Nano-Imprint - Molding Resists for Lithography

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Patterning resists by molding with a stamp opens ways for the mass-fabrication of nanostructures. The versatility of nano-imprint lithography can be greatly enhanced when copies of valuable stamp originals can be made. For the stamp copying itself we are using nano-imprint, making it possible to generate structures with inverse profiles and different depths. By considering the nanorheological behavior we were able to successfully fabricate various stamp copies for different designs.

Keywords: nano-imprint, lithography, molding, thermoplastic, squeeze flow

1. Introduction

The nano-imprint lithography process (NIL, also referred as hot embossing lithography [1,2]) is a low cost, fast method for the parallel replication of structures on the micro- and nanoscale. The unique difference from light and particle based lithographical methods is that a stamp is used instead of a mask, and that the pattern in the resist is generated by mechanical conformal contact of the stamp with a moldable material instead of resist exposure and development (see Figure 1). For many practical applications, it seems that the replication fidelity is determined by the minimum mold cavity size rather than the conformation of the polymer chain. Up to now a resolution of sub-10nm has been achieved [1], by molding a thermoplastic material (PMMA) at a temperature well above its glass transition temperature.

Nanostructured stamps used in NIL are mainly made from standard silicon wafers (e.g. 100mm diameter with 0.5mm thickness). They are compatible with cleanroom processing equipment and therefore allow a rapid processing. They have a surface quality (roughness, flatness) necessary for nanoprocessing and can also be coated with antisticking films using common silane chemistry. Further advantages are the high mechanical stiffness, and the thermal expansion behavior is very well matched with most substrate materials to be structured by NIL. This makes it possible to use them as reliable tools for replication. We inserted them into a commercial injection molding tool for Compact Disc manufacturing. With a single silicon

Fig. 1. Nanoimprint process and subsequent pattern transfer using RIE substrate etching.

mold more than 1500 cycles have been performed with a cycle time of 10sec [3], which is by far higher than the 10s of embossings per stamp in current NIL applications. However, stamps are susceptible to damage if process conditions are not optimal, e.g. when large dust particles are present between stamp and substrate during embossing or scratches during handling occur. Therefore our aim is to develop stamp copying processes which allow us to generate daughters of original stamps.

In this contribution we will present an approach of how stamp copies can be made using NIL and etching as pattern transfer, furthermore by embossing into thermoset polymers. In order to achieve a good stamp copying quality, the limitations of the process given by nanorheology will be considered. As a specific example, we will show stamp copies made from a large area checkerboard grating.

2. Molding and Rheology at the Nanoscale

For many applications, when pattern transfer has to be achieved after embossing, it is of high interest to know the final residual thickness h_f of the polymer layer (see Figure 2), and furthermore, how homogeneously this can be achieved over the embossed area. For the description of the flow process we chose a simple *squeeze flow* model with a Newtonian flow velocity distribution. The main assumption for this is that at temperatures of above 170°C, PMMA (M_w 25kg/mol) can be regarded as a purely viscous liquid with a shear viscosity η , which can be moved laterally along stamp protrusions s until it fills the cavities w of the stamp. It serves for a quick estimation of embossing times for different stamp geometries. An introduction into squeeze flow followed by a derivation of the theory and a discussion of its consequences for nano-imprint is given in [4].

Fig. 2. Geometrical definitions used for the description of the flow process. (1) before molding, (2) after demolding.

Before embossing, the polymer film has an initial thickness h_0 and the depth of the nanorelief is h_r . Applying the continuity equation (conservation of polymer volume) for the polymer film under a single line protrusion with width s and length L (equivalent to a stamp with an array of identical line protrusions), we can derive the film thickness as a function of time using a constant force F , where [3]

$$\frac{1}{h^2(t)} = \frac{1}{h_0^2} + \frac{2F}{\eta_0 L s^3} \cdot t$$

Inserting the final thickness $h_f \equiv h(t_f)$ gives the embossing time t_f , which is the time, when the stamp is fully inserted into the polymer.

$$t_f = \frac{\eta_0 L s^3}{2F} \left(\frac{1}{h_f^2} - \frac{1}{h_0^2} \right)$$

For many practical cases, where a constant pressure under each stamp protrusion $p = F/(s \cdot L)$ is assumed, this formula gives:

$$t_f = \frac{\eta_0 s^2}{2p} \left(\frac{1}{h_f^2} - \frac{1}{h_0^2} \right)$$

At identical pressure, small single stamp protrusions will sink faster than wide ones. The stamp geometry can therefore be optimized by reducing the dimensions of the protrusions. It can be shown that, for a stamp which contains an array of small structures in the center, the large single stamp protrusions surrounding the array dominate the sinking velocity (large s_i). The time to fill such a nanostructure array (in Figure 3) should be the same for an equivalent microcavity with the same stamp area and cavity volume [5].

Fig. 3. Molding of nanocavities in comparison to microstructures and possible introduction of sink microstructures for faster and more homogeneous molding. Left side: top view. Right side: side view.

However, this would mean that for many cases embossing times would be extremely large, while in practice much smaller embossing times have been observed. The reason for this is that due to the different sinking rates of protrusions of different sizes, the stamp, which is often backed by an elastic layer (e.g. a silicone mattress) for achieving a homogeneous pressure distribution, can bend locally. This results in a residual layer

height that is not uniform over the entire embossing area. To achieve good uniformity, as needed for stamp copying, the fill factor (i.e. the ratio of area covered by cavities to the total stamp area) should be kept constant, both locally (at length scales corresponding to the cavity dimensions) and across the wafer (i.e. large stamp protrusions), to ensure better lateral flow of the polymer and shorter embossing times. For this purpose, additional protrusions or cavities can be placed in intermediate areas not needed for the device's functioning (see Figure 3), or the structure can be repeated several times. For every new design, particularly for unevenly distributed cavities, transition areas between structured and unstructured areas have to be carefully considered.

Taking into account the variation of the local ratio of areas of protrusions and cavities in a stamp, we were able to calculate optimum process parameters such as initial polymer thickness and etching conditions in many cases to ensure a high fidelity of the copying process.

Fig. 4. Schematic view of the molding of a large array of nanocavities surrounded by large stamp structures. Stamp (1) and resist (2) before embossing. (3) Local bending of stamp during molding. (4) Resist after embossing with inhomogeneous residual layer. (5a) to (5c) show different states of resist thinning. (5b) is the state where complete pattern transfer is possible.

3. Stamp Copying for Nano-Imprint

The stamp copying process uses the standard NIL process sequence (see Figure 1). After embossing the stamp into a thin thermoplastic material the surface relief is thinned down to open substrate windows. The following pattern transfer process will be complete by etching only the areas of the substrate not covered by the resist. However, slight variations of the residual layer thickness after embossing are sufficient to cause an inhomogeneous pattern transfer, as can be seen

in Figure 4. A complete pattern transfer may only be possible for special cases, e.g. when density and sizes of stamp protrusions are homogeneous over the whole structured areas (see Figure 3).

Fig. 5. Micrograph of a grating embossed in resist: lighter area corresponds to the grating, higher than the surroundings. Profilometric height measurements of a cross-section schematically represented in nm indicate resist thickness variations near and within the grating border (grating structures not resolved).

Figure 5 shows a typical case where a linear grating (400nm period vertical lines in a 5x3mm² area) is surrounded by a large unstructured area. Assuming the grating alone, a fill factor of 50% ($s=w$) and a structure depth $h_r=160$ nm, a vertical movement $\Delta h = 80$ nm can be calculated. An initial PMMA thickness $h_0=320$ nm would therefore result in a final residual thickness $h_f=240$ nm and, with the fully molded structures on the top, in an overall thickness $h_f + h_r=400$ nm, which is close to the values in the center of the grating given in Figure 5. Here a transition region of about 500 μ m at the grating borders can be seen. For the structure above, it was shown that already a few additional protrusions or cavities placed in the vicinity of the nanostructures with cavity distances smaller than typical transition distances keep the transition area out of the grating structure.

The stamp copying process allows us to generate daughters of original stamps (see Figure 6). Furthermore it is of advantage to generate sets of daughter stamps with different depths. For most practical applications, particularly if high aspect ratio stamps have to be fabricated, an intermediate layer for enhancing the etching selectivity has to be used. For example, when a 20nm thick Chromium layer is placed between the resist and the substrate, it can be etched by RIE using chlorine chemistry after opening the resist windows. Because of the reversal of the pattern

polarity by etching, the stamp copying process must be continued with the inverse pattern to get a stamp with the original pattern. This pattern reversal can be avoided, when lift-off instead of etching is used.

Fig. 6. Original (top, SiO₂, depth 170nm, dark parts etched) and stamp copy (bottom, Si, 65nm, inverse profile) of a checkerboard structure fabricated by nano-imprint process and subsequent pattern transfer (grating period 400nm in squares with alternating orientation).

4. Polymer Stamp Copies

In addition to purely thermoplastic materials, the use of thermoset and UV-curable polymers suitable for nano-imprint makes it possible to fabricate stamp copies in a direct way. We developed layered stamps, which consist of a metal plate as a mechanical support covered with a thin polymer layer with a nanostructured relief. This was generated by embossing a structured silicon stamp into a thin resist layer (mr-I 9030 provided by microresist GmbH, Berlin) [6]. Before demolding, the thermoplastic precursor polymer was crosslinked and hardened by continuous heating. The profile proved to be sufficiently stable for subsequent temperature cycles in a thermal injection molding process. If suitable antiadhesive coatings are developed, as common for silicon stamps, this simple stamp copying process will surely become attractive for rapid prototyping for stamps used in NIL.

5. Conclusion

Nano-imprint is considered as another promising approach for lithography, because it is possible to go easily beyond the resolution limits set by the wavelength of light. However, further

knowledge has to be generated about process conditions and properties irrelevant for known lithographic processes, e.g. much investigation has to be put on the issue, how well nanostructures can be molded along with microstructures on flat or pre-structured substrates.

The advantage of NIL is that with a single master or stamp, identical structures can be produced as required over large surfaces. The stamps, as common with lithographic masks, can also be copied without a loss in resolution. Applications so far achieved include large area nanoscale electrode structures, gratings and sieves for biological applications, single electron transistors etc. For such devices, surrounding connection lines and pads must be included, which requires a mixture of both micro- and nanostructures in the stamp. Nanorheological considerations allow to estimate the speed of squeeze flow over large area surfaces and the thickness inhomogeneity.

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