Electronic Supplementary Information for

Well-ordered self-assembled nanostructures of block copolymer films \textit{via} synergistic integration of chemoepitaxy and zone annealing

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**Part A: Details of computational model**

To probe into the directed self-assembly of block copolymers in the presence of dual field of chemical template and zone annealing, the proposed model is based on the standard Hamiltonian in framework of polymeric field-theoretic method under a mean-field approximation. As schematically illustrated in Fig. 1 of main text, the system with volume $V$ consists of $n$ chains of AB block copolymers confined between two hard walls. The block copolymers have a chain length $N$ and ideal gyration radius $R_g$. The top wall or substrate (represented by black color) contains the chemically guiding stripes with pitch $p_s$ and width $w_s$. The top wall is neutral and represented by transparent color. The free energy functional (in unit of thermal energy $k_B T$) is given by

$$F_n = - \ln Q + \int dr \left\{ -\omega_A \varphi_A - \omega_B \varphi_B + \chi N \varphi_A \varphi_B + \frac{1}{2} \kappa (\varphi_A + \varphi_B - 1)^2 + V_0 \varphi_S (\varphi_B - \varphi_A) \right\}$$  \hspace{1cm} (S1)

where $\varphi_A$ and $\varphi_B$ are local volume fractions of A and B blocks, respectively. The parameter $\chi N$ represents the Flory-Huggins interaction parameter and $\kappa$ is the Helfand-type coefficient to control the deviation of local volume fractions from the average value. The quantity $Q$ is single-chain partition function in external potential fields $\omega_A$ and $\omega_B$ produced by the surrounding chains. The last term represents the contribution of interactions between the blocks and the chemically guiding stripes via a short-range potential field. The function $\varphi_S$ is the surface potential field for the chemical templates and their strength is denoted by $V_0$.

The kinetics of phase separation of multicomponent system is described by the Cahn-Hilliard-Cook equation, where the local volume fractions $\varphi_l(r, t)$ ($l=A$ and B blocks) at position $r$ and time $t$ are chosen as order parameters. The set of quantities obey the following diffusion equations given by
\[
\frac{\partial \phi_I(r,t)}{\partial t} = \sum_{j=A,B} \int D_{ij}(r,r') \mu_I(r') dr' + \eta_I(r,t) \tag{S2}
\]

where the intrinsic chemical potentials \( \mu_I \) are calculated from the functional derivative
\[
\mu_I(r) = \frac{\delta F[\phi_I(r)]}{\delta \phi_I}. 
\]

\( \eta_I \) are the Gaussian thermal noises satisfying the fluctuation-dissipation theorem. 
\[
D_{ij}(r,r') = \nabla_r \cdot \Lambda_{ij}(r,r') \nabla_r r',
\]
and \( \Lambda_{ij} \) are the Onsager kinetic coefficients. In order to simplify the calculation process, the local coupling approximation is utilized
\[
\Lambda_{ij}(r,r') = M_I \phi_I \delta_{ij} \delta(r-r') \tag{S3}
\]
where \( M_I \) are the mobility coefficients of blocks. The corresponding diffusion motion described in Eq. (S2) is written as
\[
\frac{\partial \phi_I(r,t)}{\partial t} = M_I \nabla \cdot \phi_I(r) \nabla \mu_I(r) + \eta_I(r,t) \tag{S4}
\]

It should be mentioned that the connectivity and entanglement of polymer chains are neglected due to the computational expense of pair-correlation functions in the numerical implementation of Rouse or reptation dynamics.

The model of zone annealing for the template-guided block copolymers is also schematically illustrated in Fig. 1 of main text. The system is divided into \( \alpha \) and \( \beta \) regions, which are determined by the spatially and temporally dependent Flory-Huggins interaction parameter \( \chi(r,t)N \). The corresponding interaction parameters in the \( \alpha \) and \( \beta \) regions are denoted by the minimum value \( (\chi N)_{\text{min}} \) and the maximum value \( (\chi N)_{\text{max}} \), respectively. The zone width or the width of \( \alpha \) region is represented by the parameter \( w \). The movement of \( \alpha \) region in the simulations is realized as follows: The center of \( \alpha \) region is shifted for one lattice space \( \Delta y \) along the \( y \) direction in each set of \( n_t \) step of discrete time \( \Delta t \), and the corresponding Flory-Huggins interaction
parameters $\chi(r, t)N$ in the $\alpha$ and $\beta$ regions are reset. The moving velocity of zone annealing is defined as

$$v \equiv \frac{\Delta y}{n_t \Delta t} = \frac{\Delta \tilde{y}}{n_t \Delta \tilde{t}}$$

(S5)

where $\Delta \tilde{y}$ and $\Delta \tilde{t}$ are the dimensionless discrete space and time, respectively. The basic velocity unit is given by $\tilde{v} = R_g/\tau$, which is specified by the basic length unit $R_g$ and time unit $\tau$ in the model.
Part B: Acceleration ratio of parallel algorithm

Fig. S1 (a) Absolute timings in seconds per time step (includes the calculation of propagators and the determination of potential fields) in a cubic box with lattice size $N\times N\times 48$. (b) Relative speedup of GPU over a single CPU. All timings are averaged over ten runs with each simulation containing 20 time steps. The simulations use the single precision architecture.
Part C: Morphological evolution of quenching block copolymers

Fig. S2 Morphological evolution of self-assembled nanostructures registered by chemical template in the quenching simulation. (a) Film thickness \( L_z=0.75L_0 \) and stripe pitch \( p_s=6L_0 \). (b) Film thickness \( L_z=1.00L_0 \) and stripe pitch \( p_s=3L_0 \). The simulation times are indicated below the images. Here and in all the morphologies of self-assembled nanostructures below, the A-rich domains and the substrates are represented by the red and black colors, respectively. The interfaces between the A- and B-rich domains are shown in green. The top wall and the B-rich domains are transparent for the sake of visualization. The solid lines on images of self-assembled nanostructures at \( t=80\tau \) highlight the positions of guiding stripes.
Part D: Three-dimensional view of self-assembled nanostructures

Fig. S3 Three-dimensional view of morphological evolution of self-assembled nanostructures programmed by dual field of chemical template and zone annealing. The zone width and the moving velocity are respectively \( w=5.0L_0 \) and \( v=0.06\tilde{v} \) (corresponding to the case of Fig. 2c in the main text).
Part E: Block copolymers at film thickness $L_z=1.25L_0$

**Fig. S4** Three-dimensional view of morphological evolution of self-assembled nanostructures programmed by dual field of chemical template and zone annealing at film thickness $L_z=1.25L_0$. The simulation time is (a) $t=0.17T_v$, (b) $t=1.38T_v$, (c) $t=2.43T_v$, (d) $t=3.47T_v$, (e) $t=4.17T_v$ and (f) $t=5.70T_v$, where the period $T_v$ of zone annealing has a value of 480$\tau$. The zone width and the moving velocity are set as $w=5.0L_0$ and $v=0.15\tilde{v}$, respectively.
Part F: Bottom view of self-assembled nanostructures

Fig. S5 Bottom view of morphological evolution of self-assembled nanostructures programmed by dual field of chemical template and zone annealing at film thickness $L_z=1.00L_0$. The simulation time is (a) $t=0.15T_v$, (b) $t=0.85T_v$ and (c) $t=4.0T_v$, where the period $T_v$ of zone annealing has a value of 480τ. The zone width and the moving velocity are set as $w=5.0L_0$ and $v=0.15\bar{v}$, respectively.
Part G: Temporal evolution of order parameters at film thickness $L_z=1.50L_0$

**Fig. S6** Temporal evolution of order parameters $S_y$ and $S_z$ of lamellar nanostructures programmed by dual field of chemical templates and zone annealing at film thickness $L_z=1.50L_0$. Other parameter settings of simulations are the same as those in Figure 7 of main text.
Part H: Steady order parameters at film thickness $L_z=1.50L_0$

![Graph](image)

**Fig. S7** Steady order parameters $S_y^*$ and $S_z^*$ of lamellar nanostructures as a function of the effective annealing time $t_a$ under various moving velocities $v$. The shaded area highlights the fact that the steady order parameters are larger than 0.9, corresponding to the case of well-ordered nanostructures. The film thickness is set as $L_z=1.50L_0$. The zone width is changed from $w=2.5L_0$ to $10.0L_0$. 