

Supporting Information to:

Polyarylenesulfonium Salt as a Novel and Versatile Nonchemically Amplified Negative Tone Photoresist for High-Resolution Extreme Ultraviolet Lithography Applications

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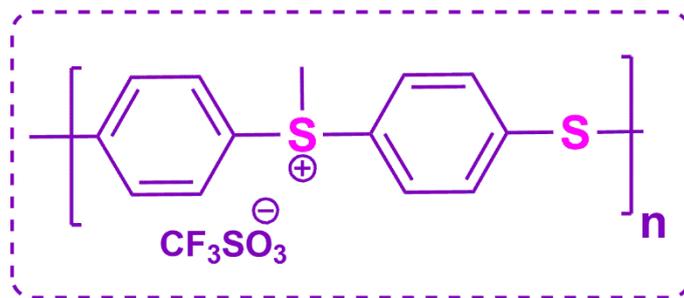


Figure S1. Chemical structure of PAS resist.

EXPERIMENTAL SECTION

Materials and methods

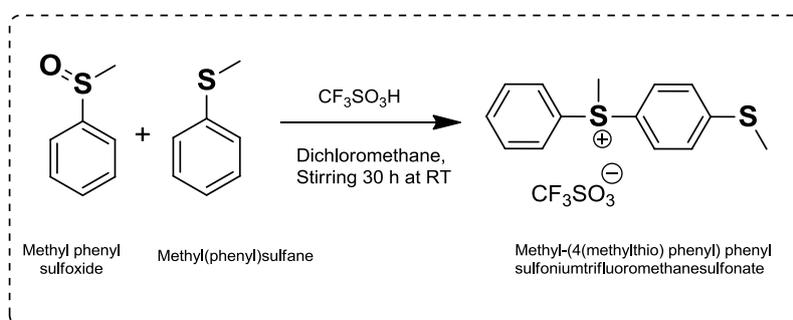
Dichloromethane (HPLC grade) was purchased from Merck, India and dried by using calcium hydride before use. Tetrabutyl ammonium hydroxide and trifluoromethane sulfonic acid were purchased from Sigma Aldrich and were used as received. Pyridine and bromine were purchased from the Alfa Aesar, India. FT-IR spectra were recorded on a Perkin Elmer Spectrum 2 spectrophotometer using KBr pellets. ¹H and ¹³C NMR spectra were recorded on Jeol JNM ECX 500 MHz spectrometer in DMSO-*d*₆. TGA measurements were performed on NETZSCH STA 449 F1 JUPITER Series instrument; the heating rate employed was 10 °C/min under N₂ atmosphere over a temperature range of 25-1000 °C. Molecular weight and polydispersity index (PDI) of PAS were determined by performing gel permeation chromatography (GPC) analyses using PL gel mixed B 10 mm column on a 1260 Infinity Series instrument from Agilent. Micro exposure tool (MET) with an Advanced Light Source (ALS) at SEMATECH Berkeley was used as the lithography tool for the EUV studies. The mask used for the nano-lithographic patterning was IMO228775. Thickness measurements were measured using NanoMap-D stylus profilometer. FE-SEM QUANTA 200FEG and

Atomic Force Microscope (AFM) (Dimension Icon, Bruker) tools were used for imaging the critical dimensions of various patterns made on silicon substrates.

Synthesis of poly[methyl(4-phenylthiophenyl)sulfoniumtrifluoromethanesulfonate], (PAS).

PAS was synthesized according to a reported procedure by Tsuchida *et al.*¹⁻³ Synthesis of PAS involved a four step process as follows:

1) Synthesis of methyl-(4-methylthio)phenyl)phenylsulfoniumtrifluoromethanesulfonate



Scheme 1. Synthetic route of methyl-(4-methylthio)phenyl)phenylsulfoniumtrifluoromethane sulfonate.

A 500 ml, three necked, round bottom flask fitted with a dropping funnel was charged with methylphenylsulfoxide (7 g, 50 mmol), methyl(phenyl)sulfane (6.2 g, 50 mmol) and dichloromethane (50 mL) under N_2 atmosphere and stirred at 0 °C. After that, trifluoromethanesulfonic acid (15 g, 100 mmol) in dichloromethane (50 ml) was added drop wise over a period of 20 minutes through the dropping funnel and stirring was continued for 30 minutes. After 30 minutes, the temperature of the reaction mixture was gradually raised to room temperature and stirred again for 20 hours. After completion of the reaction, the reaction mixture was poured into ice cold water followed by extraction with 100 ml of dichloromethane. Pure crystals of methyl-(4-

(methylthio)phenyl)phenylsulfoniumtrifluoromethanesulfonate were obtained after purification of the reaction mixture with diethyl ether. Yield: 15.7 g; 79 %. ^1H NMR (CD_3CN , 500 MHz) δ_{H} 7.5-8.0 (phenyl, 9H, m), 3.79 (methyl of sulfonium bond, 3H, s), 2.50 (methyl of sulfide bond, 3H, s). ^{13}C NMR (CD_3CN , 125 MHz) δ_{C} 147.0, 133.54, 130.78, 130.33, 129.53, 128.26 (phenyl C), 126.73, 122.04 (triflate, CF_3), 26.54 (methyl of sulfonium bond C), 13.93 (methyl of sulfide bond C). ^{19}F NMR (CD_3CN , 376 MHz) δ_{F} -77.65 (3F, s, CF_3).

The ^1H NMR chemical shifts observed in the range 7.5-8.0 ppm are due to the aromatic protons present on the phenyl rings and the resonance peaks observed at 3.79 and 2.50 ppm are due to the methyl protons present on the sulfonium and sulfide functionalities respectively. ^{13}C NMR signals observed at 147-128 ppm are due to the aromatic carbons present on the phenyl rings. The peaks observed in carbon NMR at 122.04, 26.54 and 13.93 ppm correspond to the CF_3 and CH_3 carbons present on the sulfonium and sulfide functionalities. The signal at -77.65 ppm in ^{19}F NMR is due to the fluorine atoms of the triflate functionality.

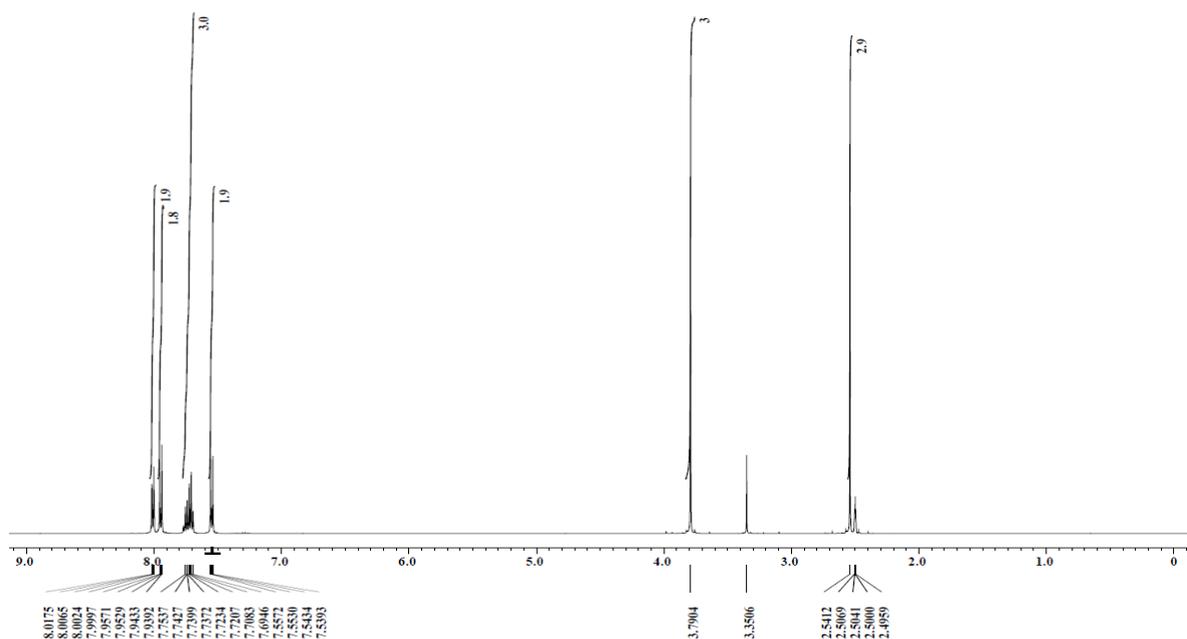


Figure S2. ^1H NMR of methyl-(4-(methylthio)phenyl)phenylsulfoniumtrifluoromethane sulfonate.

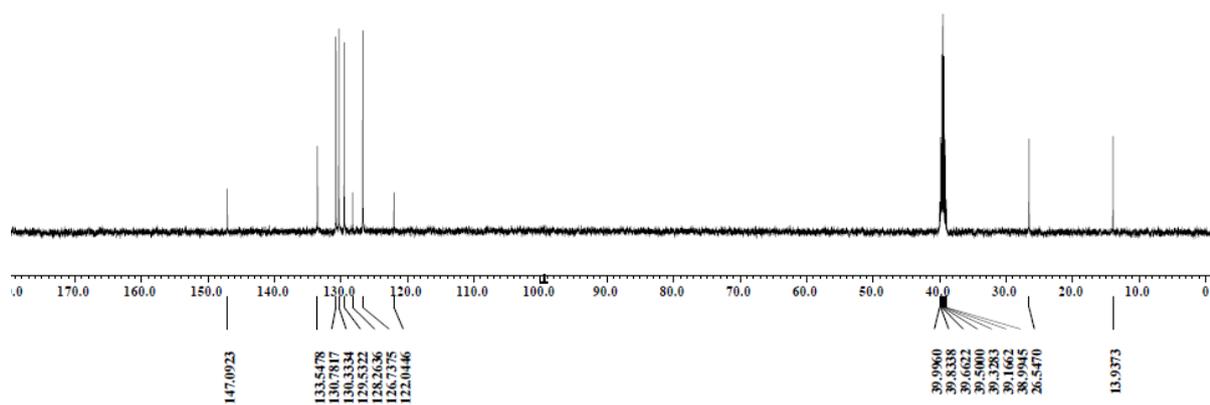


Figure S3. ^{13}C NMR of methyl-(4-(methylthio)phenyl)phenylsulfoniumtrifluoromethane sulfonate.

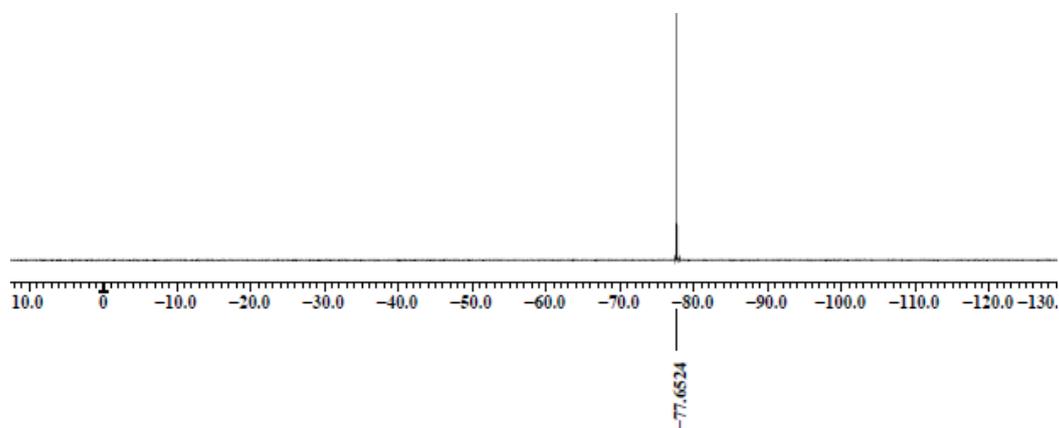
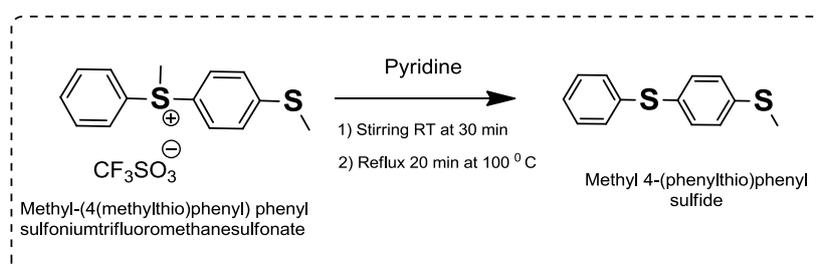


Figure S4. ^{19}F NMR of methyl-(4-(methylthio)phenyl)phenylsulfoniumtrifluoromethane sulfonate.

2) Synthesis of methyl 4-(phenylthio)phenylsulfide (MPS)



Scheme 2. Synthetic route of methyl 4-(phenylthio)phenylsulfide (MPS).

10 g (28.88 mmol) of methyl-(4-(methylthio)phenyl)phenylsulfoniumtrifluoromethane sulfonate and 50 ml pyridine were taken in a two necked round bottom flask (250 ml) equipped with a reflux condenser and a N_2 inlet. The reaction mixture was stirred at room

temperature for 30 min followed by stirring at 100 °C for 20 minutes. The reaction mixture was then poured into 10% HCl solution followed by extraction with dichloromethane. Pure, colourless liquid product was obtained on evaporation of the solvent under reduced pressure. Yield: 6.1 g; 91%. ^1H NMR (500 MHz, CDCl_3): δ_{H} 7.16-7.29 (phenyl, 9 H, m), 2.44 (methyl, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ_{C} 138.15, 136.43, 132.27, 131.23, 130.02, 129.06, 127.02, 126.62, 15.61.

The ^1H NMR chemical shifts observed in the range 7.29-7.16 ppm correspond to the aromatic protons present on the phenyl rings and the resonance peak observed at 2.44 ppm corresponds due to the methyl protons present on the sulfide functionality. ^{13}C NMR signals observed at 138-126 ppm and 15.61 ppm are due to the aromatic carbon atoms on the phenyl rings and the methyl carbon on the sulfide functionality respectively.

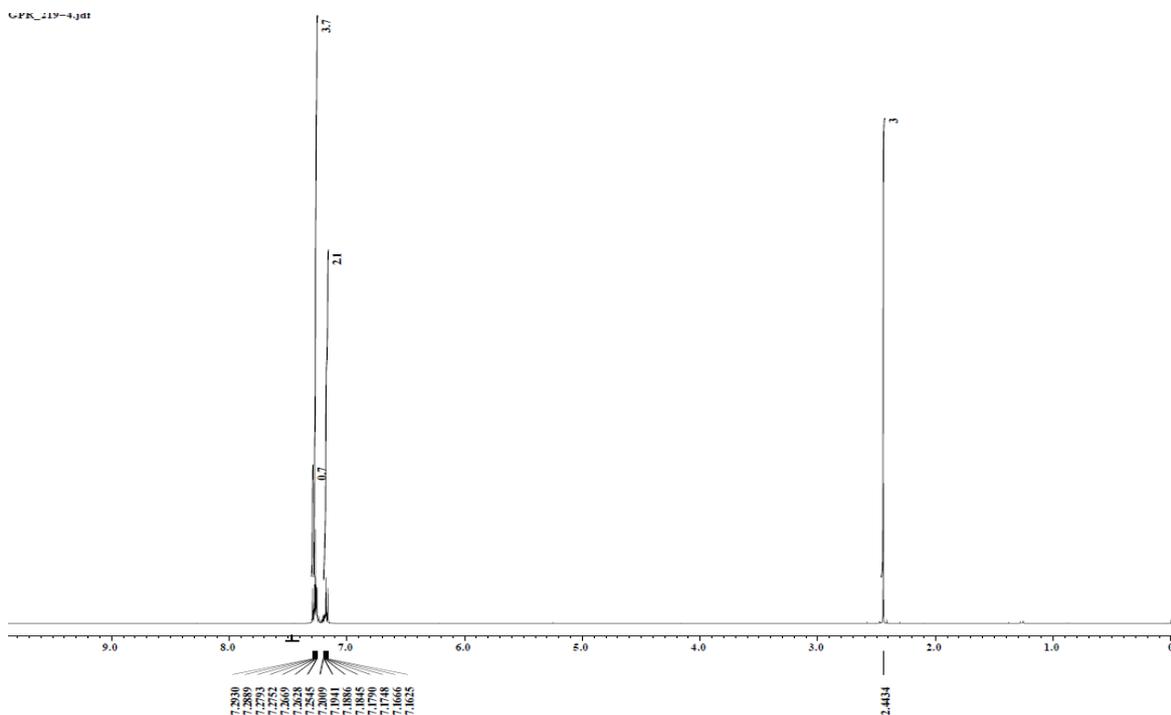


Figure S5. ^1H NMR of methyl 4-(phenylthio)phenylsulfide.

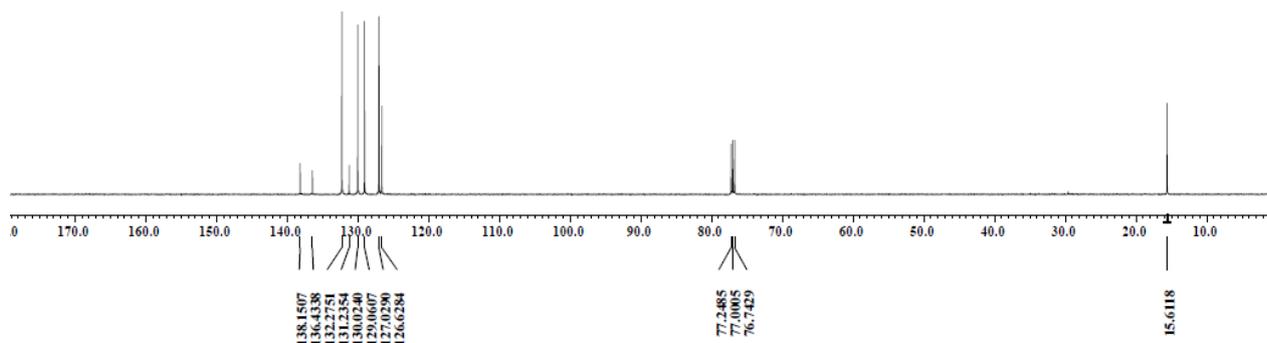
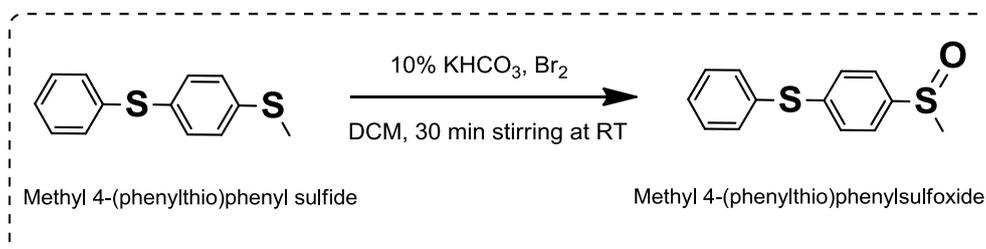


Figure S6. ^{13}C NMR of methyl 4-(phenylthio)phenylsulfide.

3) Synthesis of methyl 4-(phenylthio)phenylsulfoxide (PSO)



Scheme 3. Synthetic route of methyl 4-(phenylthio)phenylsulfoxide (PSO).

Methyl 4-(phenylthio)phenylsulfide (5 g, 21.6 mmol), 10% K_2CO_3 (43 ml) and dichloromethane (50 ml) were taken in a 500 ml two necked round bottom flask equipped with a dropping funnel. The reaction mixture was stirred for 30 min at room temperature. After this, the reaction setup was placed in an ice bath at $0\text{ }^\circ\text{C}$ and bromine (3.45 g, 21.6

mmol) in 50 ml of dichloromethane was added drop wise over a period of 10 minutes. After the addition of bromine, the reaction mixture was stirred at room temperature for 40 minutes. During this period, the reaction mixture became pale orange in color. Saturated KCl solution (100 ml) and dichloromethane (50 ml) were added to the reaction mixture and stirred for 15 minutes. The organic layer was then extracted with dichloromethane (100 ml) and washed twice with water and dried over anhydrous sodium sulfate. The reaction mixture was further washed several times with diethyl ether to get pure white solid of methyl 4-(phenylthio)phenyl sulfoxide (PSO) in 92 % yield (4.92 g). ^1H NMR (500 MHz, DMSO- d_6): δ_{H} 7.37-7.64 (phenyl, 9 H, m), 2.72 (methyl, 3H). ^{13}C NMR (125 MHz, DMSO- d_6) δ_{C} 144.55, 139.54, 132.61, 132.47, 129.95, 129.24, 128.61, 124.76, 43.13.

The ^1H NMR chemical shifts observed in the range 7.64-7.37 ppm are due to the aromatic protons present on the phenyl rings and the resonance peak observed at 2.72 ppm is due to the methyl protons on the sulfoxide functionality. ^{13}C NMR signals observed at 144-124 ppm and 43.13 ppm correspond to the aromatic carbons on the phenyl rings and the methyl carbon on the sulfoxide functionality respectively.

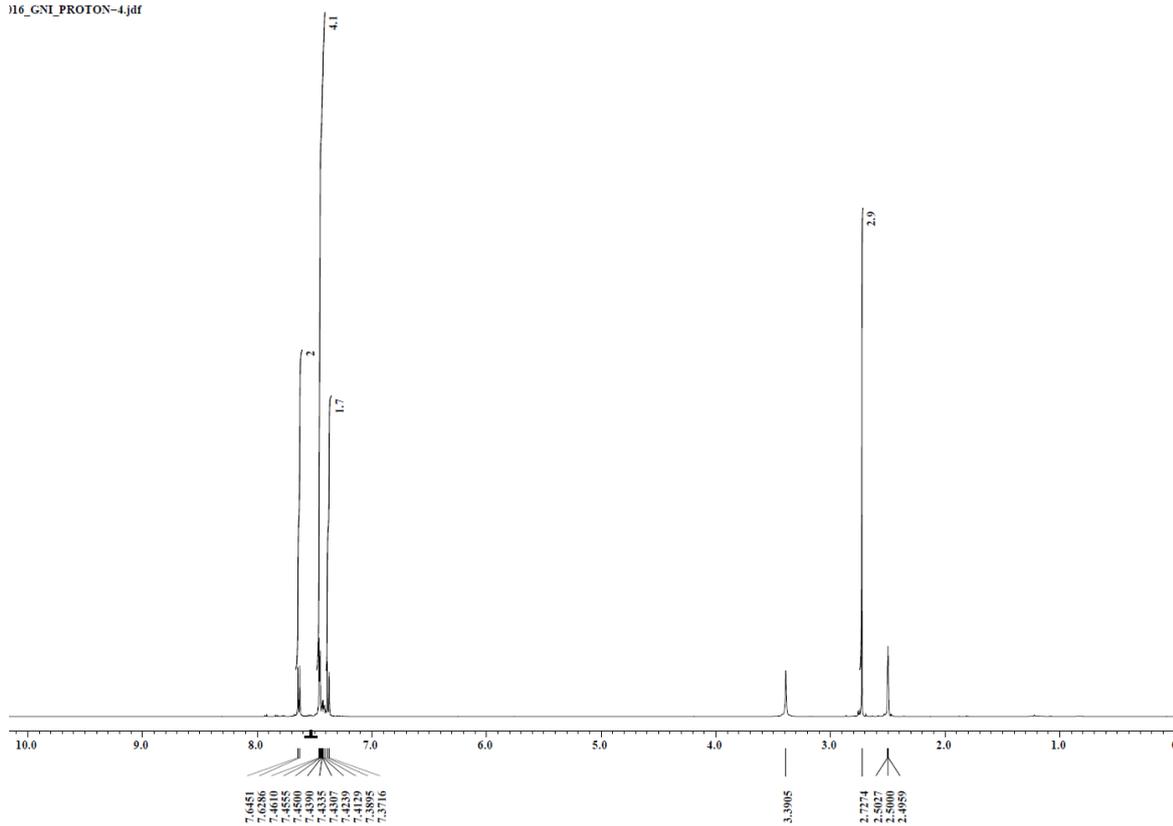


Figure S7. ^1H NMR of methyl 4-(phenylthio)phenylsulfoxide.

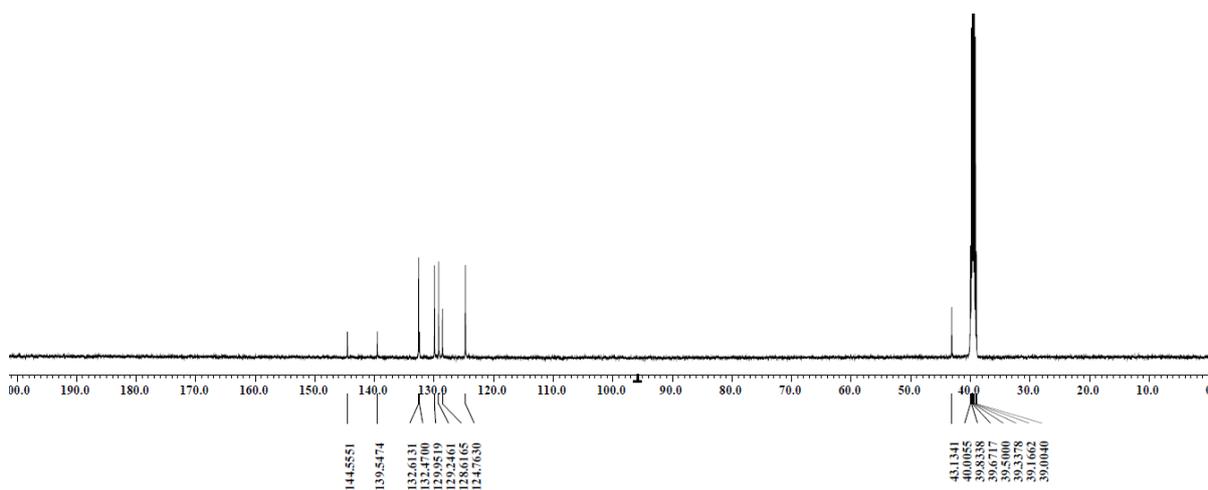
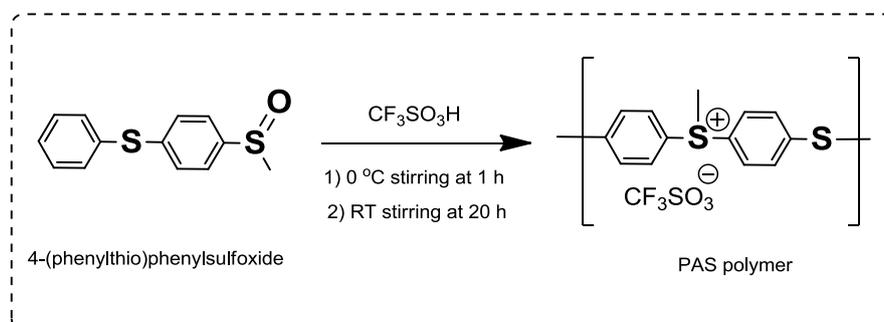


Figure S8. ^{13}C NMR of methyl 4-(phenylthio)phenylsulfoxide.

4) Synthesis of poly[methyl[4-(phenylthio)-phenyl]sulfoniumtrifluoromethanesulfonate] (PAS)



Scheme 4. Synthetic route of poly[methyl[4-(phenylthio)-phenyl]sulfoniumtrifluoromethanesulfonate] (PAS).

In a 100 ml round bottom flask, 1 g of methyl 4-(phenylthio)phenyl sulfoxide (4 mmol) was taken and cooled down to 0 °C. 5 ml of trifluoromethanesulfonic acid (which acts as a solvent as well as protonating agent) was added to the reaction mixture and stirred for 1 hour. After that, the reaction temperature was slowly raised over a period of 30 min from 0 °C to room temperature and the stirring was continued for 20 hrs. The final reaction mixture, blue in colour, was poured into ice cold water. The brown coloured polymer of PAS precipitated was filtered and washed several times with distilled water, and dried in a temperature controlled oven at 50 °C for two days. Yield: 1.2 g; 80%. ¹H NMR (500 MHz, DMSO-*d*₆): δ_H 7.6-8.0 (4 H, br.m, ArH), 3.80 (3H, s, (S-CH₃)). ¹³C NMR (125 MHz, DMSO-*d*₆) δ_C 132.26, 131.43, 129.70, 126.68, 119.37 (CF₃), 26.98 (S-CH₃). ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ_F -77.66 (3F, s, CF₃).

The broad ^1H resonance peaks observed in the range 8.0-7.6 ppm are due to the aromatic protons present on the polyarylene sulphides (PAS) chain and the methyl protons on the sulfonium functionality of the polymer skeleton appeared at 3.80 ppm. ^{13}C NMR signals observed at 133.9-126.68 ppm indicate the presence of phenyl carbons on the PAS skeleton. The ^{13}C peaks observed at 119.37 ppm and 26.98 ppm are due to the CF_3SO_3 carbon and methyl carbon on the sulfonium group respectively. The signals at -77.66 ppm in ^{19}F NMR correspond to the fluorine atoms of the triflate functionality.

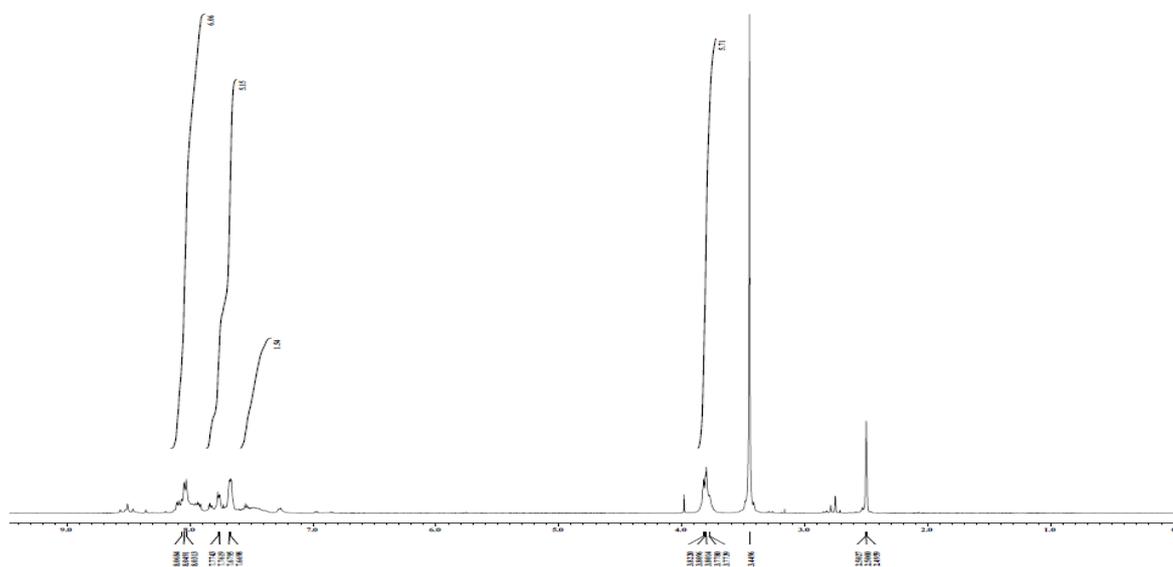


Figure S9. ^1H NMR of PAS.

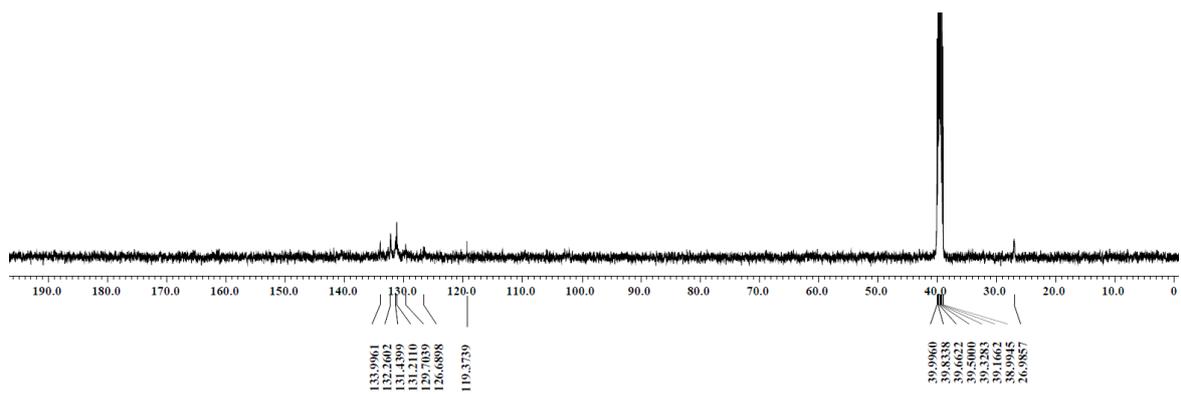


Figure S10. ^{13}C NMR of PAS.

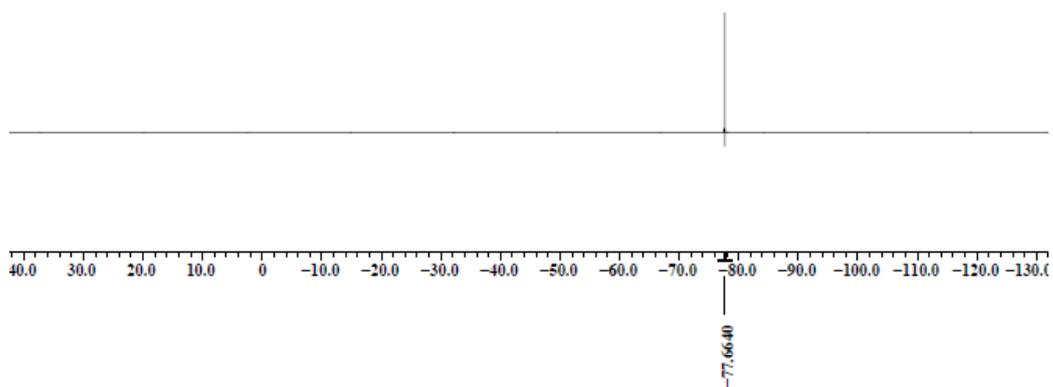


Figure S11. ^{19}F NMR of PAS.

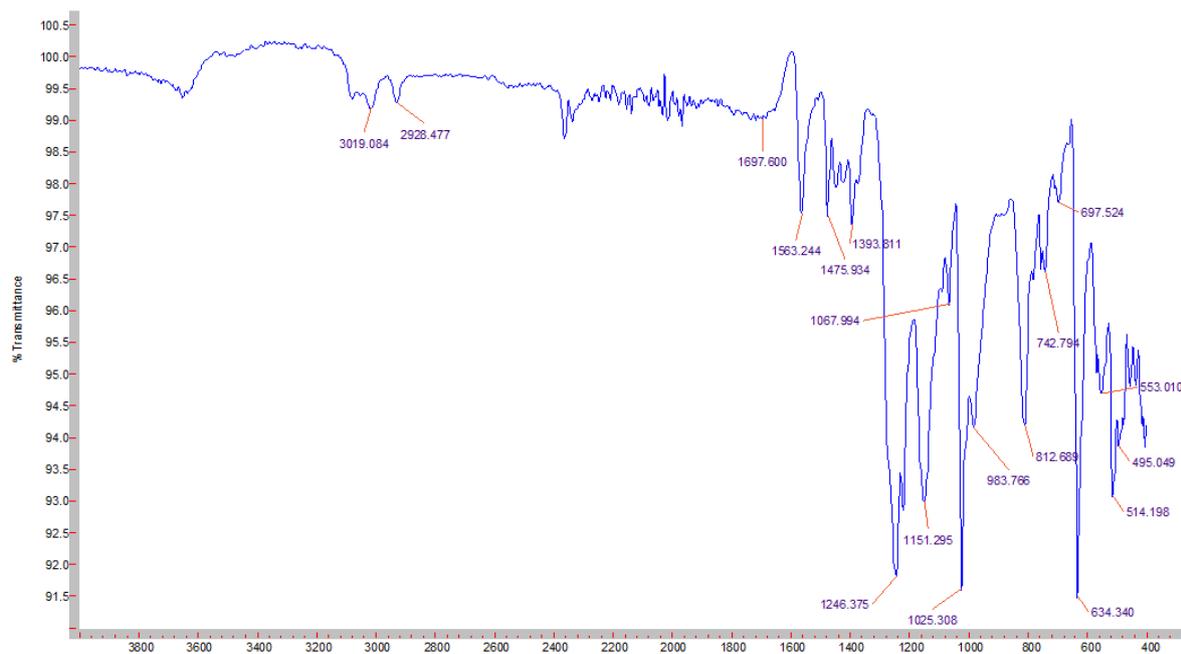


Figure S12. FT-IR of PAS.

The vibrational bands observed at 3019.08, 2928.47 and 812.68 cm^{-1} correspond to the C-H vibrations. The sharp bands at 1563.24 and 1475.93 cm^{-1} are due to the vibrations of C=C bonds in phenyl rings. The peaks at 1246.37, 1151.29 and 1025.30 cm^{-1} are due to the C-F and S=O bond vibrations of the triflate functionality respectively.

The weight average molecular weight of PAS was determined by Gel Permeation Chromatography (GPC) using mixed-B columns. Dimethylformamide (DMF) was used as the mobile phase with 1ml/min flow rate at 70 °C. Poly(ethyleneglycol) (PEG) and polyethylene oxide (PEO) were used as the standards for GPC analysis. The weight average molecular weight of PAS was calculated as 5,675 g/mol with a polydispersity index of 1.3.

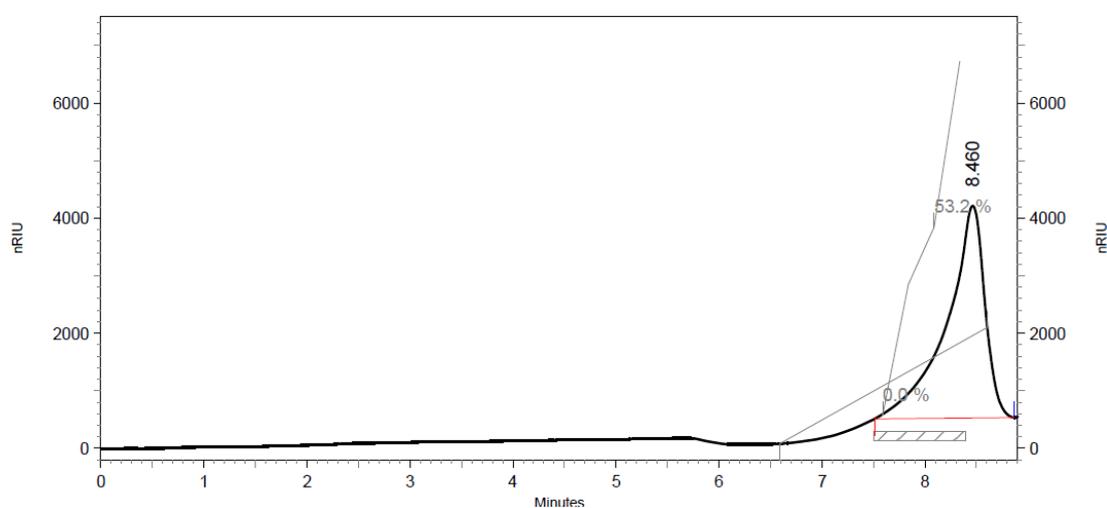


Figure S13. GPC profile of PAS resist.

The thermal stability of PAS was determined by using thermogravimetric analysis. It was observed that the polymer is stable upto 190 °C and above this temperature, the polymer starts decomposition.

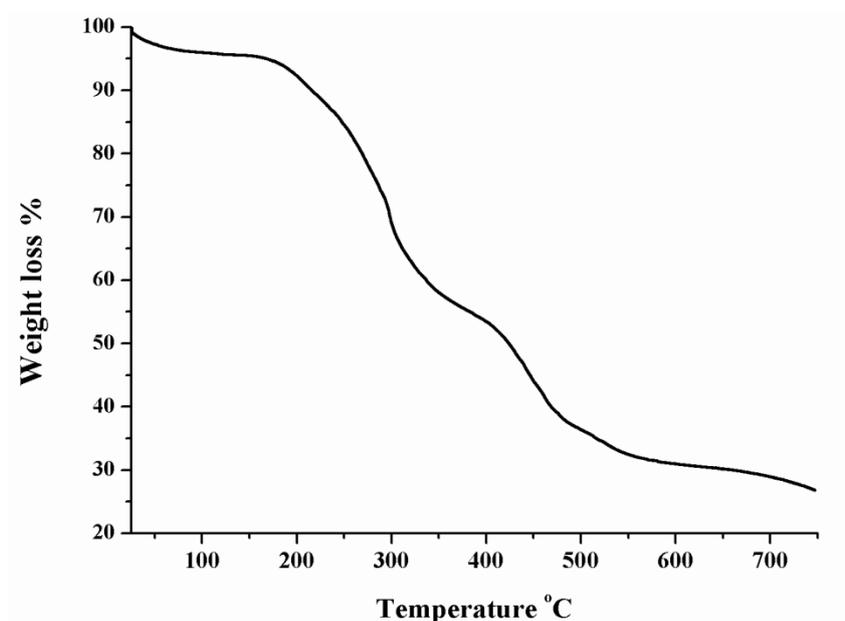


Figure S14. TGA profile of PAS resist.

The glass transition and melting temperatures of PAS, determined by using Differential Scanning Calorimetry (DSC), were found to be 76-80 °C and 132 °C respectively.

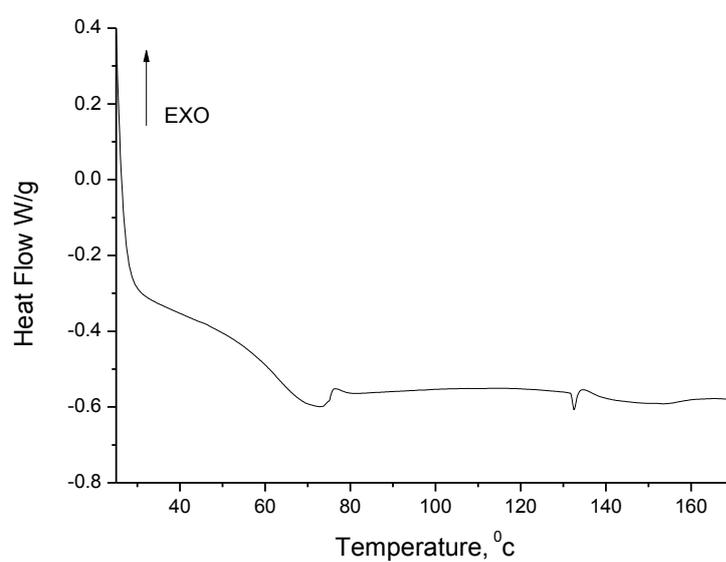


Figure S15. DSC profile of PAS resist.

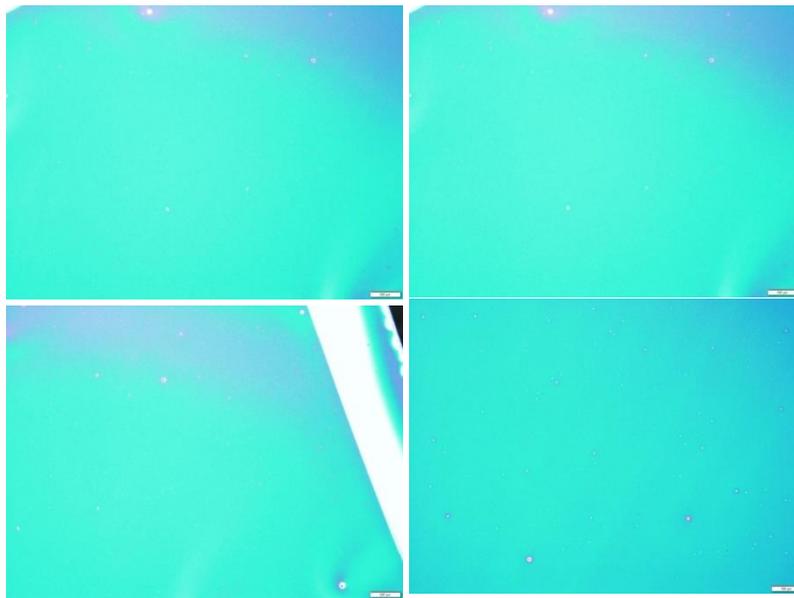


Figure S16. Optical microscope images of PAS coated on silicon substrates.

PAS coated thinfilms were characterized by using AFM tool, the *rms* roughness of the thin films was measured as ~ 0.34 nm.

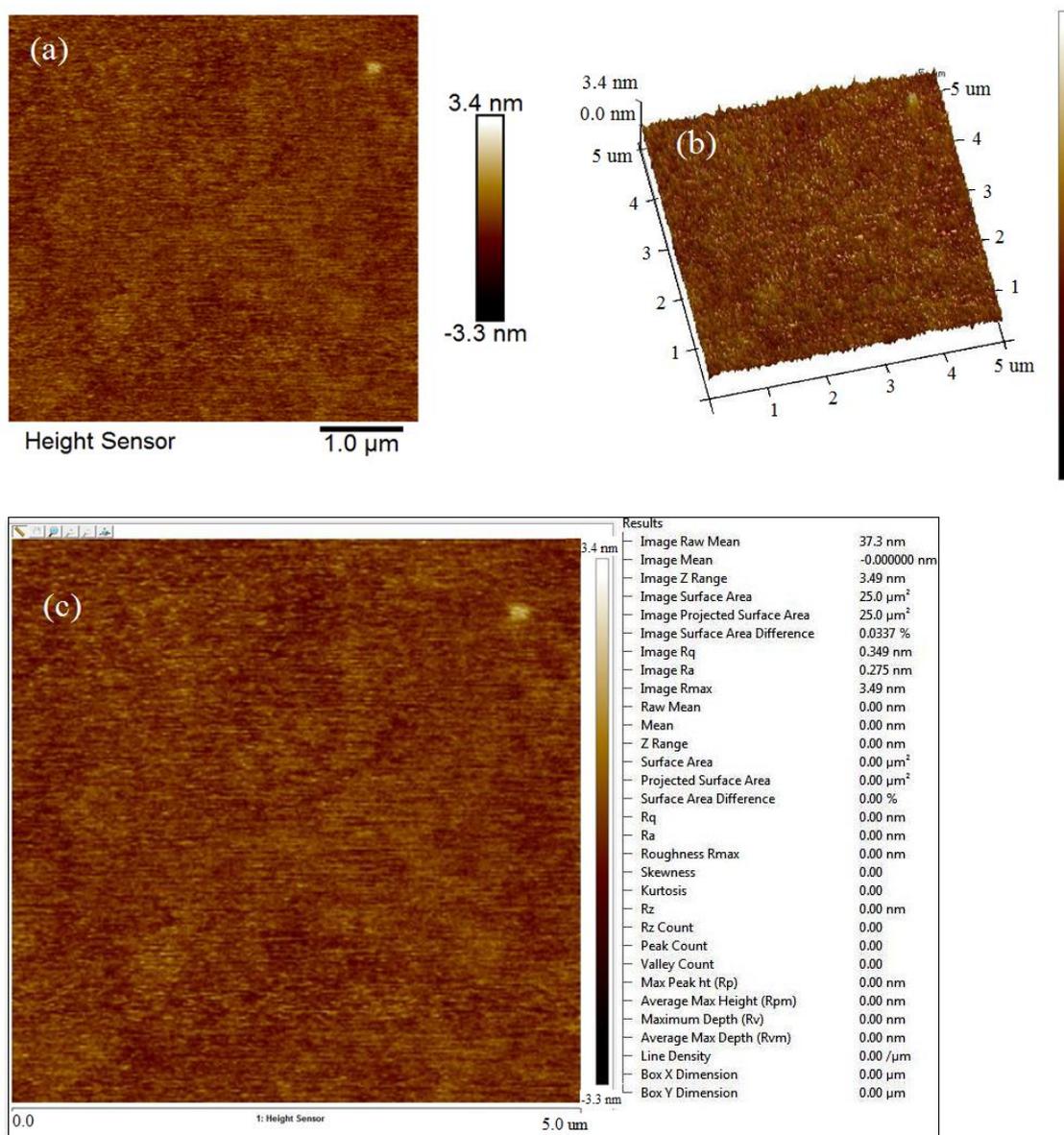


Figure S17. AFM images of the thin film of PAS. a) 2-D view of the PAS films; b) 3-D view of the PAS films; c) an image showing the roughness of the PAS film.

Thickness measurements on PAS thinfilms were performed by using stylus profilometer; the thickness was measured as 34 nm.

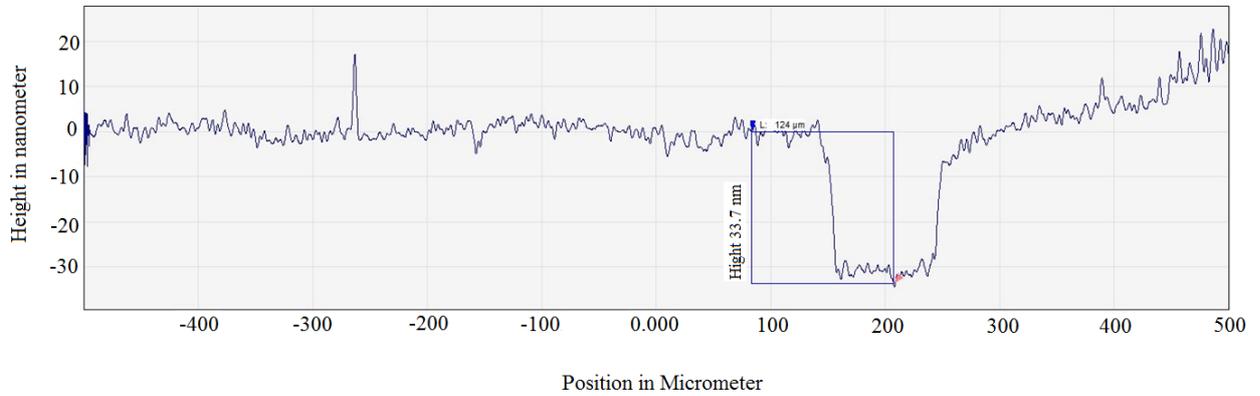


Figure S18. Thickness measurements on PAS thin film.

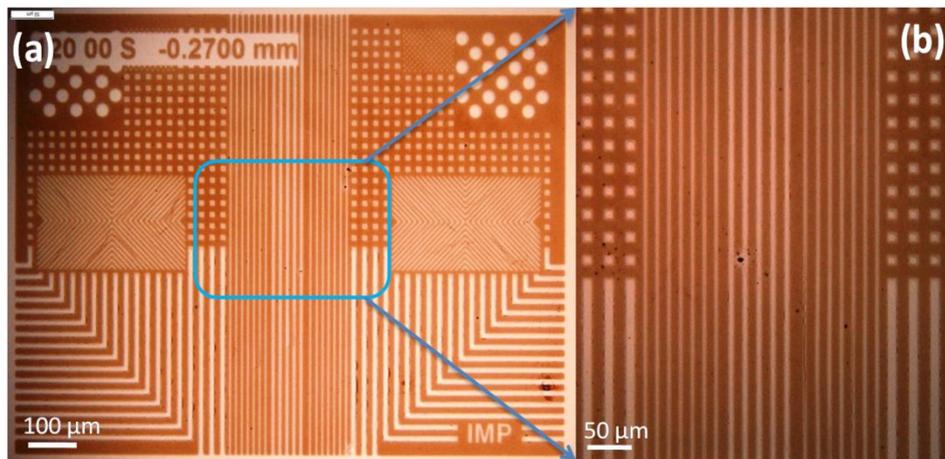


Figure S19. a) 5-100 micron size features patterned using 365 nm (i-line); (b) magnified images of micron size patterns.

The ability of PAS to act as positive tone resist was tested by using 1,4 dioxane as the developer. The UV-365 nm exposed thin films of PAS were developed in 1,4 dioxane for 10 sec followed by rinsing with water for 10 sec. The well resolved micron sized positive patterns of PAS resist obtained is given below.

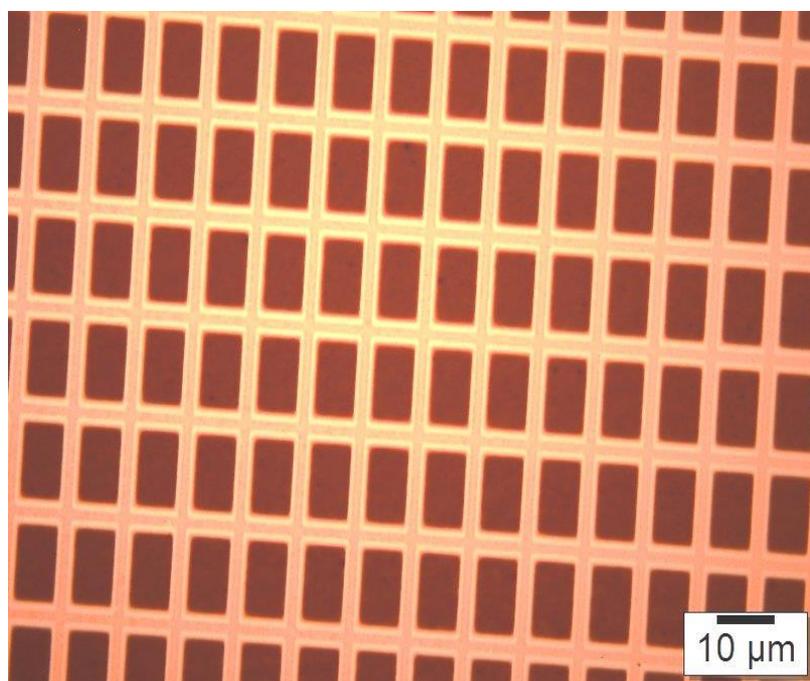


Figure S20. An image showing positive tone patterns of PAS resist.

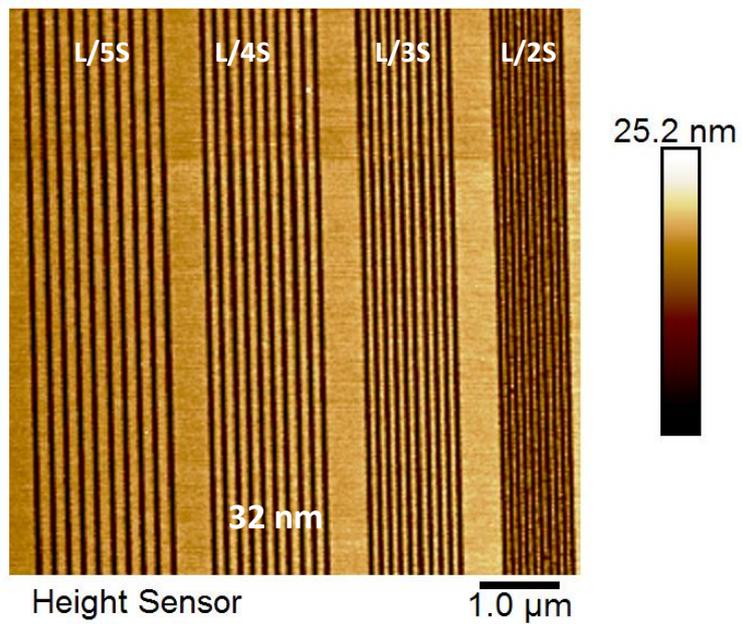


Figure S21. HR-AFM image of 32 nm line patterns with various line/spce (L/2S to L/5S) features.

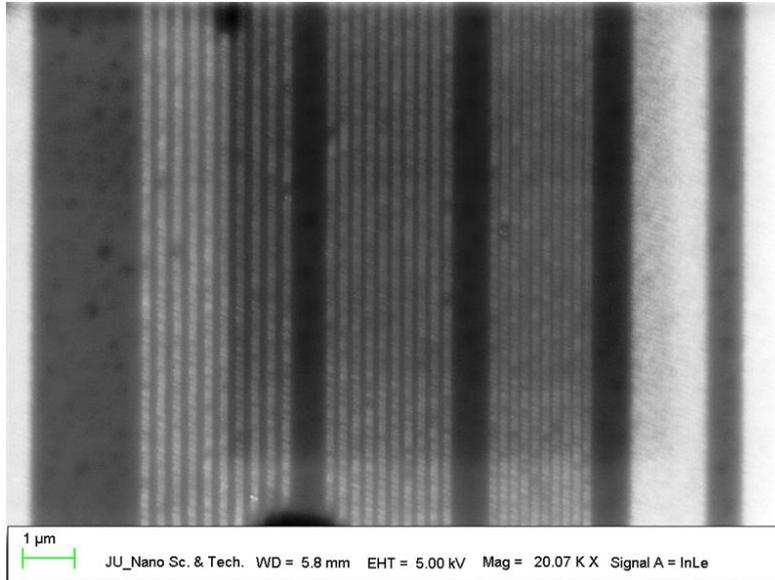


Figure S22. FE-SEM image of 30 nm line patterns with various line/spce (L/2S to L/5S) features.

Thickness measurements on 20, 25 and 30 nm line patterns of PAS resist were performed by using AFM line profilometer and the thickness was found as ~ 26.4 nm, which is less than the original film thickness measured. This could probably be due to the metrology artefact called tip convolution artefact.

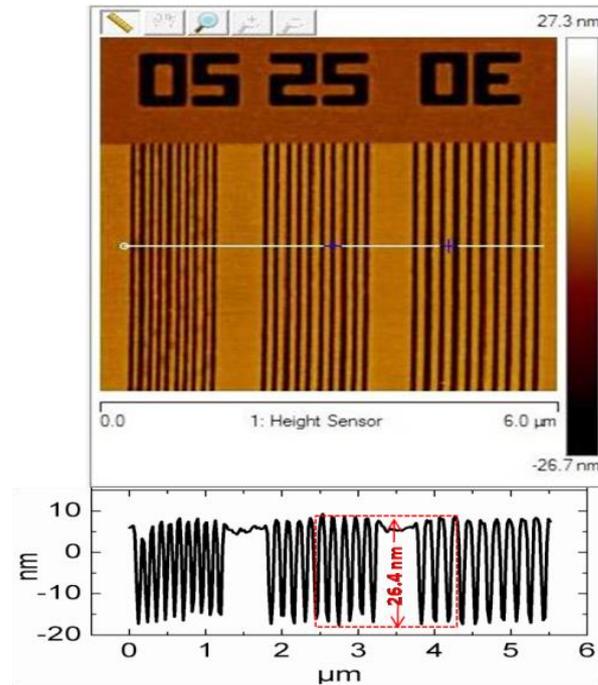


Figure S23. AFM line profile thickness measurement results on 20, 25 and 30 nm lines of PAS.

A possible mechanism for the resist action: upon exposure to UV radiation, PAS resist undergo decomposition and forms methyl(4-(phenylthio)-phenyl)sulfane leading to a polarity change as shown below.³ Previous studies have shown that the triflate group also undergoes photodegradation on EUV irradiation as shown below.⁴ As a result, neutral Ar-S-CH₃ moiety is formed during the post exposure bake and development process. This renders the irradiated area insoluble in TBAH developer because of the change in polarity from initially hydrophilic to hydrophobic.

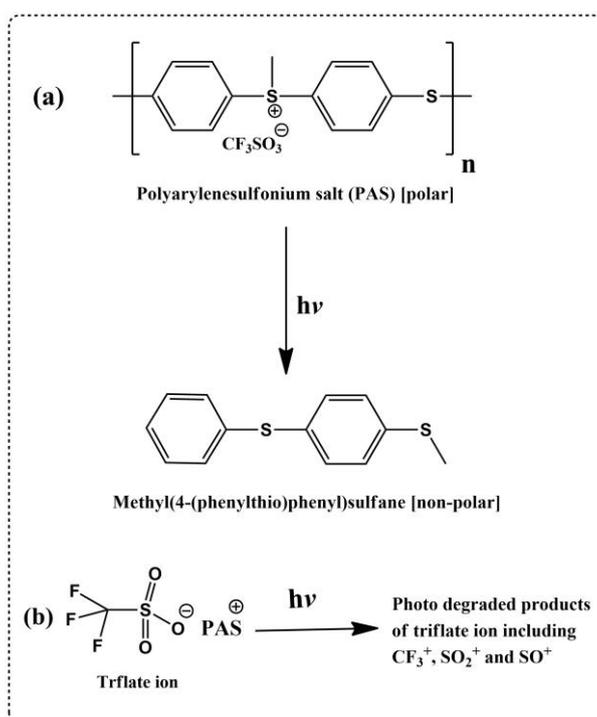


Figure S24. Possible mechanism for the radiation induced decomposition pathway of poly[methyl(4-(phenylthio)-phenyl)sulfoniumtrifluoromethanesulfonate] (PAS) resist. a) Photoinduced decomposition of polar PAS skelton into non-polar methyl (4-(phenylthio)phenyl)sulfane units; b) Photoinduced decomposition of triflate functionality of PAS polymer into the corresponding photodegraded products.

References:

- 1) Haryono, A.; Yamamoto, K.; Shouji, E.; Tsuchida, E. Synthesis and Nucleophilic Dealkylation of Poly[alkyl-(4-(phenylthio)phenyl)sulfoniumtrifluoromethanesulfonate]s. *Macromolecules*. **1998**, *31*, 1202-1207.
- 2) Tsuchida, E.; Shouji, E.; Yamamoto, K. Synthesis of High Molecular Weight Poly(phenylenesulfide) by Oxidative Polymerization via Poly(sulfonium cation) from Methyl Phenyl Sulfoxide. *Macromolecules*. **1993**, *26*, 7144-7148.
- 3) Tsuchida, E.; Yamamoto, K.; Shouji, E.; Haryono, A. Photochemical Recycling of PolyaryleneSulfide. *Chem. Commun.* **1996**, 2091-2092.
- 4) Satyanarayana, V. S. V.; Kessler, F.; Singh, V.; Scheffer, F. R.; Weibel, D. E.; Ghosh, S.; Gonsalves, K. E. Radiation-Sensitive Novel Polymeric Resist Materials: Iterative Synthesis and Their EUV Fragmentation Studies. *ACS Appl. Mater. Interfaces*. **2014**, *6*, 4223-4232.