Sidewall-angle dependent pre-filling of three-dimensional microcavities in thermal nanoimprint

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The mold filling of 3-D micro- and nanostructures in thermal NIL is barely understood, because structures with appropriate 3-D sidewalls of defined angle and low surface roughness were not available until now. Furthermore it is difficult to freeze flow states during the fast wetting and spreading of cavity sidewalls and before the onset of squeeze flow [1]. In the research presented here, stable pre-filling states were visualized in a low-pressure regime. They show that for pre-filling not only an effect dependent on surface energies of polymers and stamps have to be considered, but also cavity geometry and sidewall inclinations. Thus sidewalls have a large influence of how filling is starting, and which kind of defects might form before squeeze flow sets in. These defects, often in form of depressions leading to depleted areas, can act as *hot spots* which may be difficult to fill once the depression has formed.

We investigated sidewall and surface energy dependent filling of 3-D microcavities for different NIL polymers. In a replication study, stamp structures with vertical and sloped sidewalls [2] were imprinted into viscous material, which was cooled rapidly before demolding. The contact angles (CA) of the pre-fill states were determined from SEM micrographs of cleaved samples (see Figs.1 and 2). While for vertical sidewalls an almost horizontal surface level is seen (CA 90°), for symmetric inclined structures a lens-like meniscus of polymer below the cavity center forms. In contrast to the rather abrupt filling behavior for vertical sidewalls, in the inclined case the polymer tends to wet the surfaces gently, leading to a constant rise of polymers along extended sidewalls and stops at a specific CA before the top of the cavity is reached.

In the case of inclined sidewalls, we can see that the amount of polymer rising at the sidewalls is similar to that of the depression below the initial resist level because of volume conservation, which indicates absence of squeeze flow. Fig. 3 confirms that the shape of these cylinder-like depressions is defined by the CA of the polymer with respect to the sidewall, independent by the resist thickness. As a proof that the CA measurements in the SEM are accurate and reproducible, pre-filled states of different polymers were generated. For PMMA (molecular weight of 34.4 kg/mol), the temperature at which the CA freezes was determined to be around 190 °C as has been shown by reflowing PMMA beads at different temperatures (see Tab. 1). This indicates that the freezing is fast enough to conserve the CA of the molding temperature and not, as anticipated earlier, the glass transition temperature T_g of the polymer.

[1] H. Schift, G. Kim, J.J. Lee, and J. Gobrecht, Nanotechnol. **20** (2009) 355301 (6pp)
[2] A. Schleunitz and H. Schift, J. Micromech. Microeng. **20**(9)(2010) 095002.

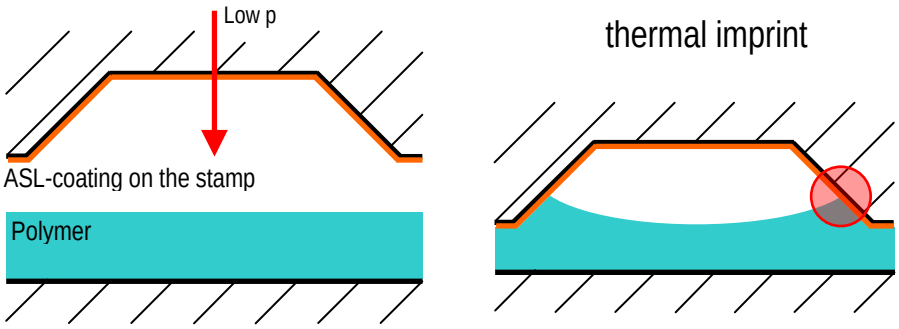

Figure 1: Resist before contact (left side) and in pre-filled state in the contact phase of thermal NIL (right side). The red circle indicates the location where the polymer forms the optimum contact angle with the sidewall.

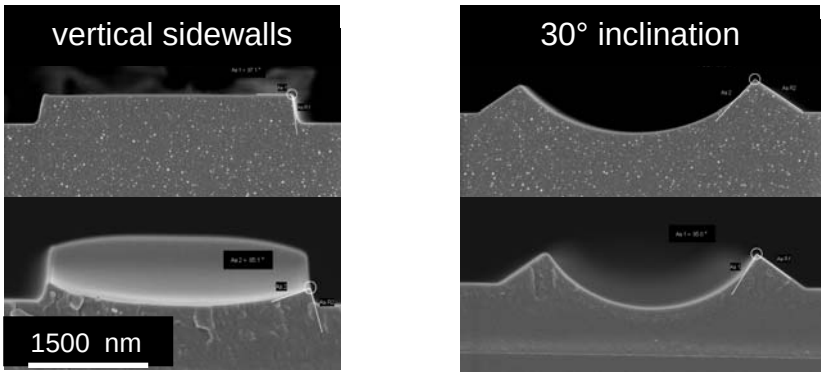

Figure 2: SEM micrographs of resist cross-sections after demolding were used to determine the CA. Top: Imprint in mr-I 8150E XP: CA 98°, bottom: Imprint in PMMA M_w 8.9k: CA 85° (thickness 990 nm).

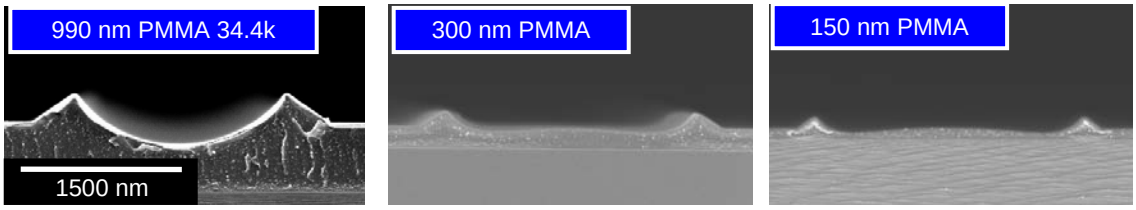

Figure 3: A lens- or cylinder-like depression below the cavity can only form for thick resist layers (in this case CA = 90°). For thin resists, the same contact angle forms at the sidewalls, but flow towards the borders is inhibited and the substrate stays wetted.

PMMA 34.4k	Reflow @ 160 °C	Reflow @ 180 °C	Reflow @ 200 °C	pre-filling ~190 °C
CA	96°	91°	85°	90°

Table 1: Measured contact angles of PMMA 34.4k beads with a diameter of 200 µm reflowed at various temperatures for 20h and cooled down rapidly to room temperature compared to CA derived from pre-filling experiment.