Smart Origination and Functional Replication: Thermal Reflow and Innovative 3D Structures

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This contribution summarizes advanced lithographic methods for polymeric 3D topographies based on the modification of the polymer molecular weight and applying thermal polymer reflow. Initial structures realized with grayscale electron beam and multi-photon lithography were reshaped due to thermal annealing close to the glass transition temperature following high-energy radiation. This allowed for new topographical functionalities such as aspheric and ultra-smooth freeform micro and nano-optics. The covered methods have in common that they exploit a specific contrast in molecular weight that enables post-processing and thus a transformation of the initial pattern by polymer reflow into a new surface topography or shape. Also, simulation methods are quickly summarized.

Keywords: Grayscale, Replication, Optics, Diffractive, Refractive, Freeform

1. Introduction

Nanoimprint lithography (NIL) is a high-resolution and high-throughput lithography method that allows for low-cost processing compared to other lithography methods [1,2]. In NIL, always the fabrication of the original – the mold – has been the most significant concern, but it is also its biggest asset. Being able to replicate any freeform surface in a vast variety of materials with ultra-high precision is the unique selling point of NIL. Directly fabricating permanent structures into functional materials, e.g., for micro-optics and integrated photonics bears a considerable application potential. This has all been considered before in the search for the killer-application in this area since the start of nanoimprint in the mid-1990s. Today, the ongoing development of new additive fabrication and 3D surface patterning methods as well as high-resolution grayscale electron beam lithography (GEBL) approaches offer a new perspective for nanoimprinting. Direct fabrication is, of course, a competitor in this field, but most processes are unfortunately still serial and slow; so replication is required for high-volume fabrication at the end. There are many new challenges for optics such as augmented/mixed reality and early adopters already employ replication techniques there. However, there is more potential to be used in the field of replication of complex surface topographies [3,4].

This article summarizes some of the latest achievements in grayscale lithography and its combination with post-processing (Fig. 1) for the fabrication of initial patterns and subsequent replication by nanoimprint lithography. The fabrication of the original patterns involves GEBL as well as multi-photon lithography (MPL). The post-processing exploits either inherent differences in material properties following the initial fabrication (Fig. 1 – (2) lateral) or it uses additional exposure to high-energy photons to create such a spatial difference in material properties (Fig. 1 – (3) vertical) in distinction to classical microlens reflow with homogeneous material [5-8].

In this work, some special focus is put on the material behavior associated with the material modification (namely molecular weight reduction) and its behavior during post-processing (namely thermal polymer reflow). There is a large collection of published work covering different aspects of this already well known process being recently reviewed.
in a large depth [10,11]. This article does not want to replicate those works but quickly summarizes the most important aspects along with some new material perspectives in this work.

2. Experimental

The typical process flow in NIL builds on the following steps and is supplemented by steps that might be unique for the techniques presented here:

(a) pattern origination in resist material,
(b) pattern modification (if required),
(c) replication into final product material.

The article covers the first two steps in the following.

2.1. Pattern origination with GEBL

For origination with GEBL, the high-resolution electron beam resist poly (methyl methacrylate) (PMMA) was used. In electron beam lithography, usually a high molecular weight $M_w$ of about 950 kg/mol is used to achieve high contrast and high spatial resolution. However, in NIL, usually the lower the $M_w$ is, the better is the polymer displacement at finite temperature and thus the imprint quality. For this reason, PMMA with an $M_w$ of about 100 kg/mol and a glass transition temperature $T_g$ of about 122 °C (micro resist technology GmbH) was selected to allow for a combination of GEBL and NIL in the same resist material [10].

PMMA was spin-coated on the silicon substrates for the required thickness and soft-baked for 2 min at 140 °C at a hotplate. Subsequently, the resist was exposed to high energy electrons (100 kV, EBPG 5000+, Raith GmbH) with a dose mapped from a respective contrast curve (Fig. 2) using a commercial software package for dose assignment and 3-dimensional pattern calculation involving proximity effect correction (BEAMER, GenISys GmbH). Finally, the pattern was developed in 100% methyl isobutyl ketone (MIBK) or mixtures of MIBK and isopropanol (IPA). Usually, a lower contrast is more suitable for GEBL due to higher resilience against dose variations [12]. However, high-resolution patterns [13] demanded minimal dark erosion for the unexposed patterns, especially in this relative low $M_w$ resist, and thus, required IPA to be used as co-solvent.

Following the development step, a discrete and stepped profile is obtained (Fig. 3). For laterally high-resolution steps, a quasi-continuous pattern might be obtained due to the non-negligible lateral development and thus an effective merging of neighboring steps [13]. Due to the variation of the GEBL dose, the $M_w$, and thus, the $T_g$ varies significantly [10]. This allows for a temperature dependent material behavior and hence the name for
2.2. Pattern origination with MPL

Multi-photon lithography is a full freeform 3D fabrication method, also known as high-resolution 3D printing and is based on the non-linear process of multi-photon absorption [14,15]. In contrast to classical laser direct writing, this method allows for the fabrication of intensively cross-linked polymer patterns without significant height restrictions, thus, it can be used for the origination of original patterns for a later mass replication [16], even with the soft-mold material poly(dimethylsiloxane) (PDMS) in an industrially appealing thermal NIL process [16,17].

2.3. Post-processing

The post-processing for GEBL was done on a hotplate at different temperatures ranging from 110 °C (slightly below the \(T_g\)) to about 130 °C (slightly above the \(T_g\)) for different times ranging from a few minutes up to several hours. In general, the lower the temperature, the slower proceeds the pattern deformation and vice versa. Thus, temperature and time allow for effective control of the final shape of the thermal reflow structure. The reflow process itself can be understood as an energy imbalance or surface-tension-driven creep process: under the constant force due to wetting of the polymer to the substrate, the initial pattern deforms towards a minimal energy shape. This shape has usually a constant curvature and is thus a semispherical (“lens-like”) pattern. This shape deformation can be stopped at any stage between the initial and the final stage by lowering the sample temperature significantly below \(T_g\).

The classical reflow [7,8] uses homogenous material, while in this work particular emphasis is put on heterogeneous material [11]. In GEBL, this material contrast is already present after exposure due to the dose induced variation in the \(T_g\) (cf. Fig. 1). For the MPL origination, PDMS replication into PMMA as typical working material was used [16]. This is required to enable modification of the PMMA \(T_g\) with vacuum UV (VUV) light of 172 nm wavelength [9]. Due to the exponential absorption of VUV, the \(T_g\) follows a comparable increase from a rather low temperature toward the bulk temperature [18]. By controlled heating of the surface close to the \(T_g\) of the bulk PMMA, a contrast in viscosity in the uppermost region compared to the bulk region (cf. Fig. 1) can be achieved. This, as a consequence, results in an ultra-smooth surface that even surpasses in quality on optimally written MPL structure [19] due to the unmatched self-perfection process of thermal reflow.

Because surface energies and surface tensions mainly determine the reflow shape, this process can be simulated with so-called soap-film concepts such as implemented in the freeware Surface Evolver (SE) [20]. With this, the process of reflow can be quite well captured in a minimalistic computational effort [21,22]. The significant reduction of the computational burden is obtained by ascribing the volume properties of the reflowing solid volume to the surface elements and by following pre-defined mathematical routines for surface tension flow well describing the reflow process. For the very early onset of reflow and the associated effects, the computationally relative cumbersome finite element methods (FEM) might be more suitable due to the dominance of volume effects [23].

For analysis, manual crystal oriented cleaving of samples to obtain cross-sectional views for scanning electron microscopy (SEM) was used.

3. Results and discussion

3.1. GEBL patterning and reflow

Figure 3 depicts a collection of initial GEBL patterns and the reflow shapes obtained for different reflow conditions. As it is visible from the pictures of different step height (Fig. 3a vs. Fig. 3b), the exposed step sidewall angle is mainly determined by the step-height and thus by the different exposure doses being required to achieve the respective step height. The closer the respective step dose comes to the dose-to-clear, the lower is the step height, and the larger is the sidewall inclination deviating from 90° vertical sidewalls [4]. As shown, different step configurations are possible. With further reduced step widths, one would obtain quasi-continuous profiles. All steps of maximum height in Fig. 3 are of non-exposed PMMA and hence have a high \(M_w\) 100 kg/mol [11]. The exposed step has a much lower \(M_w\) in the range of 5 to 15 kg/mol. This becomes visible in the mechanical behavior during cleaving in a much rougher and less regular cleaving facet for the high \(M_w\)-regions.

3.2. MPL patterning and reflow

Figure 4 summarizes the effect of exposure and reflow for MPL written patterns. Following the direct laser writing of the micro-lens array with MPL (Figs. 4a and b), the patterns were replicated via PDMS intermediate stamps into PMMA, then
exposed to VUV light and finally underwent selective thermal reflow of the surface only (Figs. 4c and d) [9]. Due to the selective surface modification, only the surface became soft enough to allow a surface tension driven material relocation and equilibration of surface undulations. In principle, the thermal reflow acts as filter that removes high-frequency roughness components [24].

3.3. Reflow modeling

FEM simulation allows for correct prediction of the onset of reflow (Fig. 5) that is in good agreement with other FEM work [23] and analytical concepts [25]. However, the computational effort is relatively high. For a principle parameter search and fast computation, the soap film method based on the Surface Evolver might be more suitable (Fig. 6).

The before mentioned difference on cleaving facet roughness was further analyzed, to understand the reflow of non-symmetric $M_w$- and thus $T_g$-distribution. As it becomes clear in Fig. 7, the lower $T_g$ region had a lower viscosity – or in other words, higher mobility of the polymer chains. The initial shape was well comparable to Fig. 3b. Thus, in a given time, the higher mobility part was reshaped to a more significant extent and moved further during wetting along the substrate. In consequence, it pulled over the other section of the pattern in this case to the right-hand side. There is still a clear border between the different regions visible in terms of different facet roughness or granularity due to different $M_w$. Thus, the shape in Fig. 7 arises from

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Fig. 3. Cross section of different patterns from a two-resist level pattern with a, d, g) 500 nm and b, e, h) a 2000 nm wide exposed step as well as c, f, i) a four-resist-level pattern with 2000 nm wide steps. (Scale bar is 1000 nm.) a-c) initial, d-f) 20 min at 120°C, g-i) 60 min 120 °C. (Reprinted with permission © Elsevier/JMSSP.)

Fig. 4. a-b) MPL written pattern with significant roughness due to the writing process (intentionally set to fast writing parameters) with b) zoom-in into the apex region between four single lenses. c-d) Same structure after transfer into PMMA, VUV exposure and reflow with d) zoom-in into the apex region. (Reprinted in parts with permission © Wiley/AMT) [8].

Fig. 5. FEM simulation of the thermal reflow of a 100 nm × 500 nm PMMA volume with a) initial volume, b) onset of reflow with typical corner rounding and double curvature as well as c) the final energy optimal shape with a constant curvature. (Note: contact angle PMMA substrate fixed to 60°.)
Fig. 7. SEM micrographs of PMMA structure written by GEBL and reflowed at 120 °C for 120 min with clear pull-over towards the low $M_w$ section along the x-axis but without significant change of the $M_w$ distribution along with the interface (solid black line) between the high and the low $M_w$ regions. The kink in the solid black line indicates the initial step position between both regions (cf. Fig. 3b).

creep and material contrast. In detail, i) fast wetting along the substrate of the more mobile region deforms the right-hand side part more than the left-hand side part and ii) due to the covalent and physical link between both material regions, this deformation translates into an additional deformation of the left hand side that is more pronounced as it would be due to wetting of this part alone. The left-hand side part is not reflowing, and deformation is almost exclusively due to the pull to the right-hand side. Figure 8 shows the SE simulation for different reflow times at 120 °C using two regions of different mobilities. The exposed part of the step-pattern (higher mobility) wets the substrate and moves along the positive x-axis. The lateral movement is due the softened polymer wetting the surface (creep). This wetting creates a force on the non-exposed part and leads to the before mentioned deformation. The comparison with the experimental results show a good agreement considering the minimal computing effort required with the SE method. Further differences arise from the fact that the SE does not take bulk effects into account.

Fig. 6. Comparison of (a) and (b) experimentally obtained scanning electron microscopy (SEM) cross sections and (c)–(e) simulation of single (isolated) 100 μm long and 1700 nm wide lines reflowed for different times at a constant temperature (scale bar: 1 μm) (simulation parameters: $\alpha_{\infty} = 27^\circ$, $\Delta \alpha = 49^\circ$, $\tau_\alpha = 3108$ s$^{-1}$, exponential contact angle decay assumed). (Reprinted with permission © IOP/JMM) [11].)
Fig. 8. Simulation and experimental verification of a double-step resist structure reflowed at 120 °C where the left-step has a 5-times lower mobility than the right step. a) Initial state, b) 20 min at 120 °C, c) 60 min at 120 °C, d) 120 min at 120 °C, e) 240 min at 120 °C and f) 480 min at 120 °C. (Reprinted with permission © AVS/JVST.)

4. Conclusion
The work has shown that thermoplastic reflow combined with a material contrast is a versatile tool for advanced topography fabrication as well as for ultra-smooth surface polishing without affecting the bulk geometry. Essential for this method is the formation of the material contrast with high-energy radiation influencing thermomechanical properties. The reflow close to the glass transition of the thermoplastic polymer involves visco-elastic behavior that can involve some residual elastic contribution, which defines the final reflow shape.

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