a master stamp, the material drop was covered with the glass substrate and spread to a film, while the air was squeezed out from the gap between glass and stamp. Thus, a moderate thickness of Ormostamp was generated, which in our case was chosen between 30 and 50 μm . The imprint was done at 300 N at room temperature. In contrast to the broadband exposure,² a narrow band expo-

FIG. 2. Scanning electron microscopy micrographs from cross sections of RIE etched master stamp with 47 nm depth, period of 76 nm, linewidth of 20 nm, and $\sim 10 \text{ nm}$ HSQ resist left after etching (initial thickness 60 nm).

sure of our Jenoptik HEX UV-module (10 nm at 365 nm) was used, with maximum intensity $I=2.8 \text{ mW}/\text{cm}^2$ in continuous mode. Because of the high sensitivity in the *i*-line range, the exposure time can be a few seconds, in contrast to the broadband exposure with maximum intensity $I=1800 \text{ mW}/\text{cm}^2$ (measured at 365 nm) for common pulsed systems. However, to assure full cross-linking, in these experiments, a relatively high exposure dose of $600 \text{ mJ}/\text{cm}^2$ was chosen. After exposure and demolding, the film was hardened in a postexposure bake (PEB) at 130 °C for 30 min. An antisticking coating with F_{13}TCS was applied from the gas phase in vacuum⁴ at room temperature. To activate silanol groups for covalent binding of silanes, prior to ASL coating an oxygen plasma flash is used. In contrast to our standard process, where 1–2 min at 20 W is chosen, here we need to reduce this time to a minimum, i.e., around 30 s, to reduce any possible deterioration. This is considered as sufficient.

For the imprint into thermoplastic materials [see Figs. 1(e)–1(h)], we chose three different materials from Micro Resist Technology, mr-NIL 6000.3, mr-I 7030 E, and 8030 E with a glass transition temperatures T_g of 40, 70, and 115 °C and appropriate imprint temperatures T_{imprint} of 110, 140, and 180 °C, respectively (see Table I). In contrast to the purely thermoplastic materials, mr-NIL 6000.3 is designed for TUV-NIL. We choose a process, where exposure is done after molding is complete, but before the stamp is detached from the substrate. All materials were spin coated to a thickness of 300 nm on standard 100 mm Si substrates, imprinted at 5–10 kN for 20 min. Demolding temperature T_{demold} was chosen to be at 30 °C. For mr-NIL 6000.3, only the bottom plate was heated, while the exposure tool at the top stamper was kept at room temperature. As with Ormostamp, the dose of $600 \text{ mJ}/\text{cm}^2$ was chosen with $I=2.8 \text{ mW}/\text{cm}^2$ at 365 nm. No PEB is needed.

For the investigation of the effect of long O_2 -plasma treatment, the stamps were treated in an Oxford Plasmalab 100 RIE using 20 SCCM (SCCM denotes cubic centimeter per minute at STP) O_2 , 20 W at 20 mtorr. For surface activation we used 5 and 10 min, which is 10–20 times more than the 30 s for one process.

TABLE I. Comparison of different thermoplastic materials replicated with Ormostamp molds.

Polymer/resist	Process	Glass transition temperature T_g (°C)	Force F (kN)	Time t (min)	Press temperature T_{top}/T_{bottom} (°C)
Imprint from Si master (zeroth generation into an Ormostamp replica (first generation)					
Ormostamp	UV-NIL	—	0.3	2	RT 20/20
Imprint with Ormostamp replica (first generation) into polymer replica (second generation)					
mr-NIL 6000.3	TUV-NIL	40	5	20	20/110
mr-I 7030	T-NIL	70	10	20	140/140
mr-I 8030	T-NIL	115	10	20	180/180

III. RESULTS

The Ormostamp replica was used as a working stamp for NIL (see Fig. 3). Faithful replication of the stamp structures is achieved using the TUV-NIL process at an imprint temperature of $T_{\text{imprint}} 110^\circ$. The 35 nm half-pitch structures with an aspect ratio of 1 are clearly replicated and show that the hardness of the Ormostamp stamp material is sufficient at process parameters of 5 kN force (on 100 mm wafers), 20 min imprint time, and elevated temperature. In contrast to

isolated small structures (e.g., pillars), where a residual elasticity of the material was found to be a disadvantage, the large grating of $0.5 \times 1 \text{ mm}^2$ proved to be well suitable for replication. The temperature is well below the maximum imprint temperature of the UV-NIL module (120°C) and makes it possible to define a standard process for mr-NIL 6000.3. This is currently not the case for T-NIL with the purely thermoplastic materials mr-I 7030 E and 8030 E. While with mr-I 7030 E only a slight structure rounding was observed, the structures were clearly smeared and ripped out by using mr-I 8030 E (see Fig. 4). The main reason for this seems to be the elevated imprint temperatures of 140 and 180°C , respectively. However, better results were obtained with larger structures, i.e., pillar structures with 400 nm period, 200 nm diameter, and 400 nm height. This suggests that not only the imprint temperature but also the residual elasticity of the material at higher temperatures may be responsible for the deformation and ripping.

FIG. 3. Imprints of 35 nm half-pitch structures into different thermoplastic resists: structures in mr-NIL 6000.3 (top) are well replicated, in mr-I 7030 (center) they are slightly rounded, and in mr-I 8030 (bottom) they are poorly replicated.

FIG. 4. Imprints of 100 nm diameter pillars into different thermoplastic resists: Structures in mr-NIL 6000.3 (top) are well replicated, in mr-I 8030 (bottom) only a part of the pillars are present (because they are either ripped away or the stamp were already filled from previous ripping).

Apart from this, the experiments with long O_2 -plasma treatment in RIE showed a visible deterioration of the surface relief on the hybrid stamps. The 200 nm pillars were reduced by 100 nm in height and diameter. In contrast to this, small plasma treatments did not show any deterioration or structural changes.

IV. DISCUSSION

Currently best results are achieved at processes with moderate temperatures (TUV-NIL). We are confident that by further optimizing the curing process for Ormostamp, process temperatures up to 140 °C, as needed for mr-I 7030 E, can be achieved without deterioration of stamp nanostructures during imprint. This would mean that standard processes for purely thermoplastic materials (with useful process resistance properties for postprocessing in RIE or lift-off) can be developed. For the imprint at higher temperatures, as needed for polymethyl methacrylate or mr-I 8030 E, probably a further development of the Ormostamp material will be needed. The current results show, however, that the resolution capability of the hybrid material is suitable for many applications. In contrast to other viscous materials such as polydimethylsiloxane precursor, where the filling of structures smaller than 100 nm is difficult to achieve, there seems to be no visible restriction.⁷ Further experiments with new stamps will aim to show even higher resolutions and aspect ratios. Here stamps with a surface relief made from HSQ or harder sol-gel materials, which are processed at high temperatures to eliminate any elastic organic component, may be alternatives.

We further showed that short oxygen plasma steps can be used for surface activation without major surface erosion before the ASL layer is applied. However, the current maximum time of 5 min may be too short for more than ten coatings. The reduction in the structure diameter from 200 to 100 nm may be accompanied by a weakening of the material. This has to be investigated in future experiments. The current experiments do not show any effect of surface weakening for short exposures to plasma; therefore it can be anticipated that a few short plasma steps can be applied without modifying

the shape, as well as the surface hardness and composition. For moderate imprint temperatures, several tens or hundreds of imprints may be possible.

V. CONCLUSION

As stated before, Ormostamp copies are inexpensive alternatives to electroplated stamps but are still restricted in lifetime and hardness. Their key advantage is that they can be cast from a multitude of originals, even replicas, e.g., in polycarbonate can be used. Therefore they enable to reduce cycle times for stamp copy fabrication and are a first step to replace expensive stamp originals by copies. Additional to this, by replication, opaque originals can be transferred into transparent copies. Furthermore by repeated copying, tone reversal is possible, which enables to copy an original into a set of stamp copies with different polarities. This is not only useful for process optimization in research but also for reducing cycle times in production by using the stamp polarity with better molding properties (e.g., pillar instead of hole arrays). In the future, several options will be evaluated, e.g., material combinations by using Ormostamp structures on prestructured substrates and on different substrate materials.

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