Electronic Supplementary Material (ESI) for RSC Applied Polymers.

Supporting Information

Iodonium Functionalized Polystyrene as Non-Chemically Amplified Resists for Electron Beam and Extreme Ultraviolet Lithography

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1. Characterization of $PSNA_{0.4}$ and the films

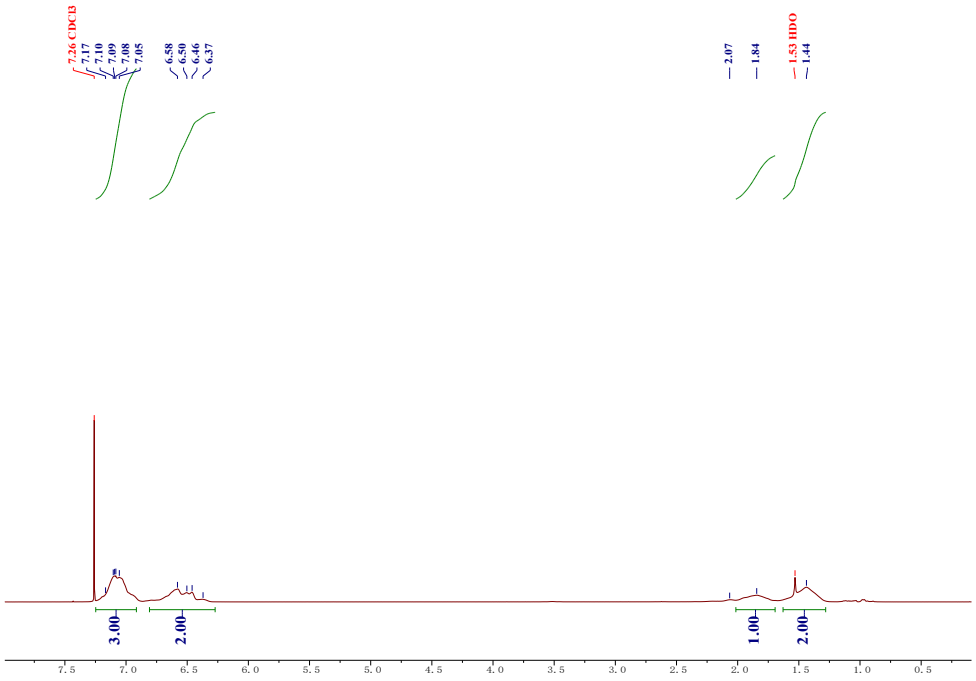

Figure S1. ^{1}H NMR spectrum of PS ($CDCl_3$, 600 MHz)

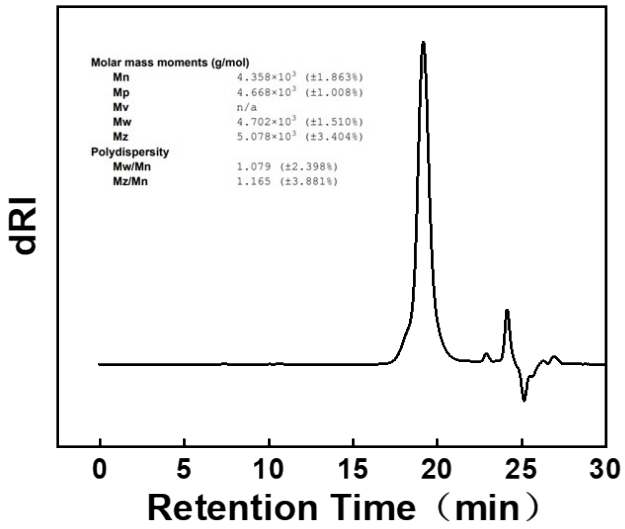

Figure S2. GPC spectrum of PS (Mw=4700, PDI=1.08)

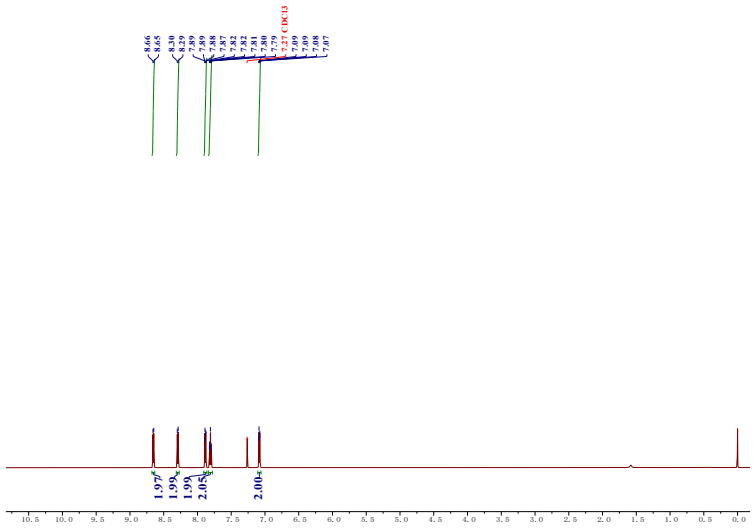

Figure S3. ^{1}H NMR spectrum of N-(p-iodophenyl)-1,8-naphthalimide ($CDCl_3$, 600 MHz)

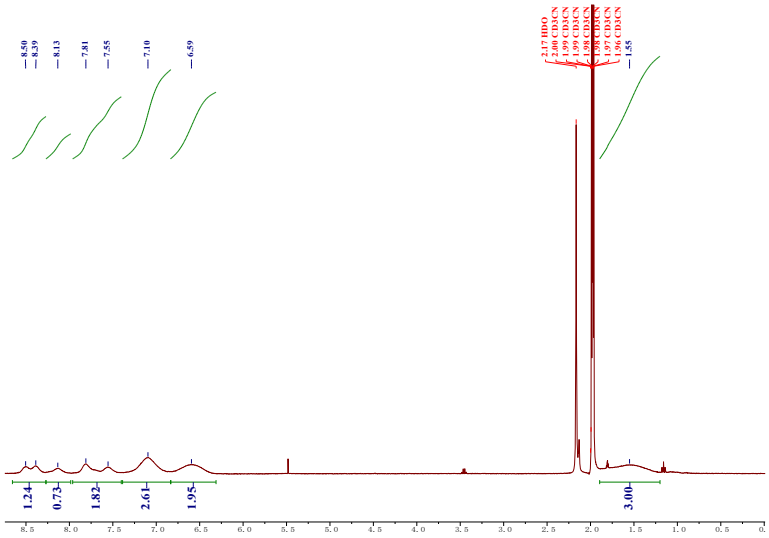

Figure S4. ^{1}H NMR spectrum $PSNA_{0.4}$ (CD_3CN, 600 MHz)

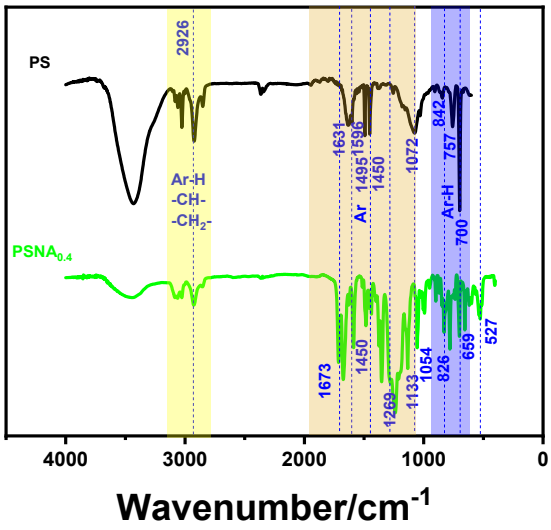

Figure S5. FTIR spectrum of PS and $PSNA_{0.4}$

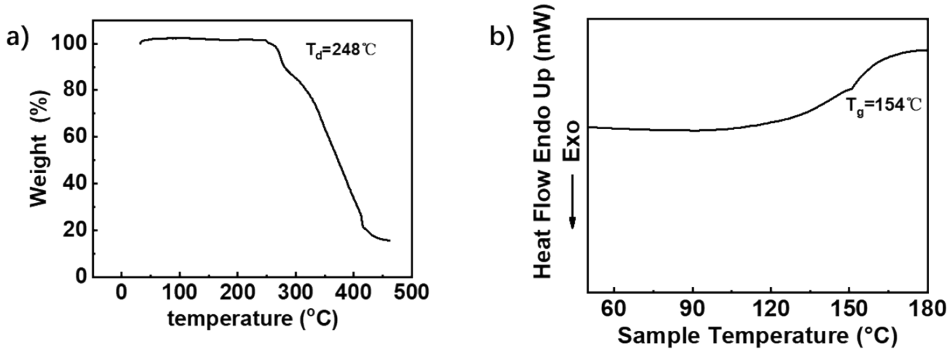

Figure S6. (a) TGA plot of the $PSNA_{0.4}$ at a heating rate of 10 °C min^{-1} under an N2 atmosphere. (b) DSC curve of the $PSNA_{0.4}$ at a heating rate of 10 °C min^{-1} under an N2 atmosphere.

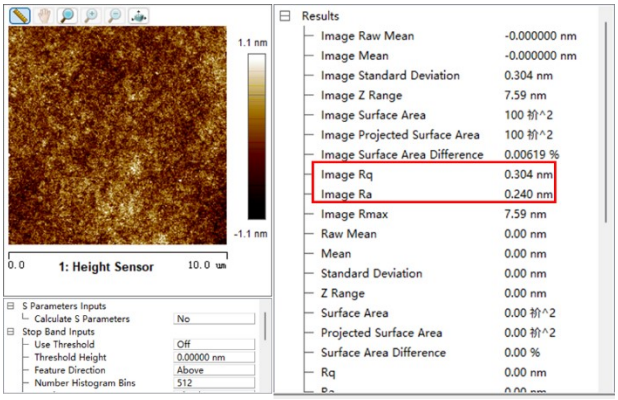

Figure S7. Roughness measurement of $PSNA_{0.4}$ using AFM

2. Solubility characterization and lithographic performances of the resist in different organic developers:

To get an optimal developer, the solubility characteristic of $PSNA_{0.4}$ film in exposed and unexposed regions was examined. The resist films were exposed to a mercury lamp (λ = 254 nm) for 180 s without masks, and then developed for 60 s with different developer solutions. The results are summarized in Table S1.

Table S1. Solubility of $PSNA_{0.4}$ films before and after 254 nm exposure performed at room temperature and Hansen parameters of related solvents

Solvent	Before exposure (%) [a]	After exposure (%) [a]	Hansen solubility parameter（HSP）		
			Dispersion（δD）	Polarity（δP）	Hydrogen bonding（δP）
Cyclohexyl chloride	− (97)	− (75)	17.3	5.5	2.0
Toluene	− (98)	− (70)	18.0	1.4	2.0
n-Butyl acetate	− (95)	+− (54)	15.8	3.7	6.3
MIBK	− (84)	+− (40)	15.3	6.1	4.1
Dimethyl sulfoxide（DMSO）	+ (0)	+ (9)	18.4	16.4	10.2
1,4-Dioxane	+ (98)	+− (44)	19.0	1.8	7.4
Isopropyl alcohol (IPA)	− (96)	− (81)	15.8	6.1	16.4
Acetonitrile	+ (0)	− (75)	15.3	18.0	6.1
Butyl lactate	+ (0)	− (61)	15.8	6.5	10.2

+: Soluble at room temperature; + −: partly soluble; and −: insoluble.

[a] The remaining thickness before / after exposure and developed in different solvents for 60s.

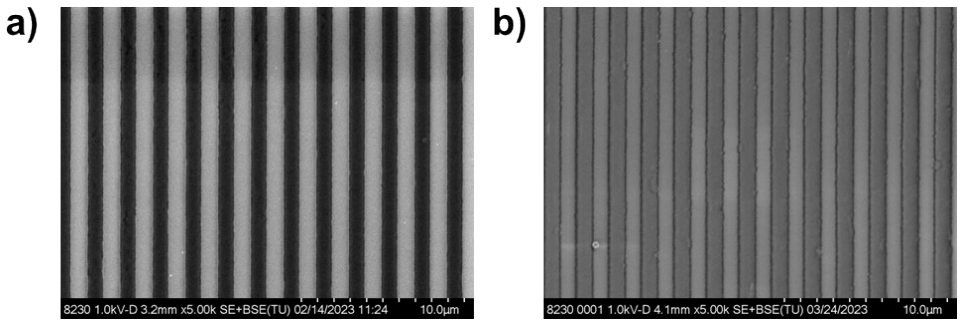

Figure S8. SEM images of 1 um line-space patterns formed by $PSNA_{0.4}$ developed by (a) Acetonitrile (b) n-Butyl lactate

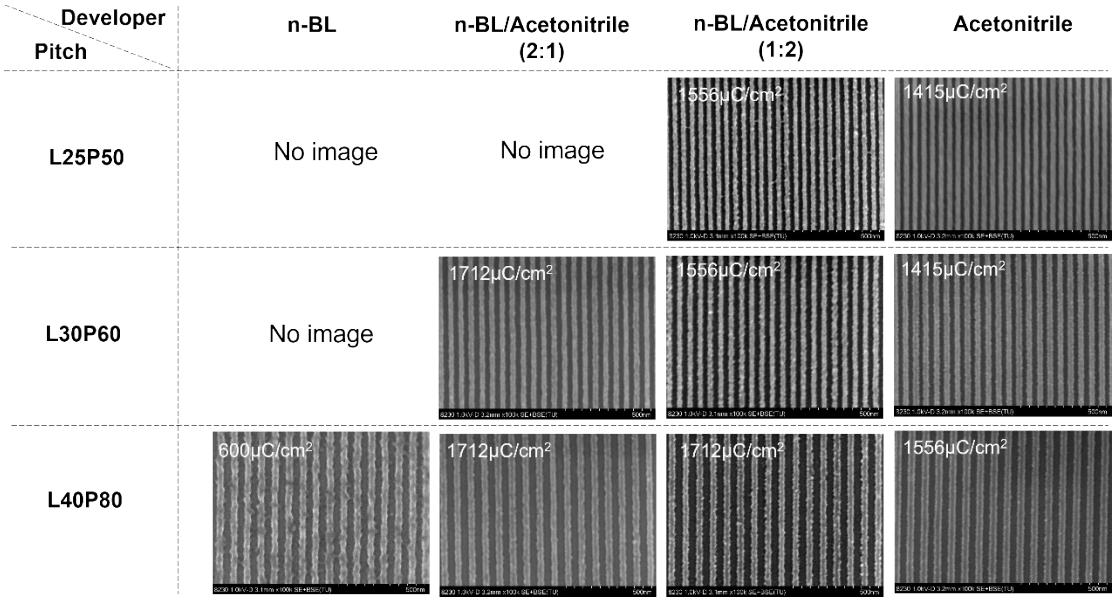

Figure S9. SEM images of negative patterns at HP 25/30/40 nm of $PSNA_{0.4}$ resist developed in n-BL/Acetonitrile developers.

3. Normalized remaining thickness (NRT) analysis

The normalized remaining thickness (NRT) scatter plots with different development conditions were given as shown in Figure S11. After nonlinear fitting the NRT scatter plot by logistic function (a common S-shaped curve),[1] tangent was produced at 0.5 (NRT = 0.5) of the fitted S-shaped curve, as shown in Figure S11 (corresponding to the red line). It is considered that the NRT of photoresist increased linearly on this tangent until it increases to 1, and then stay constant. The sensitivity is defined as the lower limit of dose required to totally retain the resist (D_{100}). The dose of the point with NRT = 0 on the tangent is considered to be the upper limit to keep the thickness of resist films unchanged (D_0). The contrast value (γ) is derived from the following formula;

$$\gamma = \frac{1}{\left\{log\left(\frac{D_{100}}{D_0}\right)\right\}}$$

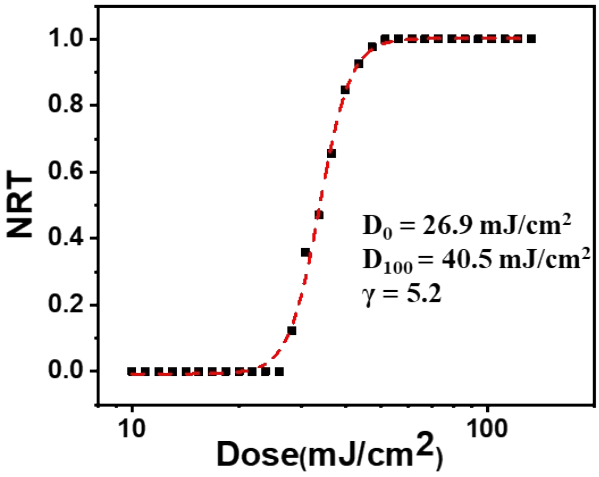

Figure S10. The NRT curves of $PSNA_{0.4}$ resist developed in acetonitrile by EUV irradiation.

4. LER measurement of high-resolution SEM images

The LER parameters for all the patterns were analyzed by the software ProSEM. All the lines in the image were selected for analysis, and the LER on the left and the right were obtained respectively. The average value of them was taken as the LER value of the image.

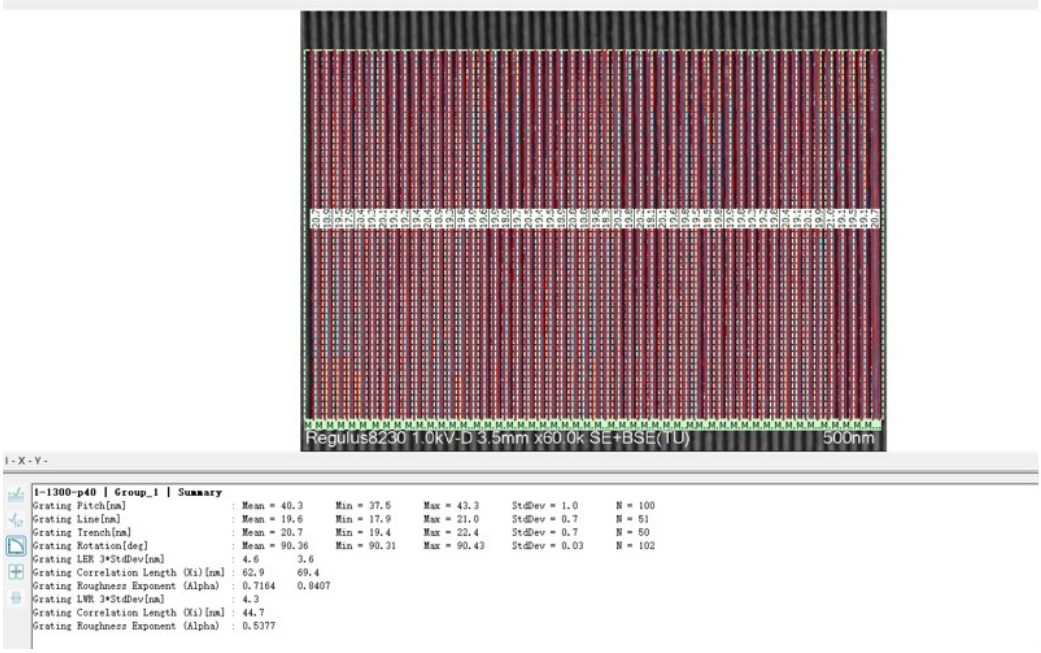

Figure S11. LER measurement of 20 nm L/S pattern of $PSNA_{0.4}$ resist in EBL.

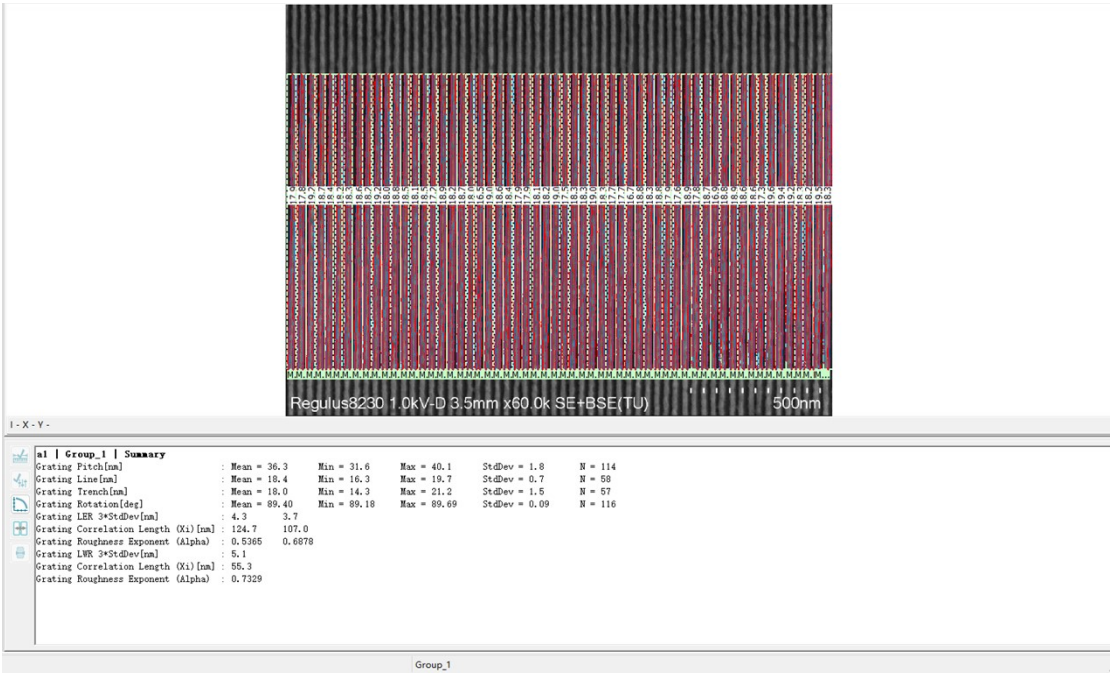

Figure S12. LER measurement of 18 nm L/S pattern of $PSNA_{0.4}$ resist in EBL.

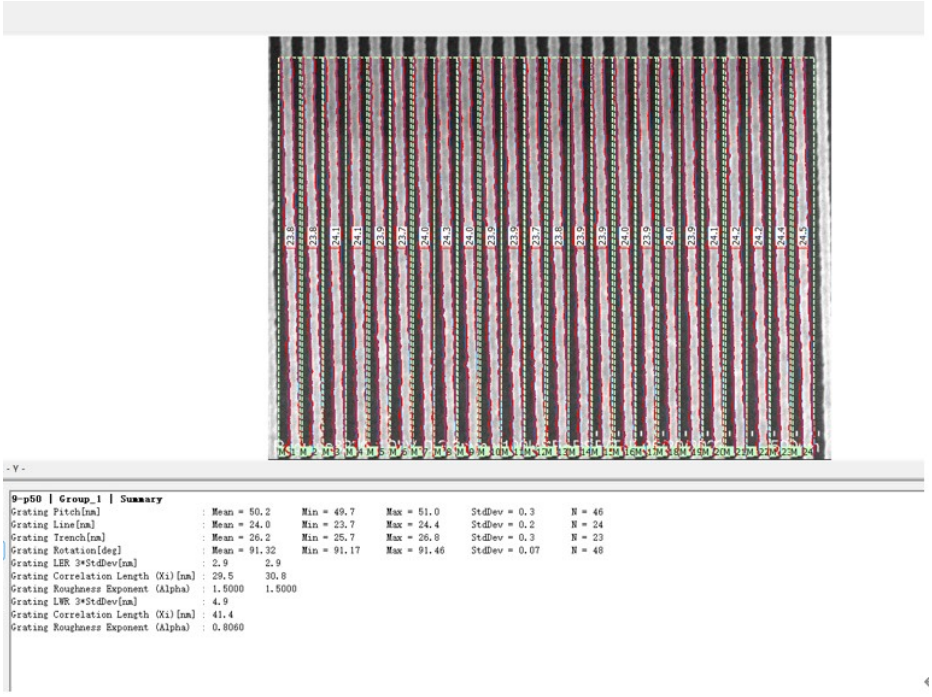

Figure S13. LER measurement of 25 nm L/S pattern of $PSNA_{0.4}$ resist in EUVL

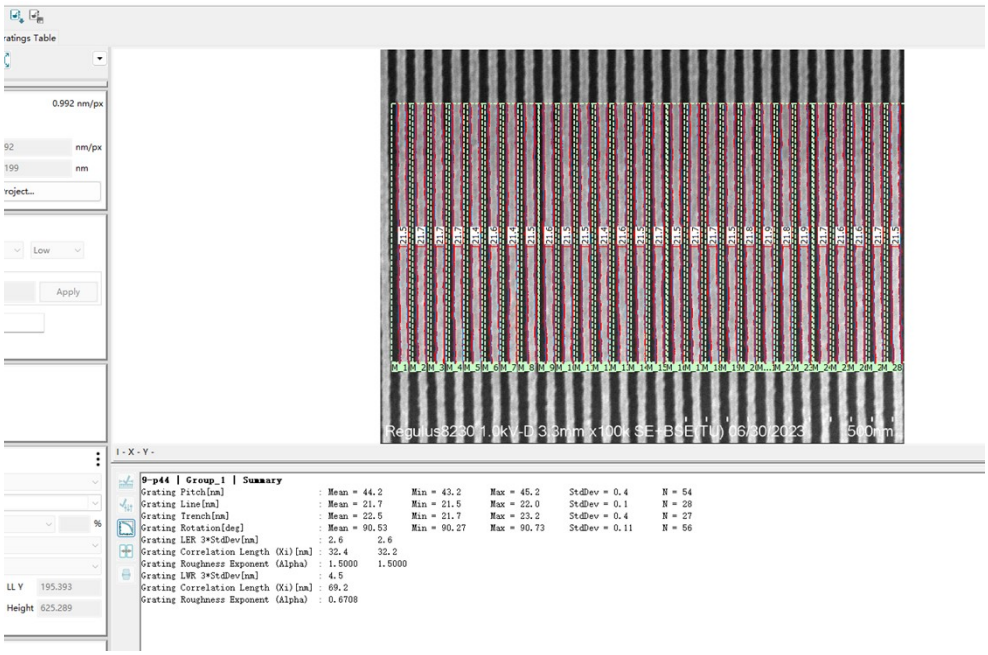

Figure S14. LER measurement of 22 nm L/S pattern of $PSNA_{0.4}$ resist in EUVL.

5. Mechanistic analysis of $PSNA_{0.4}$ resist pattern generations

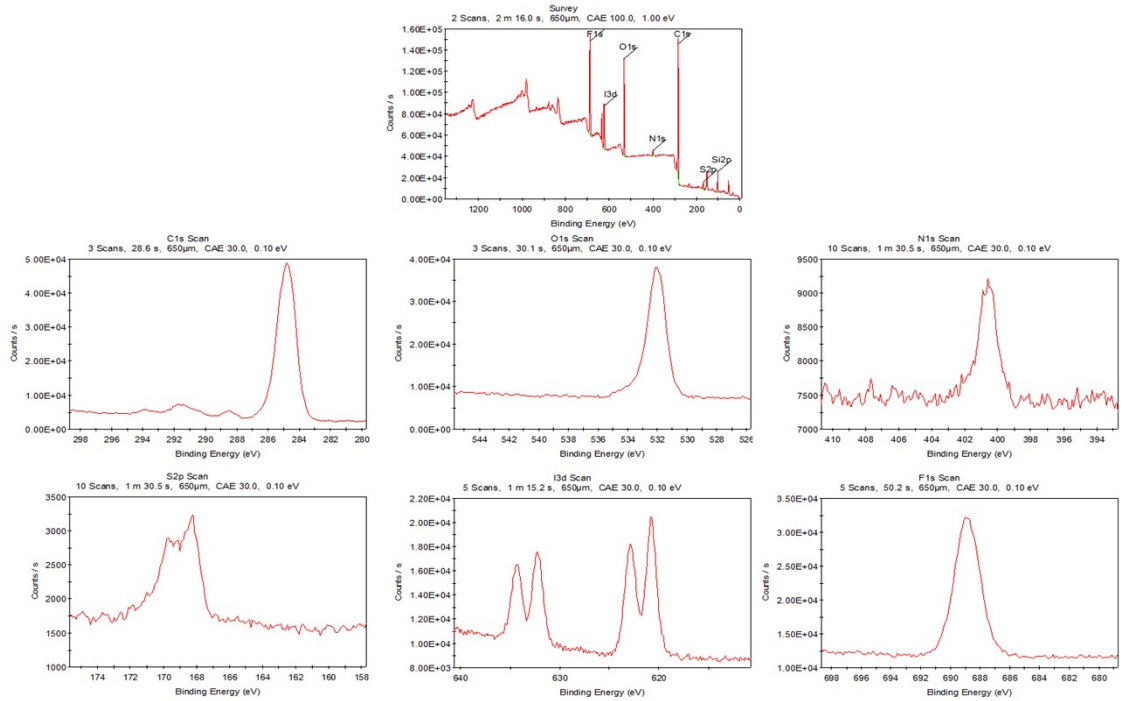

Figure S15. The XPS survey spectrums and high-resolution XPS spectra of C 1s, S 2p, F 1s, N1s, I 3d and O 1s for the pristine film of PSNA0.4 resist.

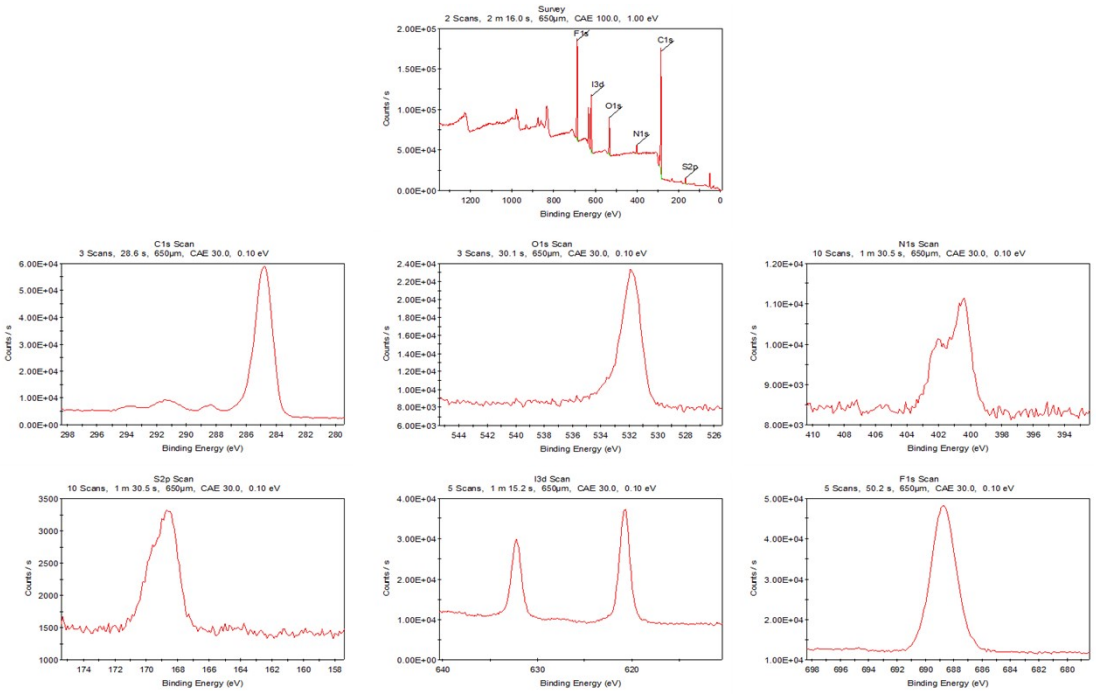

Figure S16. The XPS survey spectrums and high-resolution XPS spectra of C 1s, S 2p, F 1s, N1s, I 3d and O 1s for the PSNA0.4 resist films after e-beam exposure.

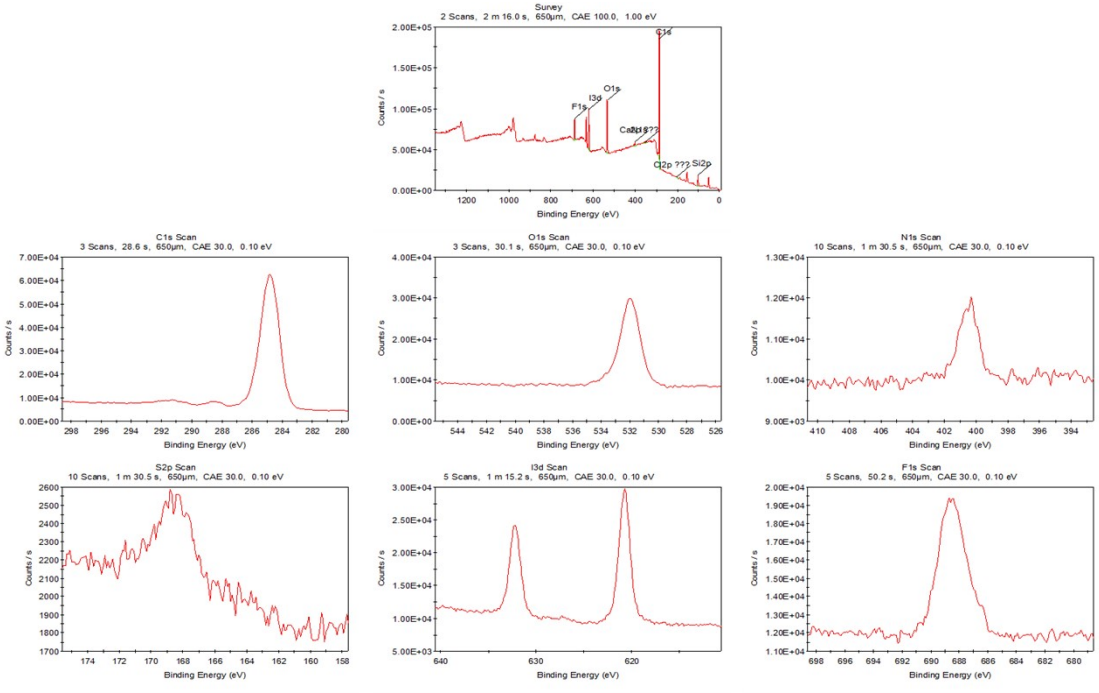

Figure S17. The XPS survey spectrums and high-resolution XPS spectra of of C 1s, S 2p, F 1s, N1s, I 3d and O 1s for the PSNA0.4 resist films after development.

6. Etch Resistance and Pattern Transfer Capability of the $PSNA_{0.4}$ Resist

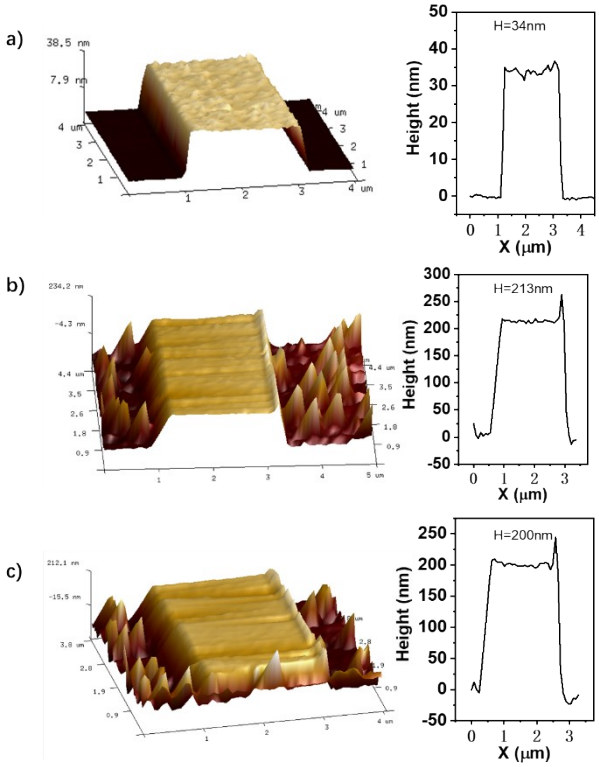

Figure S18. The 3D AFM topography images of the exposed $PSNA_{0.4}$ resist after (a) development, (b) etching and (c) resist-strip, together with height values.

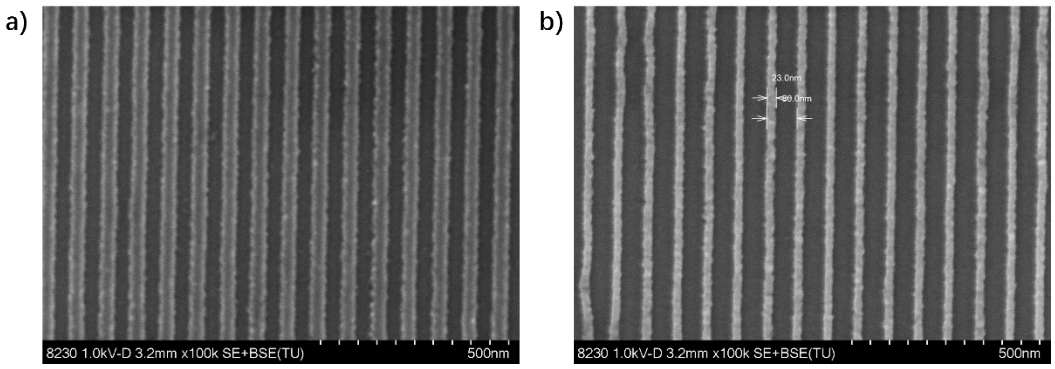

Figure S19. The SEM pictures of (a) 40 nm L/S (b) 20nm L/3S patterns of $PSNA_{0.4}$ resist upon electron beam exposure. (The samples were selected for further etching process, presented in Figure 7).

1. X.-Y. Lu, H. Luo, K. Wang, Y.-Y. Zhang, X.-F. Zhu, D. Li, B. Ma, S. Xiong, P. F. Nealey, Q. Li and G.-P. Wu, *Advanced Functional Materials*, 2021, **31**,2007417.