Relevance of stamp material for vertical phase separation of block copolymers in nanoimprint

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Lamella forming block copolymers (BCP, block ratio 1:1) have the capability to self-assemble perpendicular to the substrate with a period of a few tens of nanometers. Vertical lamella are obtained in a simple way by annealing the BCP film, when the layer thickness is adequate; with a 'neutral' substrate in an asymmetric configuration it should be a multiple of the lamella thickness L_0. Nevertheless, for the guidance of the lamella a pre-structured substrate is required that provides a chemical or topographical pattern [1].

When thermal nanoimprint (T-NIL) is used instead, no substrate pre-preparation is needed. Then the stamp is used for guiding, and it can be used several times. In addition, T-NIL features the advantage that free-standing, non-embedded polymer structures are achieved. We recently could demonstrate that it is possible to imprint a lamellar PS/PMMA block copolymer and to achieve ordered vertical lamella (Fig. 1a) [2]. We found that this also works for structure heights that do not match $n \cdot L_0$, in contrast to a 'non-imprint' situation, and without providing a 'neutral' substrate. When the layer thickness is not so critical the realization of precise lateral geometries is less demanding.

Quite likely, the reason for this different behavior is the interaction of the BCP with the stamp sidewalls, featuring a low surface energy due to the anti-sticking layer applied. The geometries and the surfaces involved are sketched in (Fig. 1b). Whereas the surface energy of the substrate, γ_{sub}, induces lamella parallel to the substrate, the surface energy of the stamp, γ_{st}, induces the desired lamella perpendicular to the substrate; the question is which of the surfaces is dominating. Analogous to the literature [3], Fig. 2 shows the interaction energy of the BCP with the respective surfaces. The stamp is dominant with narrow cavities when the layer thickness is not too low, in accordance with our experiments. This argument should hold independent of the stamp material used, due to the anti-sticking layer applied. Against expectations, this is not the case. Our experiments with a replica stamp from OrmoStamp show that no vertical lamella can be obtained under the same processing condition as with Si stamps, see Fig 3.

We will indicate and discuss potential reasons for this difference.

[1] Koo et al., Soft Matter, 2013, 9059 - 9071
[2] A. Mayer et. al., accepted for publication, Microelectronic Engineering 2017
[3] D. G. Walton et. al., Macromolecules, 1994, **27**, 6225-6228

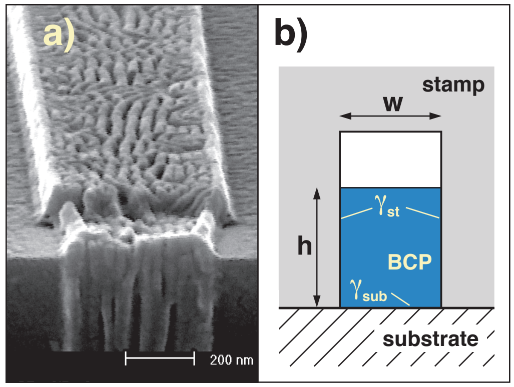

Figure 1. Vertical lamella of PS/PMMA-BCP in stamp cavities with T-NIL.

a) Experimental result within a cavity of 500 nm. (190/170°C, 100 bar, 1 h)

b) Imprint at partial cavity filling, interaction with stamp γ_{st} and substrate $\gamma_{sub.}$

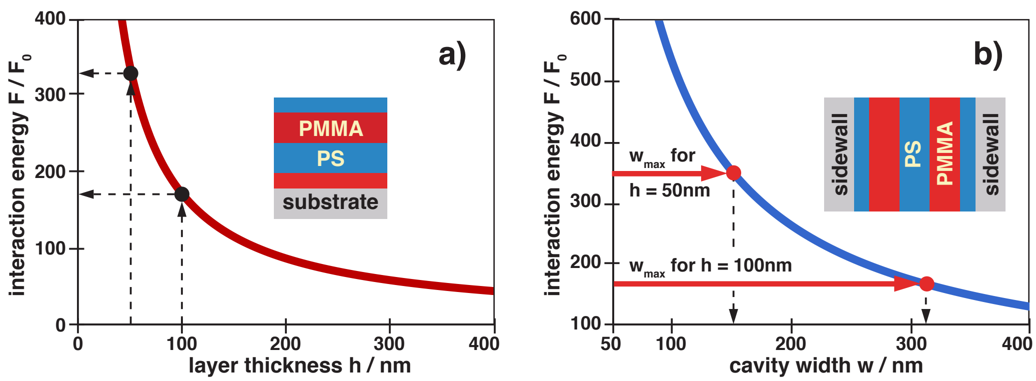

Figure 2. Reach of interaction of BCP with the confining surfaces.

a) Interaction with substrate as a function of the layer thickness.

b) Interaction with the stamp sidewalls as a function of the cavity width.

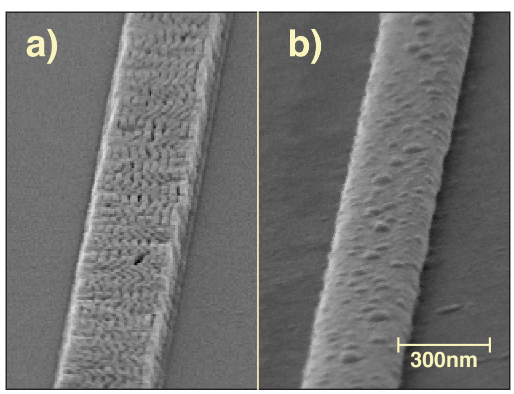

Figure 3. Influence of the stamp material on lamella formation.

(190/170°C, 100 bar, 1 h)

a) Si stamp, vertical lamella; b) OrmoStamp, no clear lamella visible.