

ADVANCED MATERIALS

Supporting Information

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Tailoring Nanostructures Using Copolymer Nanoimprint Lithography

*Pascal Thébault , Stefan Niedermayer , Stefan Landis , Nicolas
Chaix , Patrick Guenoun ,* Jean Daillant , Xingkun Man ,* David
Andelman , and Henri Orland*

Supporting Information, "Tailoring Nano-Structures Using Copolymer Nanoimprint Lithography" by Thébault et al

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Selective PMMA etching

For selective phase etching of PMMA, the same UV/O₃ apparatus as for wafer cleaning and OTS SAM oxidation was employed. To avoid ozone formation that can degrade both polymer blocks, the reaction chamber was flushed for 30 min with nitrogen before and during the UV-irradiation. Samples were irradiated for 30 min and subsequently treated with glacial acetic acid during 1h to ensure complete removal of degraded PMMA fragments.

Self-consistent field theory modeling

In the Self-Consistent Field Theory (SCFT) calculations, the BCP chains consist each of $N = N_A + N_B$ monomers (each having a Kuhn length a) with symmetric $N_A = N_B$ block lengths. The BCP system is slowly quenched starting from the disordered state, with $\chi N = 10.4$, above the Order-Disorder Temperature (ODT). Then, the χN parameter is gradually increased passing through the values: 10.6, 10.8, 11.5 and 20 that are inside the micro-phase separation region, below the ODT.

In the calculation the bottom surface is chosen to have the same interaction with the two blocks, while the top surface (the mold) is modelled to have a preferred interaction $u = u_A - u_B > 0$, mimicking the difference in surface tension between the mold and the PS and PMMA blocks. The two surface parameters are chosen to be $u_A = 2.0$ and $u_B = 1.98$, representing the short-range interaction of the mold with the A and B blocks, respectively. All lengths are expressed in terms of the bulk periodicity of the BCP lamellae, $L_0 \sim 4.05R_g$, where R_g is the chain radius of gyration $R_g = Na^2/6$.

Thin film nano-rheology

The geometry of polymer flow is given in Fig. A below.

Assuming Newtonian flow properties for the thin BCP film and within the lubrication approximation, the flow is governed by the equation $\eta \frac{\partial^2 v_y}{\partial z^2} = \frac{\partial p}{\partial y}$ and $\frac{\partial p}{\partial z} = 0$, where $v_y(y, z, t)$ is the velocity profile at time t after the onset of pressure, at distance y from the groove center and height z , and η is the viscosity. Using no-slip boundary conditions at the bottom ($z = 0$) and top $z = h(t)$ surfaces we have:

$$v_y(y, z, t) = \frac{1}{2\eta} \frac{\partial p(y, t)}{\partial y} z [z - h(t)]. \quad (1)$$

Integrating over y and using mass conservation we can relate the integrated velocity profile to $\partial h / \partial t$ at the groove exit $y = \omega_l / 2$, and find:

$$p(y, t) = -\frac{3\eta}{2h^3} \frac{\partial h}{\partial t} (l^2 - 4y^2). \quad (2)$$

Calculating the average stress $\langle p \rangle$, which equals to the applied pressure, $\langle p \rangle = P$, we get $P = -\eta l^2 h^{-3} \frac{\partial h}{\partial t}$, which can then be integrated to obtain

$$h(t) = \frac{L_A}{\sqrt{1 + t/\tau}} \quad (3)$$

where τ is the characteristic timescale, $\tau = \eta \omega_l^2 / 8PL_A^2$, and L_A the initial film thickness. Finally, the shear rate is found to be:

$$\dot{\gamma} = \frac{\partial v_y}{\partial z} = \frac{24yPL_A}{\eta \omega_l^2} \left(\frac{1}{\sqrt{1 + t/\tau}} - \frac{2z}{L_A} \right), \quad (4)$$

where $0 \leq z \leq h(t)$. The maximum shear rate is obtained close to the top and bottom surfaces (at $z = h$ and $z = 0$, respectively) for $y = \omega_l / 2$ (groove exit). With $L_A = 50$ nm, $\omega_l = 500$ nm, $P = 15$ bars, the maximum shear rate at the groove is $\dot{\gamma} \approx 0.1 \text{ s}^{-1}$ at 110° C ($\eta \approx 2 \times 10^7$ Pa.s) and $\dot{\gamma} \approx 100 \text{ s}^{-1}$ at 170° C ($\eta \approx 2 \times 10^4$ Pa.s).

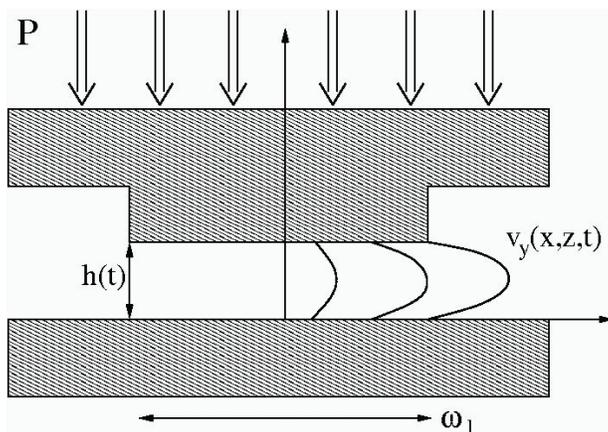


Fig. A: Schematic representation of the polymer nano-rheology inside the mold during the NIL press stage. The figure is a cut in the $y - z$ plane, where the pressure and film thickness $h(t)$ are along the z -axis, while the width ω_l is in the y -direction.

Silicon wafer etching by reactive ion etching (RIE)

The PMMA phase was first selectively removed with UV-irradiation and subsequent etching with glacial acetic acid as described above. Then the PS resist pattern (26 nm height) was used as a resist mask to etch, 20 nm deep, the underneath silicon substrate with RIE process (See Fig. B). ICP etching mode was used with the following process conditions: HBr/Cl₂/O₂ gases (112/68/7 sscm), under a 10 mT pressure with bias of 60 W and a source of 500 W. The residual resist was then stripped away with pure oxygen plasma.

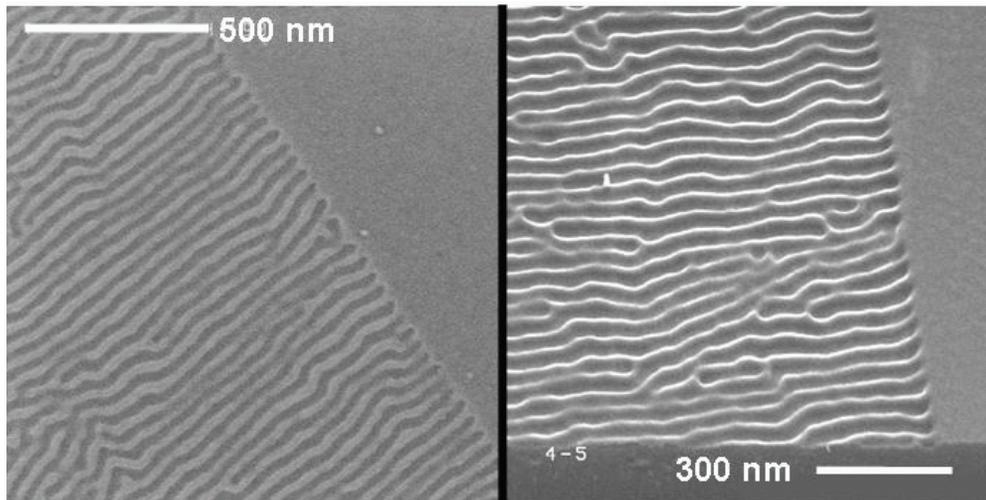


Fig. B: SEM top view (left) and cross-section view (right) of 20 nm deep etched silicon. A NIL processed PS-PMMA film was used as mask for reactive ion etching (RIE) process after removal of the PMMA.