Supporting Information

A Novel Water Developable Tetraphenyltin Based Nonchemically-Amplified Molecular Resist for Sub-13nm Lithography

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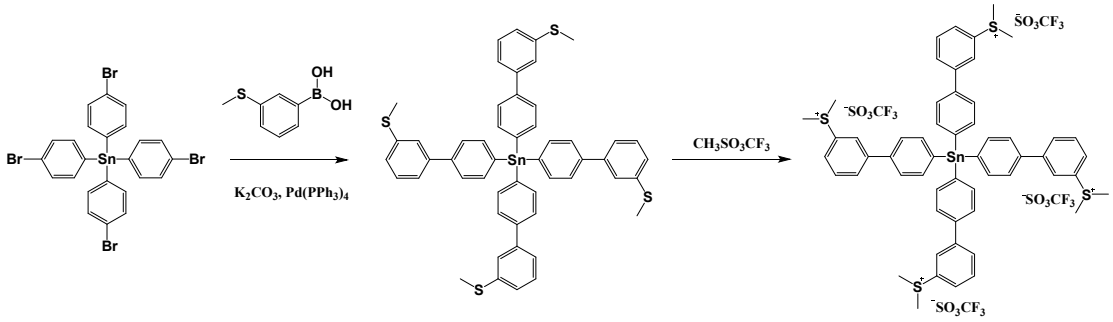
1. Synthesis and Characterization of $SnMS_4$ and $SnMSF_4$



Scheme S1 Synthesis of $SnMSF_4$

Chemicals and Reagents. All the standard reagents and chemicals were purchased from commercial sources and used without any further purification. Sn(*p*-$C_6H_4Br)_4$ was synthesized according to the method reported in previous literature.[1, 2]

Synthesis of tetrakis(3'-(methylthio)-[1,1'-biphenyl]-4-yl)stannane ($SnMS_4$). Sn(*p*-$C_6H_4Br)_4$ (4 g, 5.4 mmol), 3-methylthiophenylphenylboric acid (5.44 g, 32.4 mmol), and anhydrous potassium carbonate (6.00 g, 43.4 mmol) were added to a 200 mL Schlenk flask, which was purged with argon and then charged with water (15 mL) and toluene (30 mL). Then tetratriphenylpalladium (0.40g, 0.35mmol) was added under a nitrogen atmosphere. The mixture was stirred at reflux overnight under a nitrogen atmosphere. The solution was cooled to room temperature and extracted with toluene/H_2O three times. The combined organic layer was washed with brine, and dried over Mg_2SO_4. The solvent was removed under vacuum, and the crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2=1:1, v/v) to give $SnMS_4$ as a white solid (0.96 g, 19 %).^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.76 (d, *J* = 8.1 Hz, 8H, benzene), 7.68 (d, *J* = 8.1 Hz, 8H, benzene), 7.51 (s, 4H, benzene), 7.43 – 7.35 (m, 8H, benzene), 7.30 – 7.22 (m, 4H, benzene), 2.53 (s, 12H, CH_3).**Synthesis of (stannanetetrayltetrakis([1,1'-biphenyl]-4',3-diyl))tetrakis (dimethylsulfonium)**

trifluoromethanesulfonate ($SnMSF_4$). $SnMS_4$ (0.24 g, 0.26 mmol) was added to a 250 mL round-bottomed flask with 120 mL dry CH_2Cl_2. Then methyl trifluoromethanesulfonate (0.52 g, 3.2 mmol) was added at room temperature. After stirring in the dark for 24 h, a large number of white solids were precipitated in the solution, which was filtered and washed with ether to give white solid of 0.38 g with a yield of 93%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.19 (s, 4H, benzene), 8.09 (d, J = 7.9 Hz, 4H, benzene), 7.99 – 7.76 (m, 24H, benzene), 3.21 (s, 24H, CH_3). ^{19}F NMR (600 MHz, CD_3CN) δ -79.29 (s, 1H). HRMS (ESI) m/z: $[M]^{4+}$ calcd for $C_{56}H_{56}S_4Sn^{4+}$ 244.0566, found 244.0566; $[M]^-$ calcd for $CF_3SO_3^-$ 148.9526, found 148.9525. FT-IR: ν_{max}/cm^{-1} 3061, 3024 and 2935 (CH), 1258 (CF_3), 1161 and 640 (SO_2), 1030 (S-O). Elemental analysis (%) calcd for $C_{60}H_{56}F_{12}O_{12}S_8Sn$: C, 45.84; H, 3.59; S, 16.31; found: C, 46.64; H, 3.68; S, 16.06.

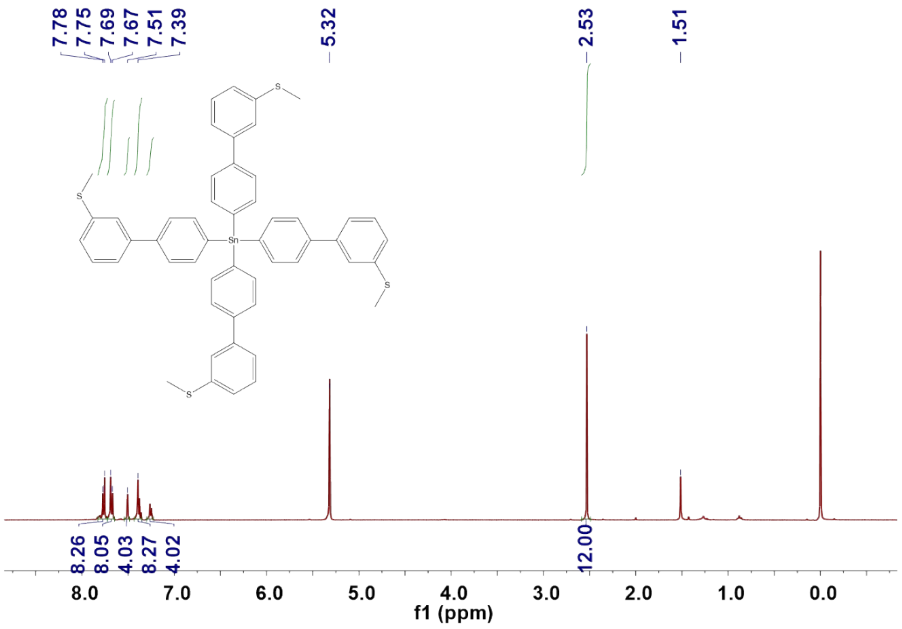


Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of SnMS.

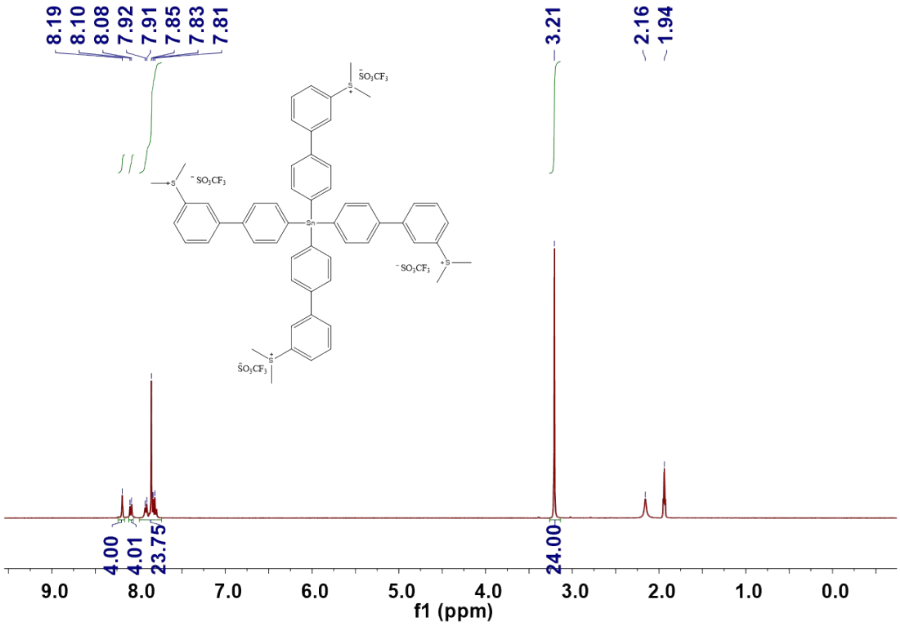


Figure S2. ^{1}H NMR (400 MHz, CD_3CN) spectrum of $SnMSF_4$.

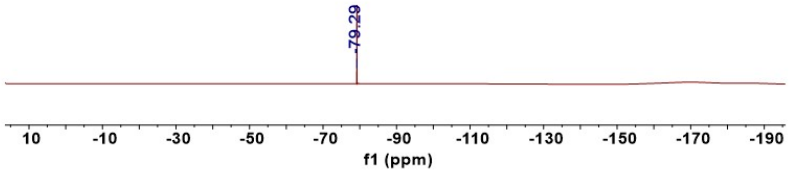


Figure S3. ^{19}F NMR (400 MHz, CD_3CN) spectrum of $SnMSF_4$.

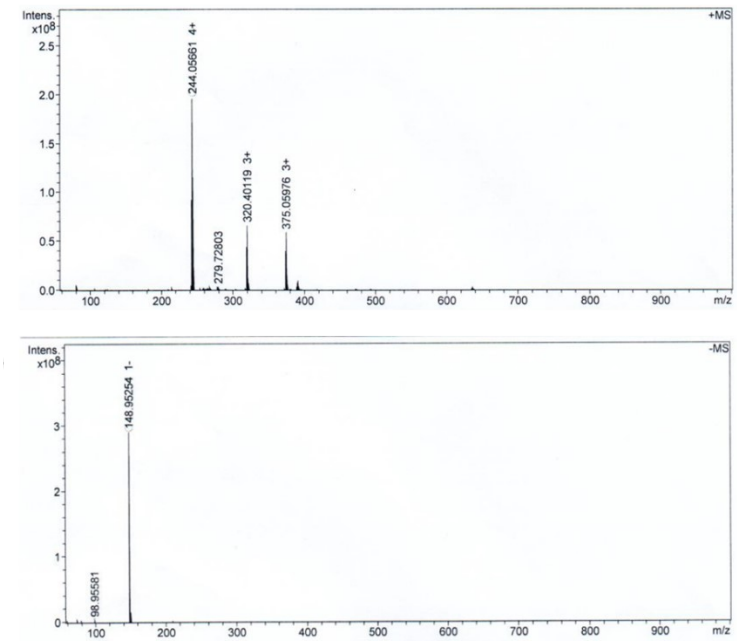


Figure S4. HRMS (ESI) spectrum of $SnMSF_4$.

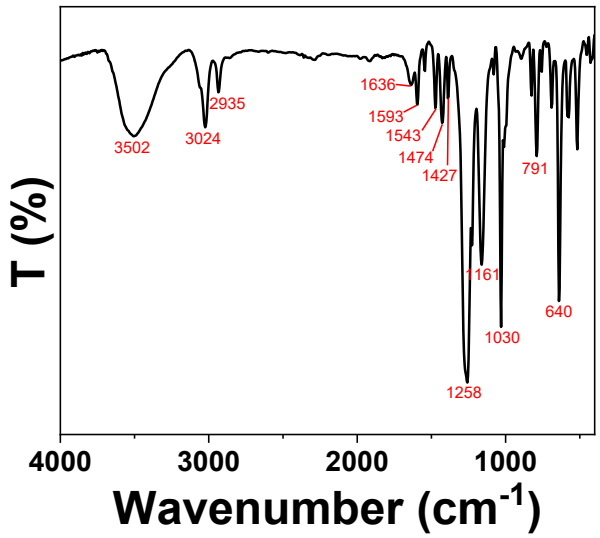


Figure S5. FT-IR spectrum of $SnMSF_4$.

2. Normalized remaining thickness (NRT) analysis

The contrast curves were obtained by fitting the film thickness data using a logistic function. According to the contrast curve, the tangent line at y = 0.5 can be obtained. The dose of tangent at y = 0 and 1 are considered as D_0 and D_{100}. The contrast could be calculated by the equation 1:

$$\gamma = \frac{1}{log(D_{100}/D_0)} \quad (1)$$

3. EUV lithographic patterns with different exposure doses for $SnMSF_4$ resist

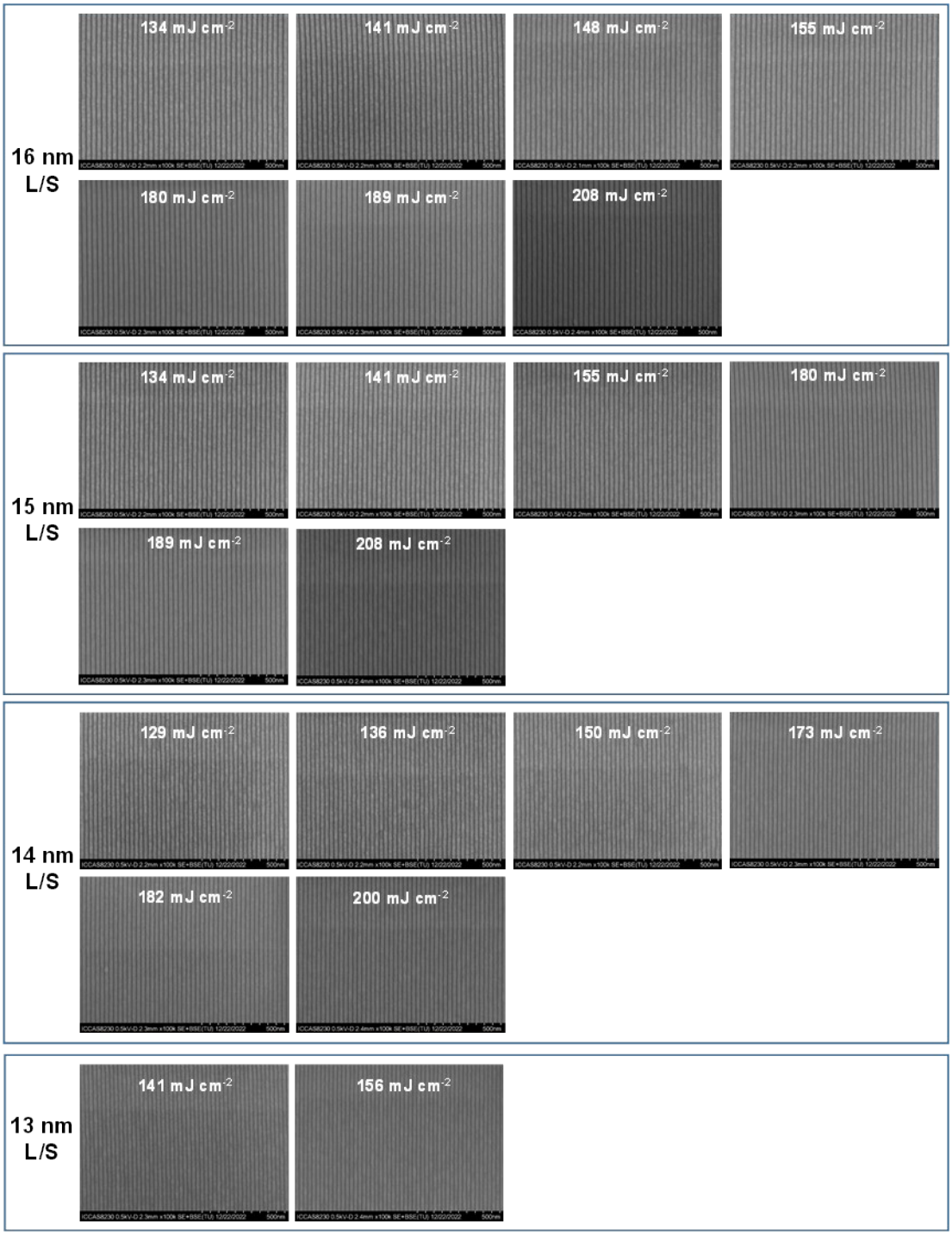


Figure S6. The 16, 15, 14 and 13 nm L/S line patterns of $SnMSF_4$ resist under different exposure doses for EUVL (Developer：H_2O).

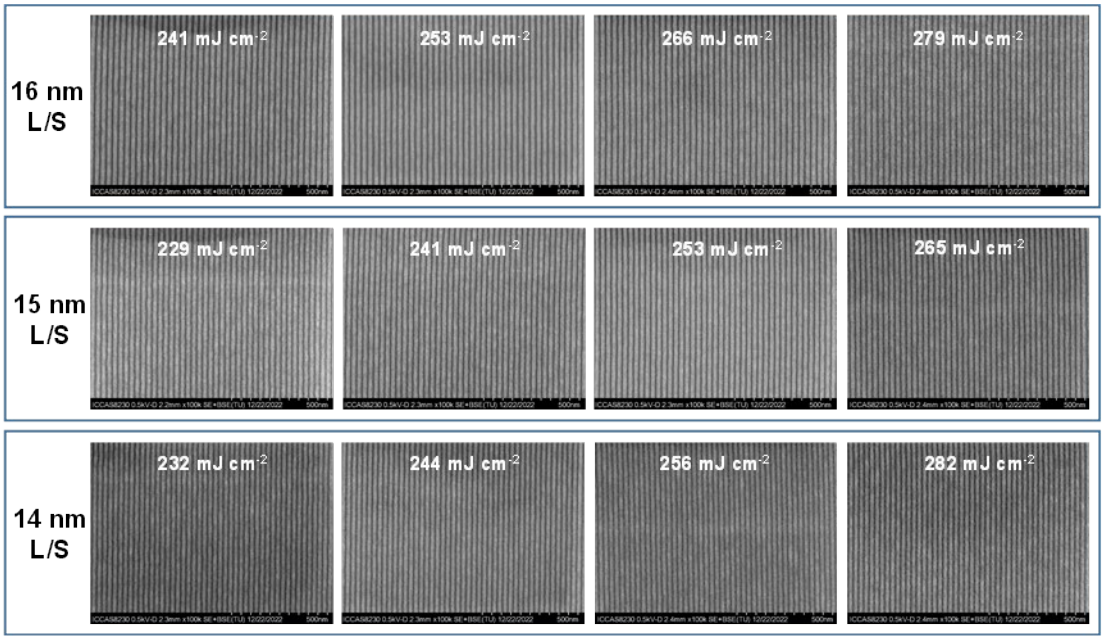


Figure S7. The 16, 15 and 14 nm L/S line patterns of $SnMSF_4$ resist under different exposure doses for EUVL (Developer：IPA/H_2O=1/10).

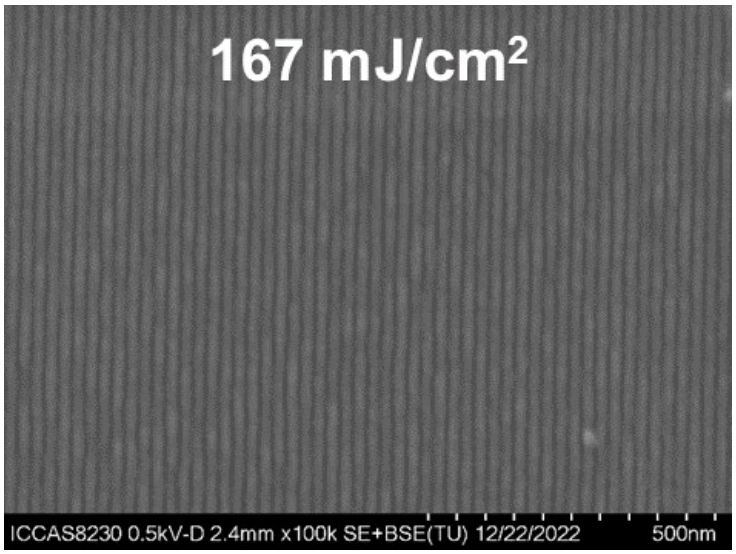


Figure S8 The 12 nm L/S line patterns of $SnMSF_4$ resist for EUVL (Developer: H_2O).

4. LER measurement of high-resolution SEM images

The information on the SEM images was listed as following:

Data Size = 1280x960; Pixel Size=0.9921876; Signal Name=SE+BSE(TU); Magnification = 100000

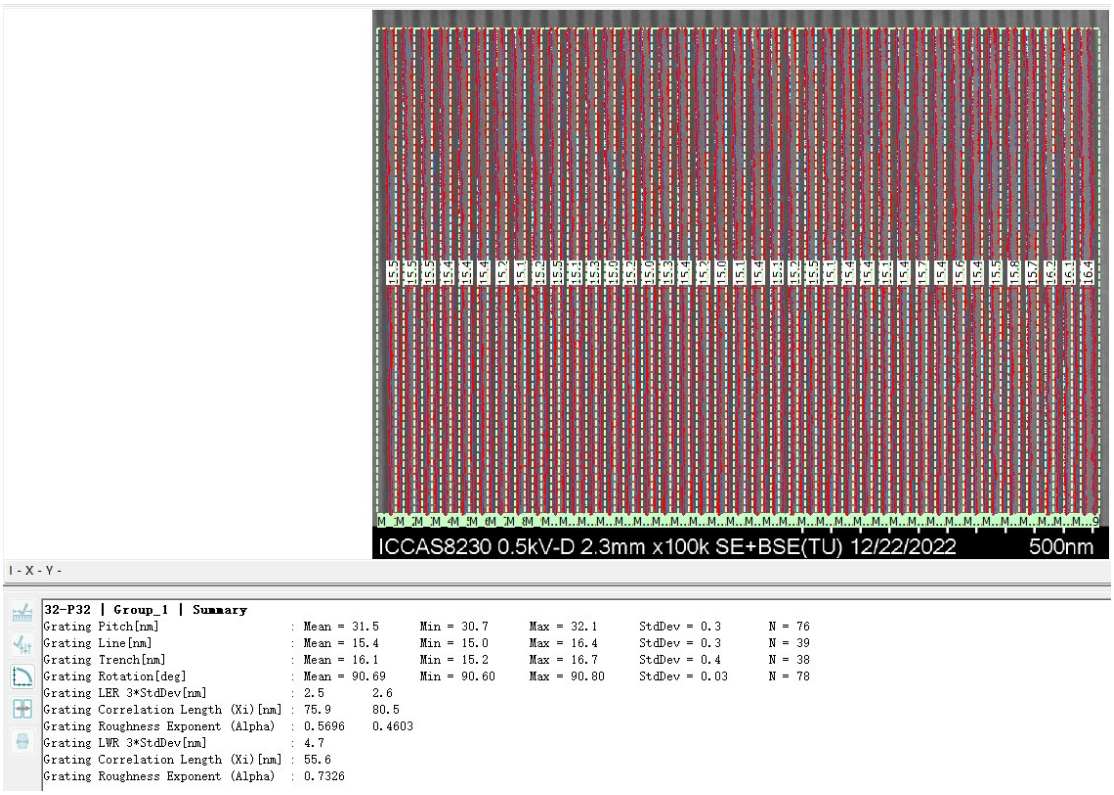


Figure S9. The LER and LWR measurement of 16 nm L/S pattern of $SnMSF_4$ resist (Developer：H_2O).

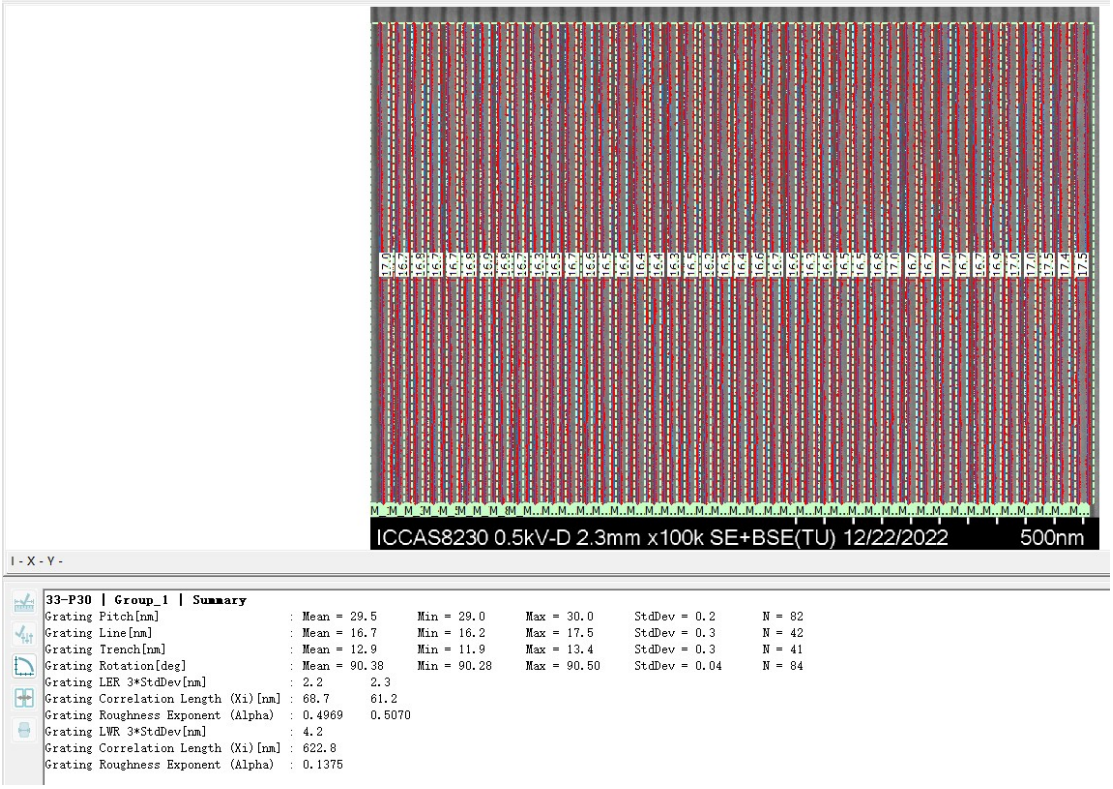


Figure S10. The LER and LWR measurement of 15 nm L/S pattern of $SnMSF_4$ resist (Developer：H_2O).

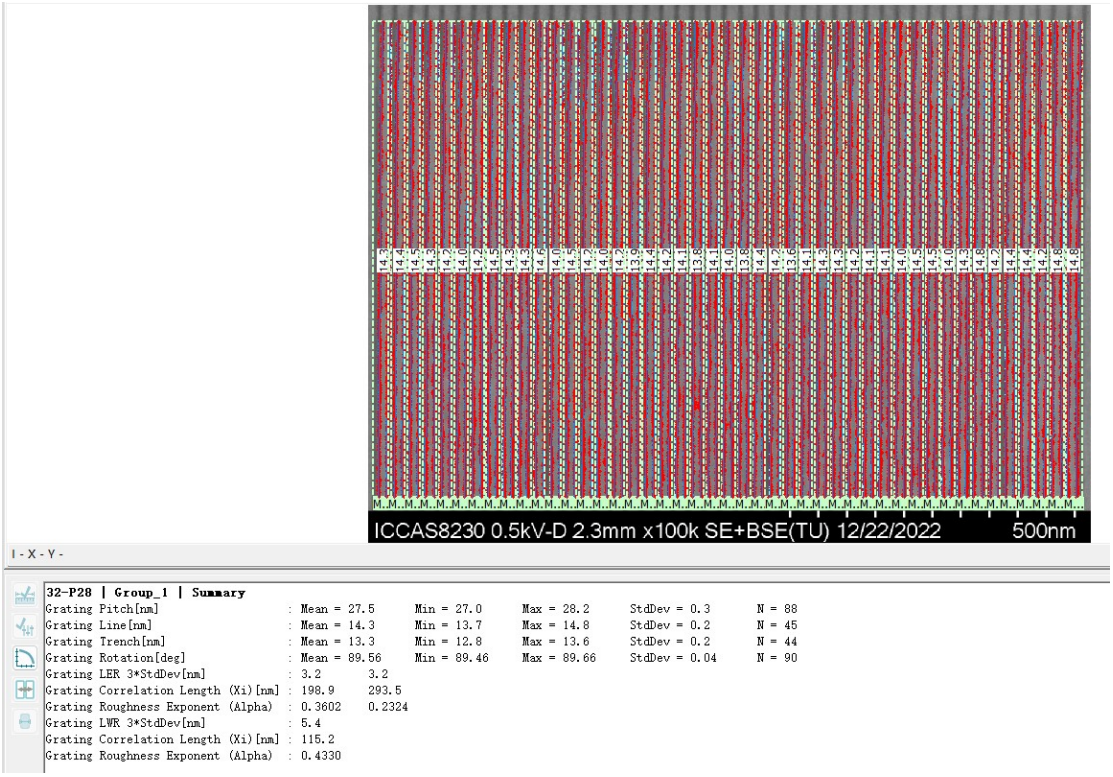


Figure S11. The LER and LWR measurement of 14 nm L/S pattern of $SnMSF_4$ resist (Developer：H_2O).

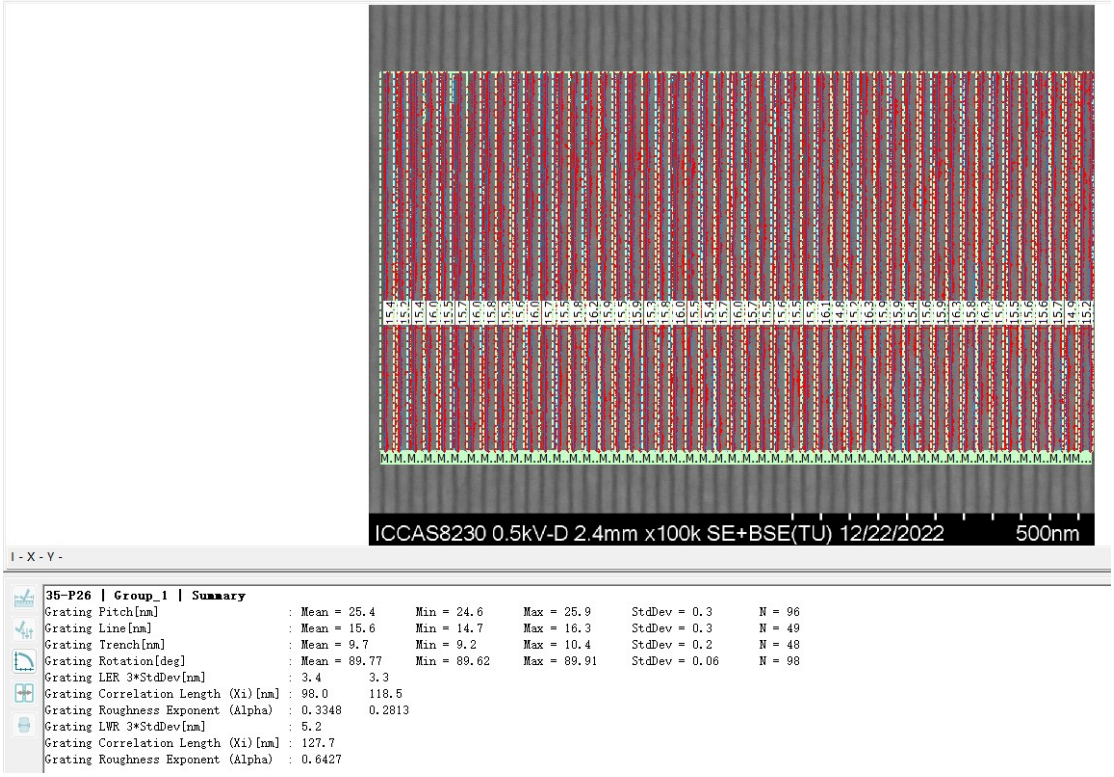


Figure S12. The LER and LWR measurement of 13 nm L/S pattern of $SnMSF_4$ resist (Developer：H_2O).

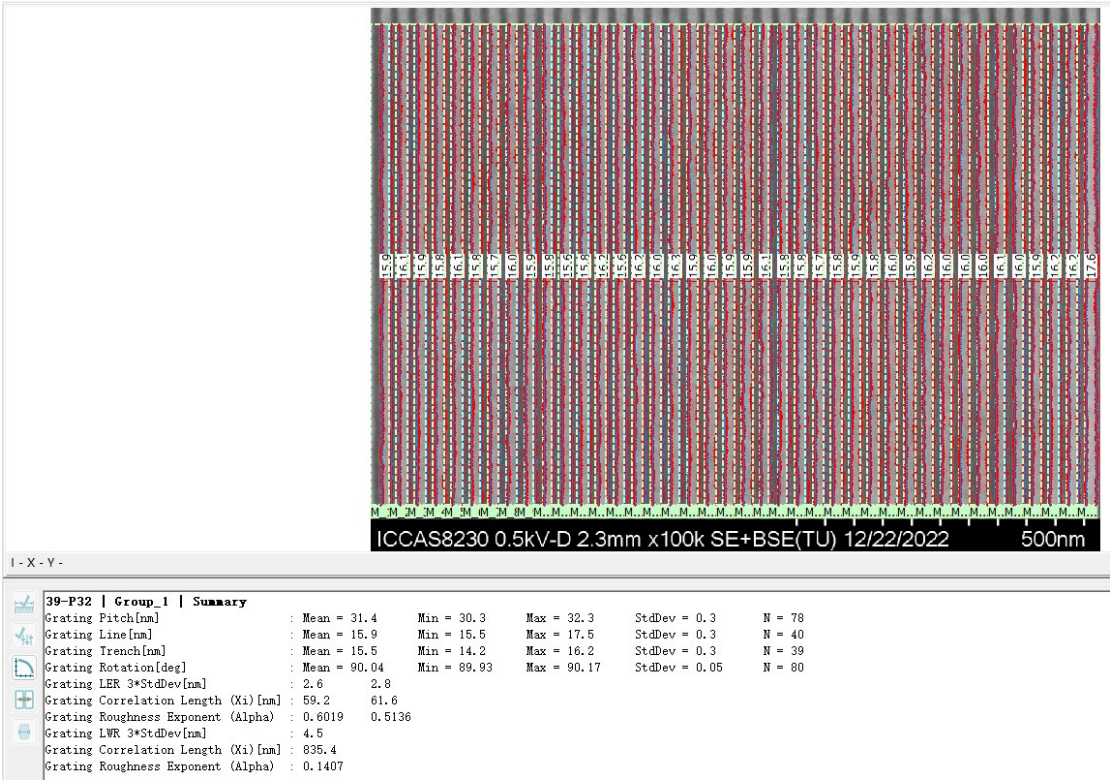


Figure S13. The LER and LWR measurement of 16 nm L/S pattern of $SnMSF_4$ resist (Developer：IPA/H_2O=1/10).

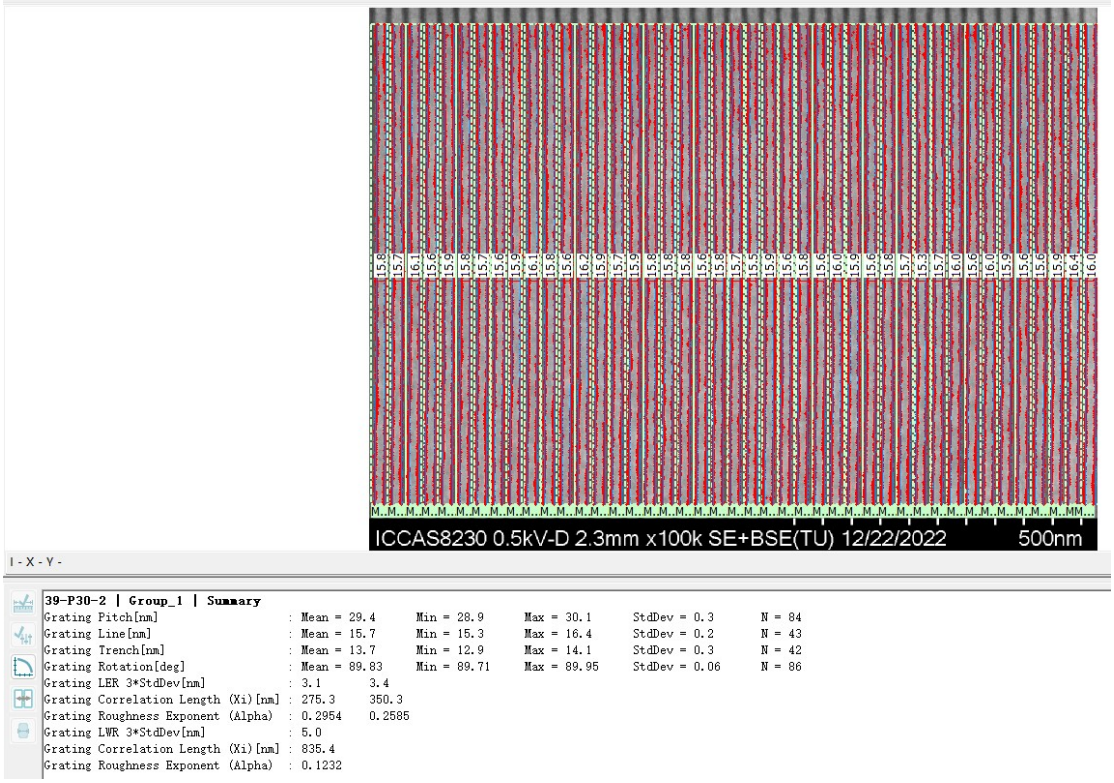


Figure S14. The LER and LWR measurement of 15 nm L/S pattern of $SnMSF_4$ resist (Developer：IPA/H_2O=1/10).

5. XPS test results for mechanism analysis

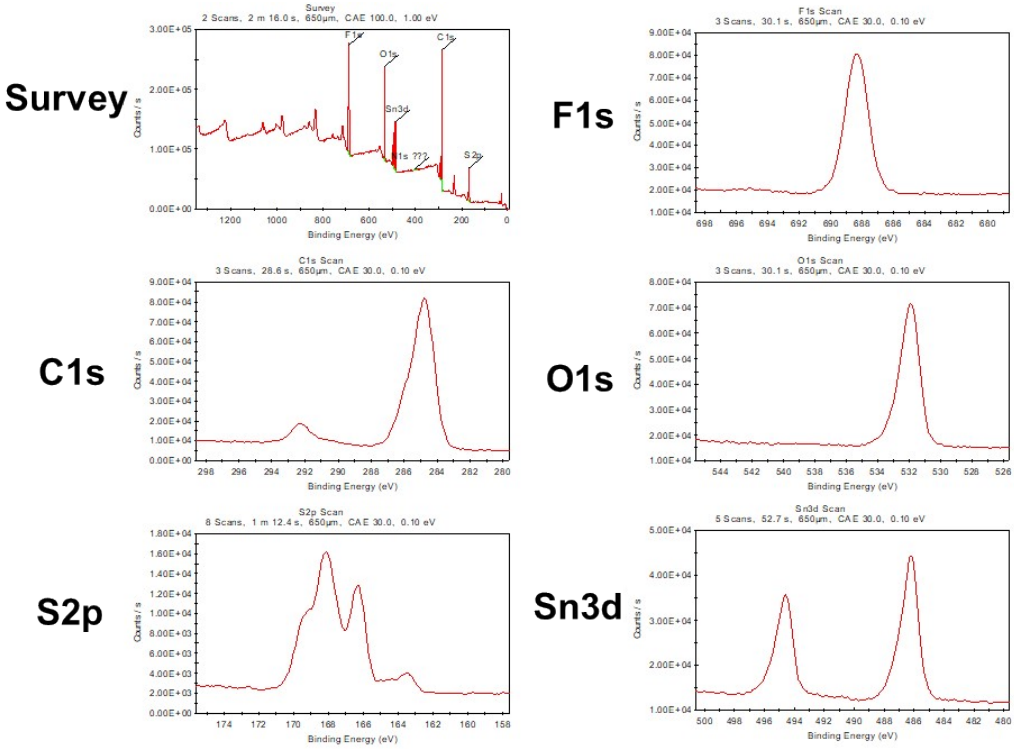


Figure S15. The XPS survey spectrums and high-resolution XPS spectra of C 1s, S 2p, F 1s, O 1s and Sn 3d for the pristine film of $SnMSF_4$ resist.

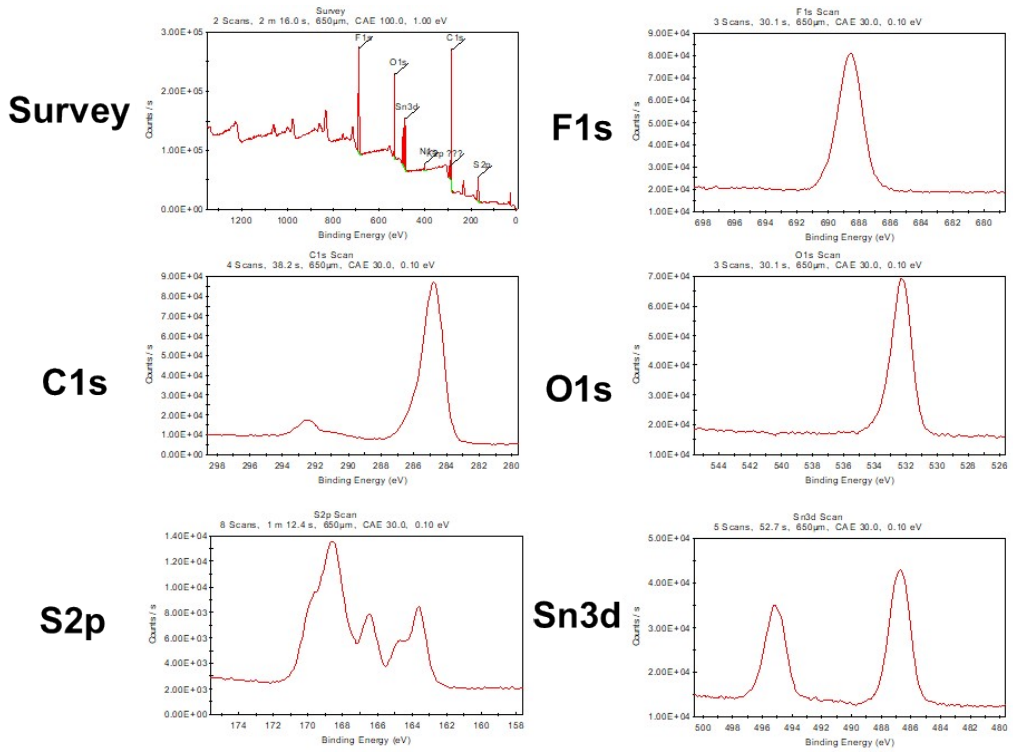


Figure S16. The XPS survey spectrums and high-resolution XPS spectra of C 1s, S 2p, F 1s, O 1s and Sn 3d for the $SnMSF_4$ resist films after e-beam exposure.

1. Yang, Y.; Beele, B.; Bluemel, J., Easily immobilized di- and tetraphosphine linkers: Rigid scaffolds that prevent interactions of metal complexes with oxide supports. *Journal of the American Chemical Society* **2008,** *130* (12), 3771-3773.
2. Uptmoor, A. C.; Geyer, F. L.; Rominger, F.; Freudenberg, J.; Bunz, U. H. F., Tetrahedral Tetrakis(p-ethynylphenyl) Group IV Compounds in Microporous Polymers: Effect of Tetrel on Porosity. *Chempluschem* **2018,** *83* (5), 448-454.