Supplementary Information

Siliconized silsesquioxane-based nonstick molds for ultrahigh-resolution lithography

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Experimental section

Viscosity measurements. The viscosities of the Si-SSQA/acrylic blends containing 4 wt.% Darocur 1173 were determined at 25 °C using a Brookfield viscometer Model DV-II Pro (Brookfield Engineering Labs Inc.). Measurements were acquired from 0.5–0.7-mL samples with a CPE-51 spindle at a rotation speed of 5–50 rpm.

Ultraviolet-visible spectroscopy. The UV-Vis transparency of the samples was measured over the wavelength range of 200−800 nm using a spectrophotometer (UVmini-1240; Shimadzu). For this purpose, the Si-SSQA/acrylic blends containing 4 wt.% photoinitiator (Darocur 1173) were spin-coated onto the quartz substrate modified with TMSPM to form a 500 nm thick film. The samples were then fully cured for approximately 3 h under vacuum by an 80-W mercury short Arc lamp (INNO-CURE 100N; Lichtzen Co., Ltd.).

Swelling measurements. The free-standing samples cured by UV irradiation at 365 nm for 3 h under vacuum with an 80-W mercury short Arc lamp were immersed in an excess of organic solvents such as ethanol, dehydrated toluene and methyl methacrylate at room temperature. After 48 h, the samples were removed from the organic solvent, and excess surface organic solvents were dried with filter paper. The swollen mass (W_s) was weighed until the samples reached a constant weight. The samples were subsequently dried for 48 h in vacuum desiccators at room temperature, and their dry weights (W_d) were recorded. The swelling ratio (Q_r) of the cross-linked samples was calculated according to the following equation: $Q_r = 100 \times (W_s - W_d)/W_d$.

Table S1. The viscosities of the Si-SSQA/acrylic blends.

Si-SSQA/acrylics	Viscosity at 25°C [cP] [a]	
[wt.%]	EGDMA	DEGDA
100:0	4570	4570
50:50	43	121
20:80	18	52
1:90	4	12
0:100	3.2	9

[a] The viscosities of the Si-SSQA/acrylic blends containing 4-wt.% Darocur 1173 were determined at 25°C.

Table S2. The swelling ratios (Q_r) of the cured Si-SSQA/acrylic networks.

Compositions	Swelling ratio, Q_r [wt.%]		
	Ethanol	Toluene	Methyl methacrylate
20Si-SSQA/80EGDMA	≤ 0.5 ± 0.3	≤ 0.4 ± 0.3	≤ 0.6 ± 0.3
50Si-SSQA/50EGDMA	≤ 0.2 ± 0.2	≤ 0.4 ± 0.2	≤ 0.6 ± 0.3
20Si-SSQA/80DEGDA	≤ 1.2 ± 0.4	≤ 0.9 ± 0.4	≤ 1.2 ± 0.5
50Si-SSQA/50DEGDA	≤ 0.8 ± 0.4	≤ 0.8 ± 0.2	≤ 0.9 ± 0.3

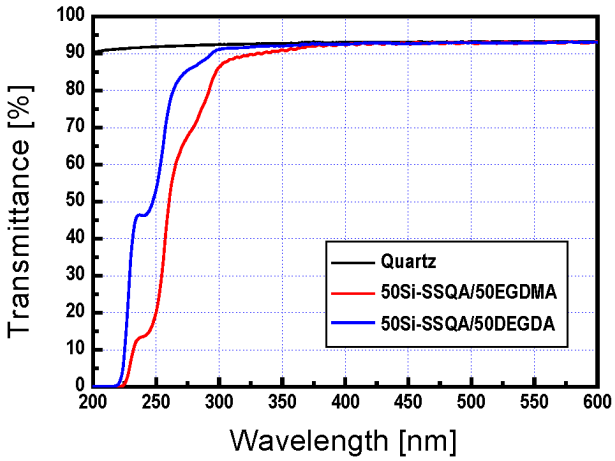

Fig. S1 UV-Vis transmission spectra of the cured Si-SSQA/acrylic networks on a quartz substrate.

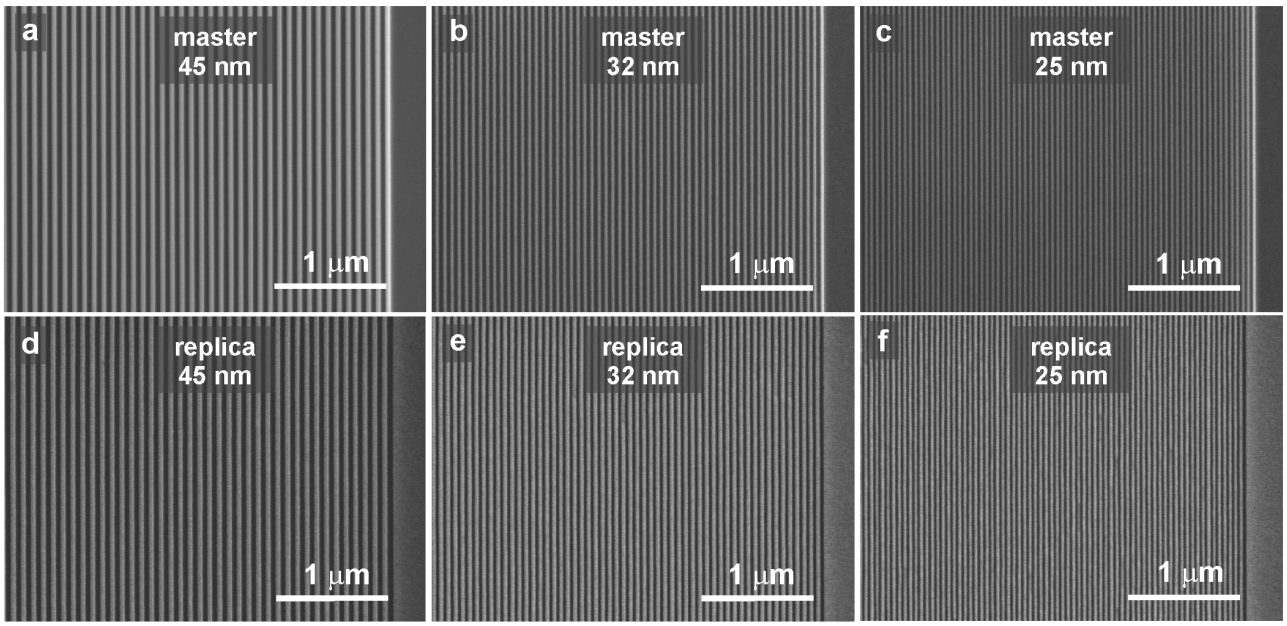

Fig. S2 FE-SEM images of (a-c) the Si masters (NIM-25L/100; NTT-AT) and (d-f) the first replicas of the 50Si-SSQA/50DEGDA with different feature sizes: (a, d) 45 nm, (b, e) 32 nm, and (c, f) 25 nm. The Si masters (NIM-25L/100; NTT-AT) have a line-to-space ratio of 1:1 and a height of 100 nm.

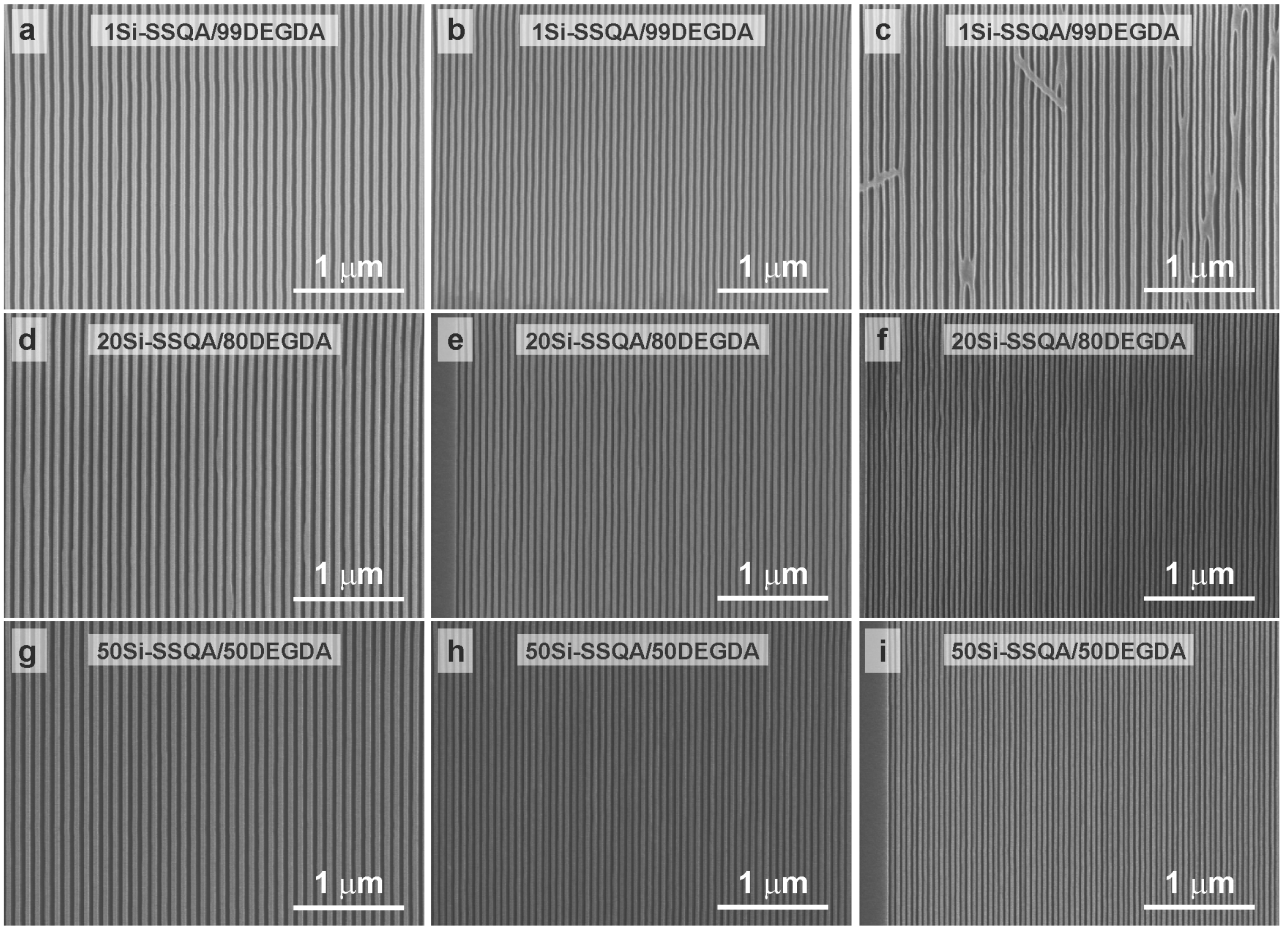

Fig. S3 FE-SEM images of the first replica molds of (a-c) the 1Si-SSQA/99DEGDA, (d-f) the 20Si-SSQA/80DEGDA, and (g-i) the 50Si-SSQA/50DEGDA with different feature sizes: (a, d, g) 45 nm, (b, e, h) 32 nm, and (c, f, i) 25 nm. The images of the first replica molds were captured after demolding the second replica molds.

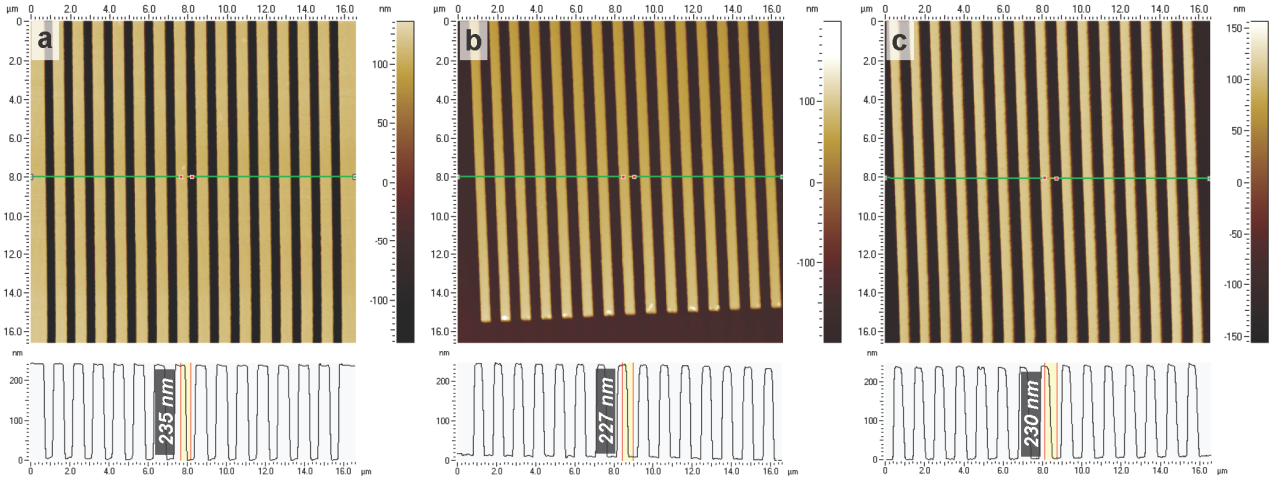

Fig. S4 Height and cross-sectional AFM images of (a) the master mold (NIM-80L, NTT-AT), (b) the UV-molded 50Si-SSQA/50EGDMA, and (c) the 50Si-SSQA/50DEGDA networks. From the cross-sectional images, the photopolymerization-induced shrinkage ratios for the 50Si-SSQA/50EGDMA and 50Si-SSQA/50DEGDA networks were estimated to be 3.4% and 2.1%, respectively.

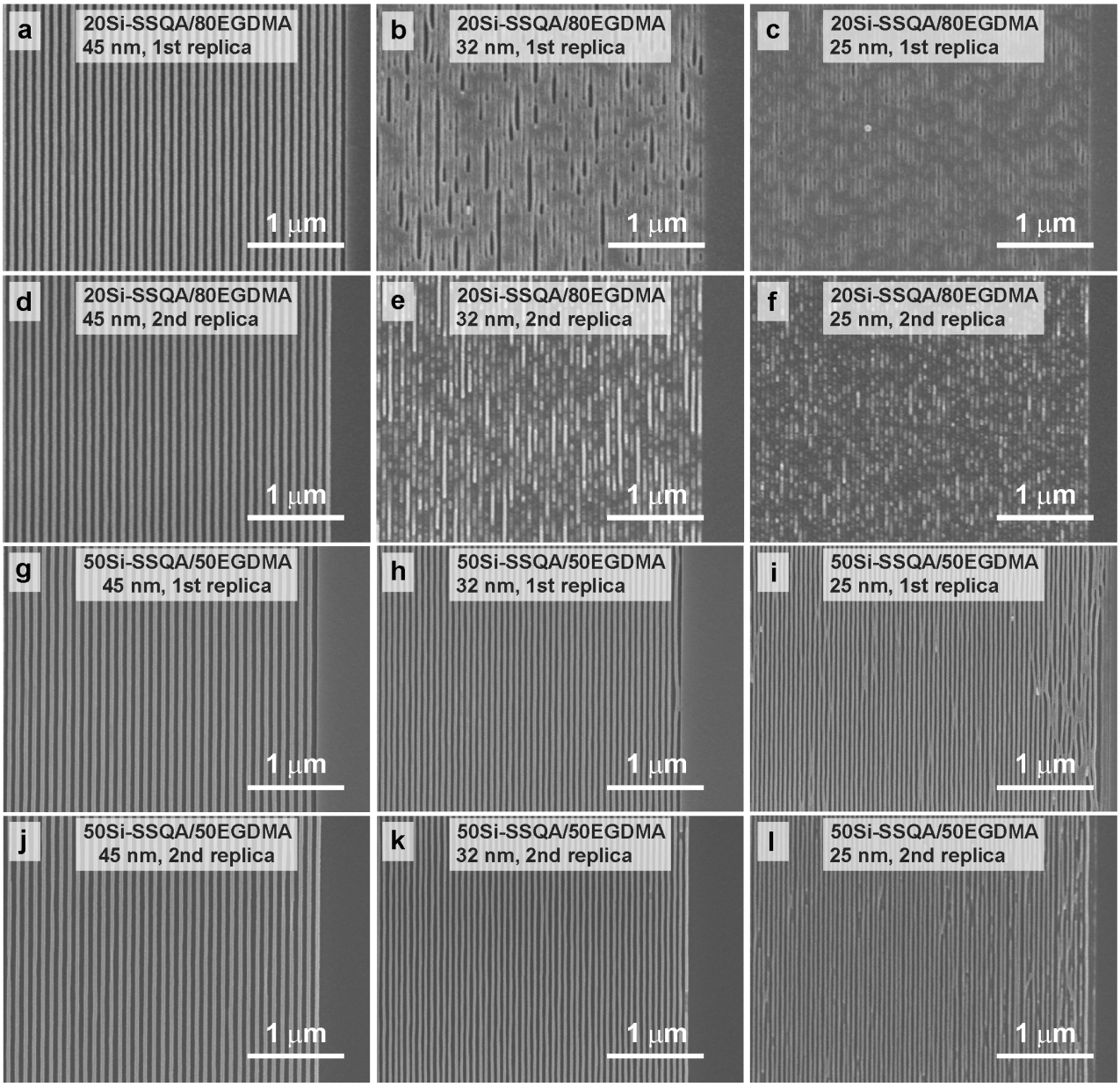

Fig. S5 FE-SEM images of (a–c) the first replicas and (d–f) the second replicas of the 20Si-SSQA/80EGDMA and (g–i) the first replicas and (j–l) the second replicas of the 50Si-SSQA/50EGDMA. Each second replica was duplicated from each first replica.