Supplementary Information

Three-Dimensional Electroactive ZnO Nanomesh Directly Derived from Hierarchically Self-Assembled Block Copolymer Thin Films

Ashwanth Subramanian, [a] Gregory Doerk, [b] Kim Kisslinger, [b] Daniel H. Yi, [c] Robert B. Grubbs, [c] and Chang-Yong Nam *[a, b]

[a]Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York 11794, USA.

[b]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA.

[c]Department of Chemistry, Stony Brook University, Stony Brook, New York, 11974, USA.

*Email: cynam@bnl.gov

Determination of ZnO Crystallite Size by Scherrer Analysis

The crystallite size can be deduced from the width of X-ray diffraction (XRD) peak by the Scherrer's equation expressed as: $D = (K \cdot \lambda)/(B \cdot \cos(\theta))$, where D is the average crystallite size (nm), K Scherrer constant (typically varying from 0.68 to 2.08; ~0.94 for the hexagonal wurtzite ZnO [Zak et al., *Solid State Sciences* 13, 251-256 (2011)]), λ X-ray wavelength (1.54178 Å for Cu K_α), B full width at half maxium (FWHM) of a given XRD peak, and θ one half of the position of X-ray diffraction peak (2θ). We fit the XRD peaks in Figure 7 using Gaussian function to obtain 2θ, B, and, finally, D as summarized below Table S1.

Synthesis of PS-*r*-P2VP Random Copolymer Brush

Materials: 2,2'-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA-086) was purchased from Wako Chemicals USA (Richmond, VA). Dichloromethane (anhydrous) and diethyl ether (anhydrous, stabilized, HPLC) were purchased from Fisher Scientific (Pittsburgh, PA). *N*,*N*-dimethylformamide (DMF) (99.9%), *n*-hexane (95%), and tetrahydrofuran (THF) (99.9%) were purchased from VWR International (Radnor, PA). Activated alumina (basic type, Brockmann I grade), styrene (S) (≥99%), 2-vinylpyridine (2VP) (97%), (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO) (98%), and toluene (HPLC grade) were purchased from Sigma-Aldrich (St. Louis, MO). S and 2VP were flushed through activated alumina, degassed by three freeze-pump-thaw cycles, flushed with argon, and transferred into a N_2-filled glovebox immediately before use. All materials were used as received unless otherwise noted.

Synthesis Procedures: A mixture of VA-086 (7.19 mg, 0.0249 mmol) and TEMPO (5.53 mg, 0.0354 mmol) in S (454.7 mg, 4.366 mmol) and 2VP (302.7 mg, 2.879 mmol) was added to a reaction vial with a magnetic stir bar, and the vial was sealed in a N_2-filled glovebox. The sealed vial was removed from the glovebox and heated to 130 °C in an aluminum block on a hot plate. After heating with stirring for 68 h, the vial was removed from the aluminum block and cooled in liquid N_2. The viscous mixture was allowed to warm to room temperature then diluted with a 1:13 (v/v) mixture of DMF/THF (7 mL) and precipitated in *n*-hexane (45 mL), initially forming a precipitate in solution that ultimately adhered to the glass wall as a gel. The supernatant was decanted, and the gel was dried under vacuum (623.3 mg, 80.9% yield). The dried gel was dissolved in CH_2Cl_2 (6 mL) and precipitated in a 1:9 (v/v) mixture of diethyl ether/*n*-hexane (100 mL), again forming a precipitate in solution that afterwards adhered to the glass wall as a gel. The supernatant was decanted, the gel was dried and dissolved in CH_2Cl_2 (2.5 mL), and the resulting solution (~100

mg mL^{-1}) was transferred to a vial to store until further use. Conversions (^{1}H NMR): S, 79%; 2VP 93%. ^{1}H NMR (500 MHz, CD_2Cl_2, δ): 8.6–8.0 (br, 1H per unit of P2VP, Ar H), 7.6–6.0 (br; 5H per unit of PS, Ar H; 3H per unit of P2VP, Ar H), 2.5–0.7 (br, 3H per unit of PS, 3H per unit of P2VP).

The isolated PS-*r*-P2VP sample with 58% PS fraction as measured by ^{1}H NMR was analyzed by size exclusion chromatography (SEC) in $CHCl_3$ (35 °C, 1.0 ml/min) and in 1% triethylamine containing THF (40 °C, 1.0 ml/min). In $CHCl_3$, an M_n and $Đ$ could not be measured under the elution conditions used because the only visible SEC peak appeared at elution volumes higher than the total permeation limit. For comparison, a PS homopolymer synthesized under similar conditions ([TEMPO]/[VA-086] = 1.5:1; [S]/[VA-086] = 300:1; 130 °C, 68 h) was found by SEC under these conditions to have an M_n of ~9 kg/mol and $Đ$ of 1.5. In 1% triethylamine containing THF, an M_n of ~22 kg/mol and $Đ$ of 1.7 were measured.

Preparation of PS-r-P2VP Solutions: PS-*r*-P2VP solutions for spin-coating were prepared from dried aliquots of a stock PS-*r*-P2VP solution before adding toluene for a 1% (w/w) solution. The dilute PS-*r*-P2VP solutions were stirred overnight and filtered gently through a 0.45 μm PTFE syringe filter.

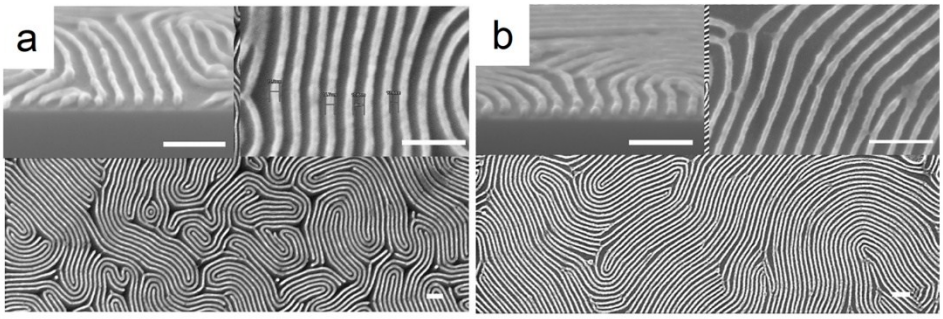
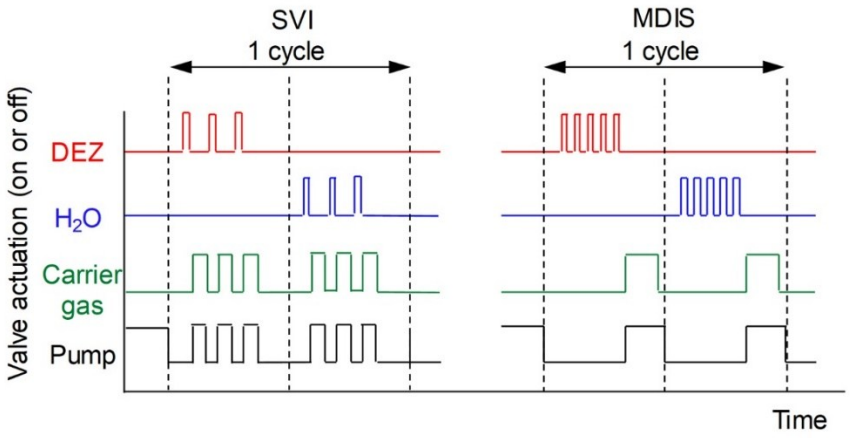


Figure S1. SEM micrographs of AlO_x infiltration-synthesized by the normal infiltration protocol (4 cycles) on different self-assembled lamellar BCP thin film templates: (a) PS-*b*-PMMA and (b) PS-*b*-P2VP. All scale bars denote100 nm.



Scheme S1. Schematic comparison of SVI (left) and MDIS (right) protocols, differentiated by the precursor dosing and purging sequences.

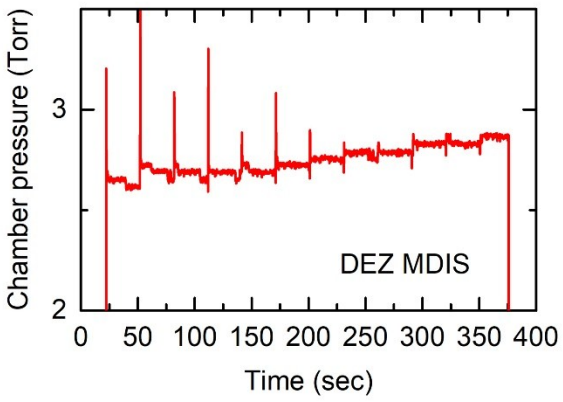


Figure S2. Temporal pressure profile in the ALD reaction chamber measured during the DEZ exposure half cycle (micro-doses) in MDIS.

Table S1. Summary of crystallite size calculated using Scherrer analysis. 2θ, FWHM, D, and D_{avg} denote: Peak position, full width at half maximum, crystallite size, and average crystallite size, respectively. A detailed description of Scherrer analysis is provided below.

Sample	Plane	2θ (degree)	FWHM (degree)	D (nm)	D_{avg} (nm)
ZnO RTP without TiO_2 coating	[100]	31.8	0.51	16.28	15.78
	[002]	34.4	0.5	16.65	
	[101]	36.2	0.59	14.4	
ZnO RTP with TiO_2 coating	[100]	31.8	0.93	8.95	7.41
	[002]	34.4	1.19	7.25	
	[101]	36.2	1.36	6.03	