Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supporting Information

Photoacid generator integrated terpolymer for electron beam lithography applications: sensitive resist with pattern transfer potential

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Experimental Section

Materials and methods

Acetonitrile and tetrahydrofuran (HPLC grade) were purchased from Merck, India and well dried before use. Tetramethyl ammonium hydroxide was purchased from Sigma Aldrich, India and used as received. FT-IR spectra were recorded on a Perkin Elmer Spectrum 2 spectrophotometer using KBr pellets. ^{1}H, ^{13}C and ^{19}F 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 ºC/min under N_2 atmosphere over a temperature range of 25-1000 ºC. Molecular weight and polydispersity index (PDI) of GBLMA-MAMA-MAPDST was determined by performing gel permeation chromatography (GPC) analyses using PL gel mixed B 10 mm column on a 1260 Infinity Series instrument from Agilent. RAITH 150-Two was used as experimental tool for the electron beam lithography studies with 20 KV E.H.T. NanoMap-D stylus profilometer is used for the thickness measurements. FE-SEM Nova Nano SEM 450 FEI, Zeiss ultra 55 and Atomic Force Microscope (AFM) (Dimension Icon, Bruker) tools were used for imaging the critical dimensions of various patterns made on silicon substrates.

Synthesis and characterization of GBLMA-MAMA-MAPDST Resist

GBLMA,[1] MAMA[2] and MAPDST[3] were synthesized according to the literature reports and characterized using spectroscopic techniques. GBLMA (0.3 gm, 1 eq), MAMA (1.15 gm, 2.8 eq), MAPDST (0.131 gm, 0.2 eq) and AIBN (0.023 gm, 0.08 eq, relative to all monomers) were dissolved in dry acetonitrile/tetrahydrofuran mixed solvents (1:2; V/V) under N_2

atmosphere. After that, resulting solution was filtered through 0.4 μm Teflon filters in a single armed polymerization flask which was equipped with rubber septum and magnetic stirring bar. After several freeze-pump- thaw cycles, the polymerization flask was placed in a preheated oil bath at 65 °C and allow the stirring in dark for 24 hours. After completion, the reaction mixture was poured into the petroleum ether and the resultant crude product was re-dissolved in minimum amount of methanol and re-precipitated in diethyl ether. The pure white solid of GBLMA-MAMA-MAPDST was filtered and dried over 50 °C for 12 h in a temperature controlled hot air oven. Yield: 0.650 gm. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.14 (brs, 2H, Ar H), 7.4 (brs, 2H, Ar H), 5.5 (brs, ^{1}H; CH, (cyclic GBLMA unit)), 4.33 (brd, 2H, CH_2, (cyclic GBLMA unit)), 3.27 (s, 6H; $S(CH_3)_2$), 2.4-1.0 (br peak, 3H, (Aliphatic CH_3 & CH_2 units); ^{13}C NMR (125 MHz, DMSO-d_6) δ_C 176.17, 174.93, 172.67 (C=O), 153.87, 131.83, 129.62, 127.09, 125.15, 123.93, 122.96, 121.94, 119.39, 117.21(aromatic, CF_3), 86.63, 68.42, 65.15, 54.92, 46.93, 44.87 (CH_2), 37.59, 35.11, 33.86, 32.50, 28.73 (SCH_3), 28.68, 26.11, 21. 36, 15.0 (CH_3 aliphatic). ^{19}F NMR (DMSO, 376 MHz, δ): -77.65 (3F, s, CF_3); IR (KBr): v = 2910 (CH_2), 1790-1719 (C=O), 1586.6, 1462.6, 1448.7 (C=C), 1380.8, 1257.3 (CF_3), 1220.6, 1148.1-1131.9 (C-O), 1029.8 (S=O), 954.7, 886.00, 842.0, 815.74, 756.10, 639.20, 573.9, 520.0.

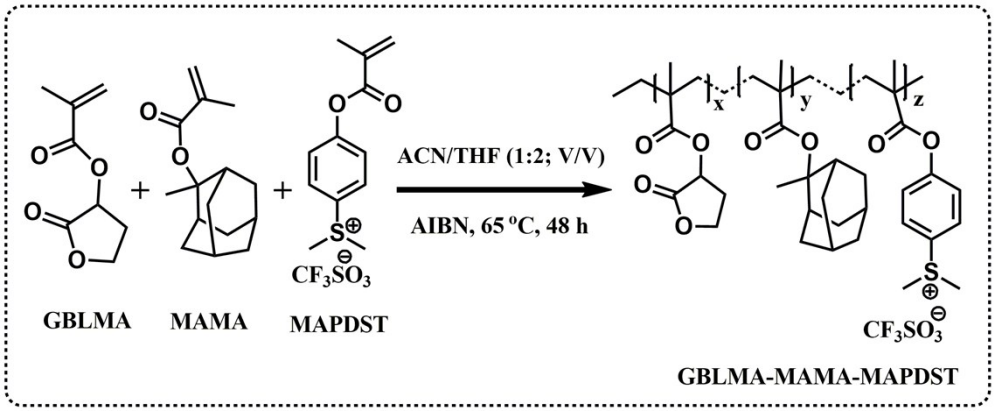


Figure S1. Synthetic route of GBLMA-MAMA-MAPDST resist.

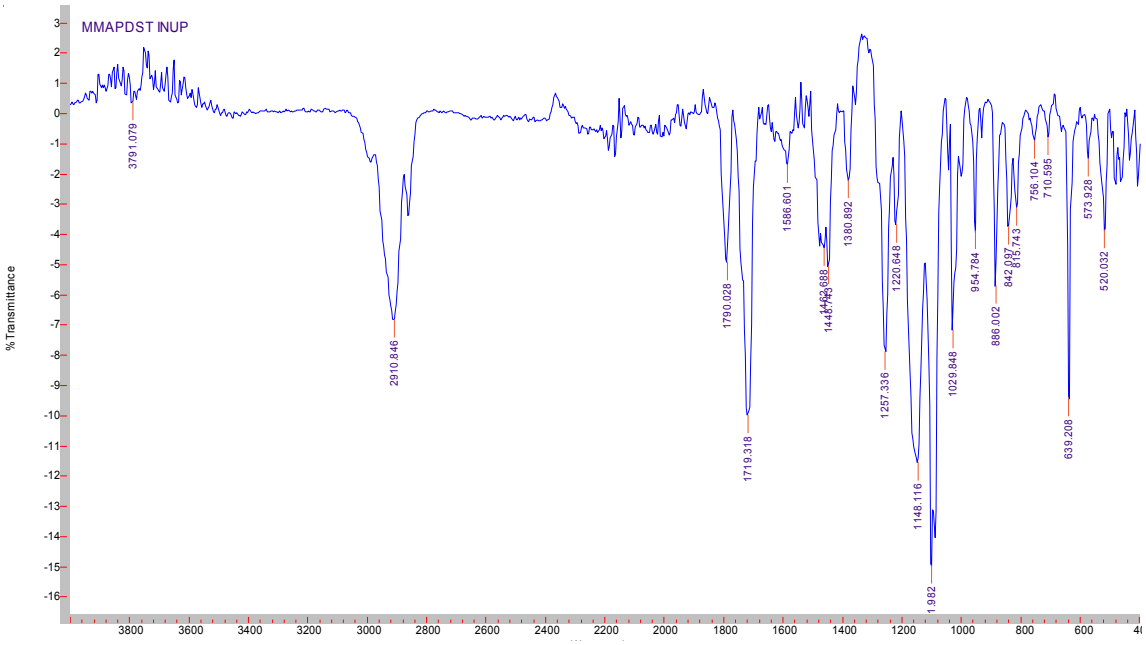


Figure S2. IR-profile of GBLMA-MAMA-MAPDST resist.

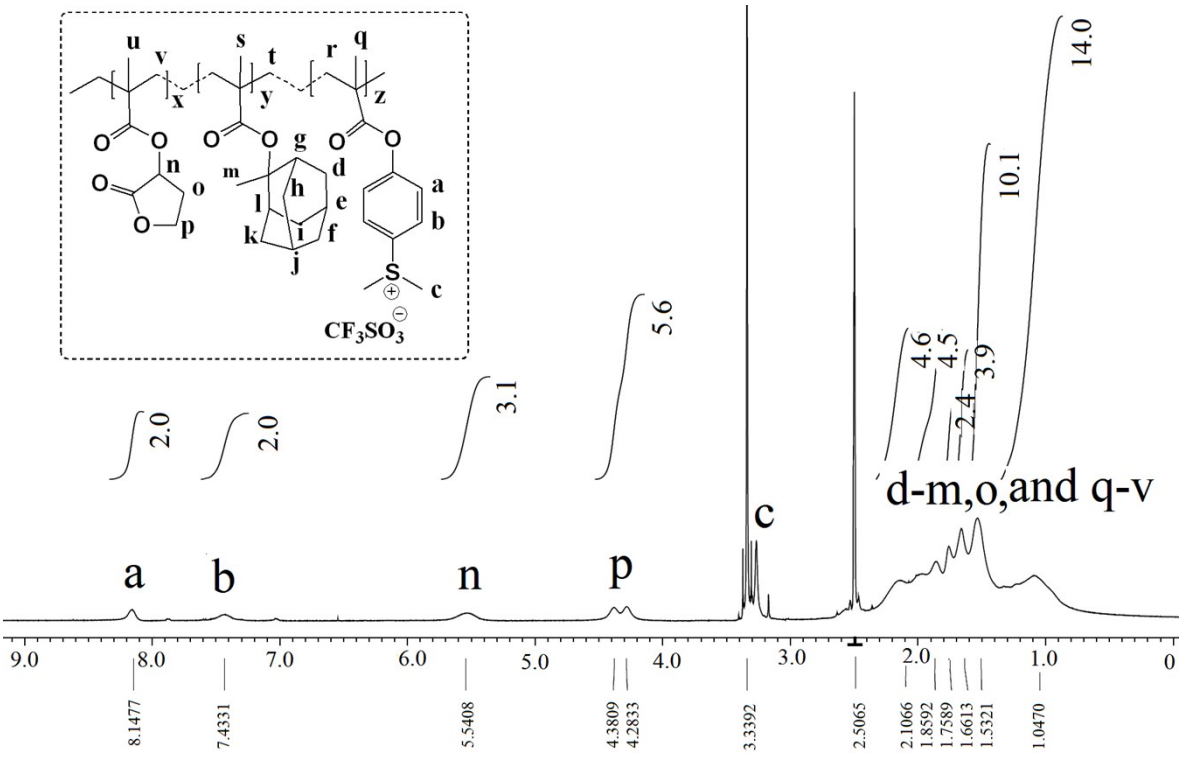


Figure S3. ^{1}H NMR of GBLMA-MAMA-MAPDST resist.

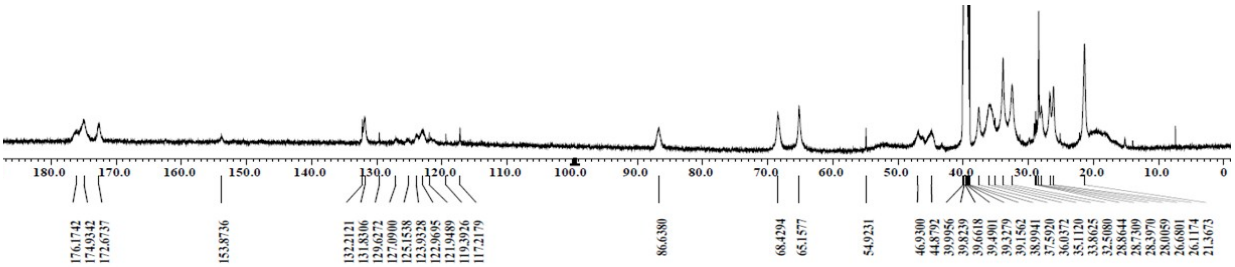


Figure S4. ^{13}C NMR of GBLMA-MAMA-MAPDST resist.

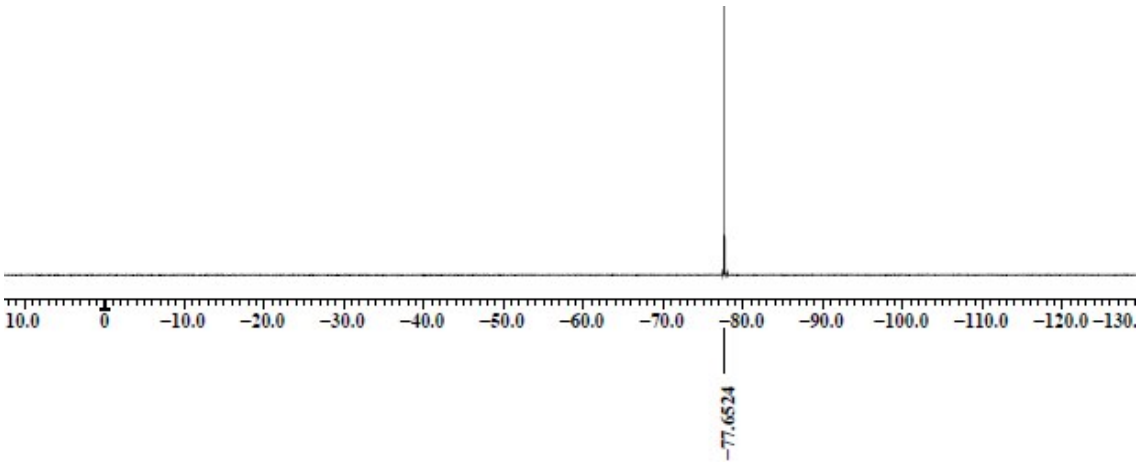
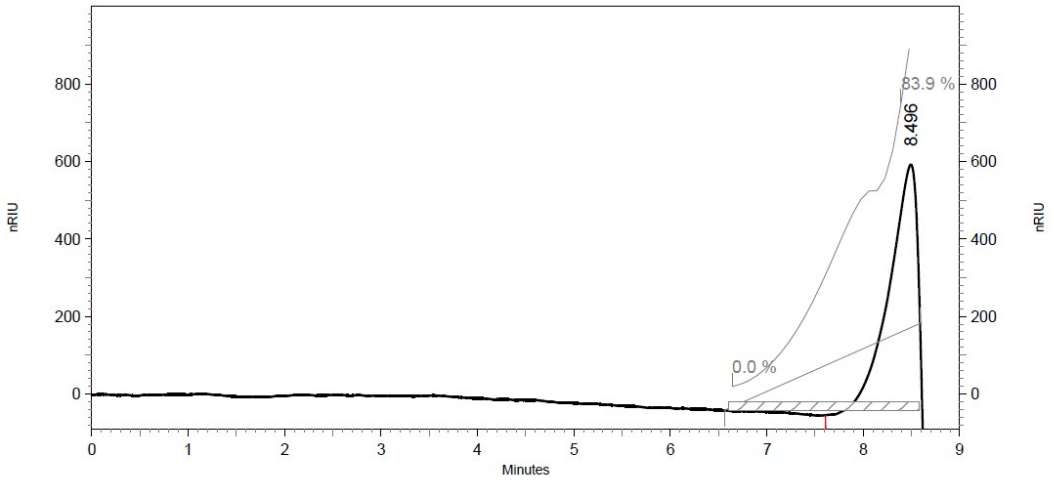


Figure S5. ^{19}F NMR of GBLMA-MAMA-MAPDST resist.



SEC Summary information

RID: RI Signal	
Processing Start Time(min) =	6.600
Processing Stop Time(min) =	8.580
Number of Slices =	24
Weight Average Molecular Weight =	13147
Number Average Molecular Weight =	3556
Z Average Molecular Weight =	39542
Z+1 Average Molecular Weight =	66153
Polydispersity index =	3.697
Peak Molecular Weight =	1250
Z Average / Weight Average =	3.008
Z+1 Average / Weight Average =	5.032

SEC Slice Data — RID: RI Signal Results

Volume	Mol Wt	Area	Cum. % Area	Cum. Area
RID: RI Signal				
6.601	134313	3021	0.23	3021
6.684	107118	8680	0.90	11701
6.767	85951	13459	1.93	25160
6.851	69346	18565	3.36	43725

Figure S6. GPC data of GBLMA-MAMA-MAPDST resist.

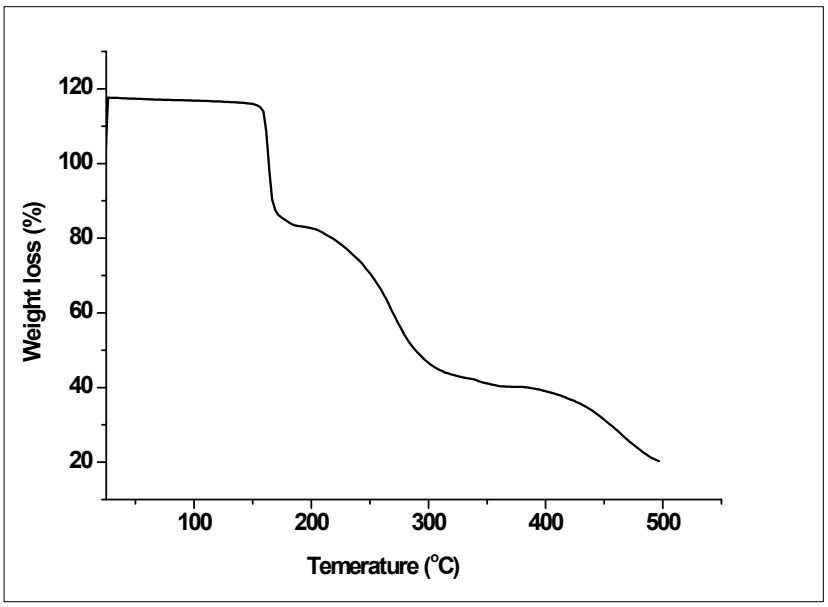


Figure S7. TGA profile of GBLMA-MAMA-MAPDST polymer.

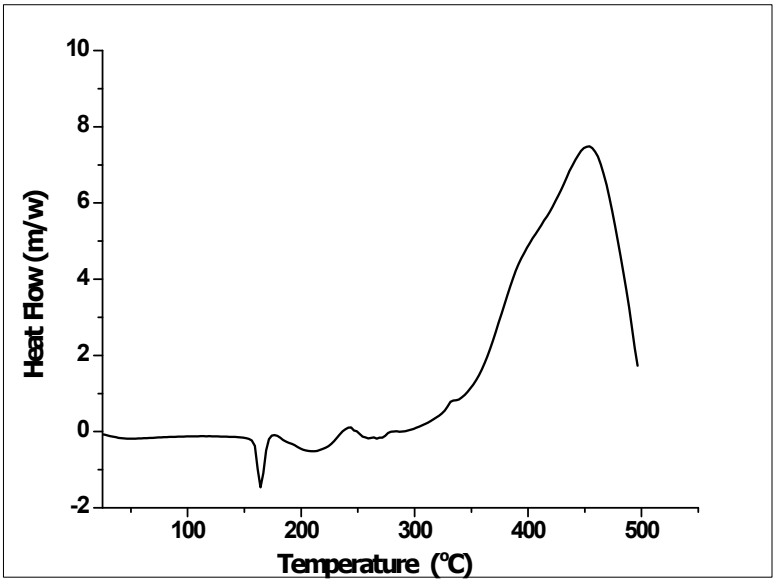


Figure S8. DSC profile of GBLMA-MAMA-MAPDST polymer.

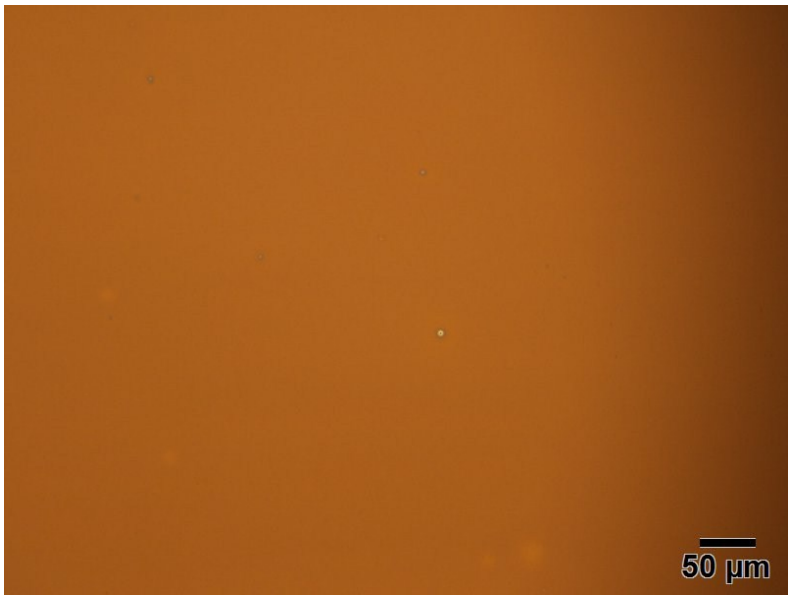


Figure S9. Optical microscope image of GBLMA-MAMA-MAPDST resists coated on silicon substrate indicating uniform film formation.

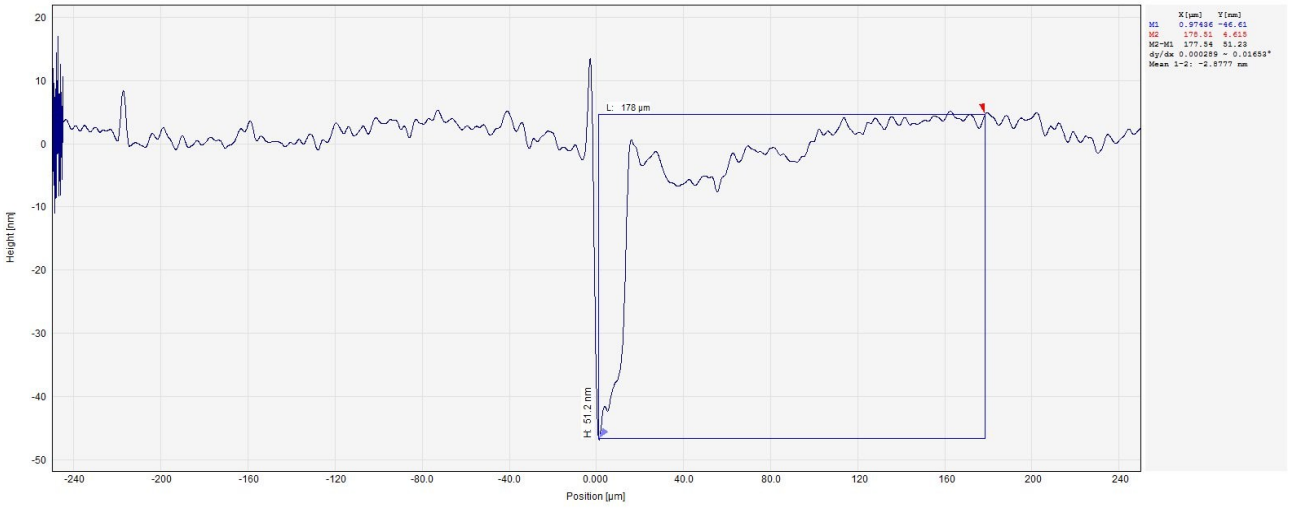


Figure S10. Thickness measurements on GBLMA-MAMA-MAPDST polymer.

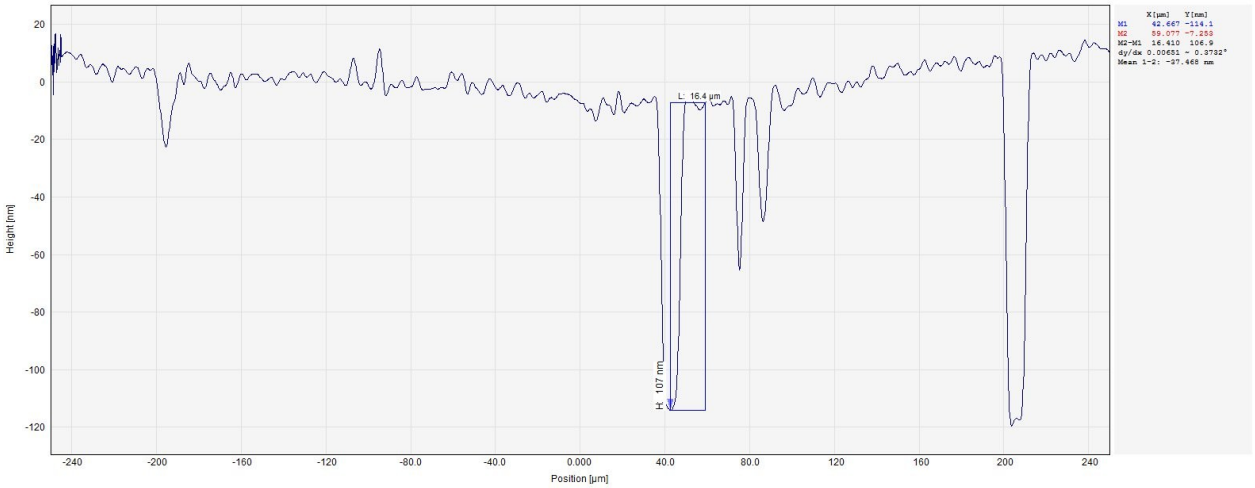


Figure S11. Thickness measurements of transferred line features on the silicon substrate at the etch time of 15 sec.

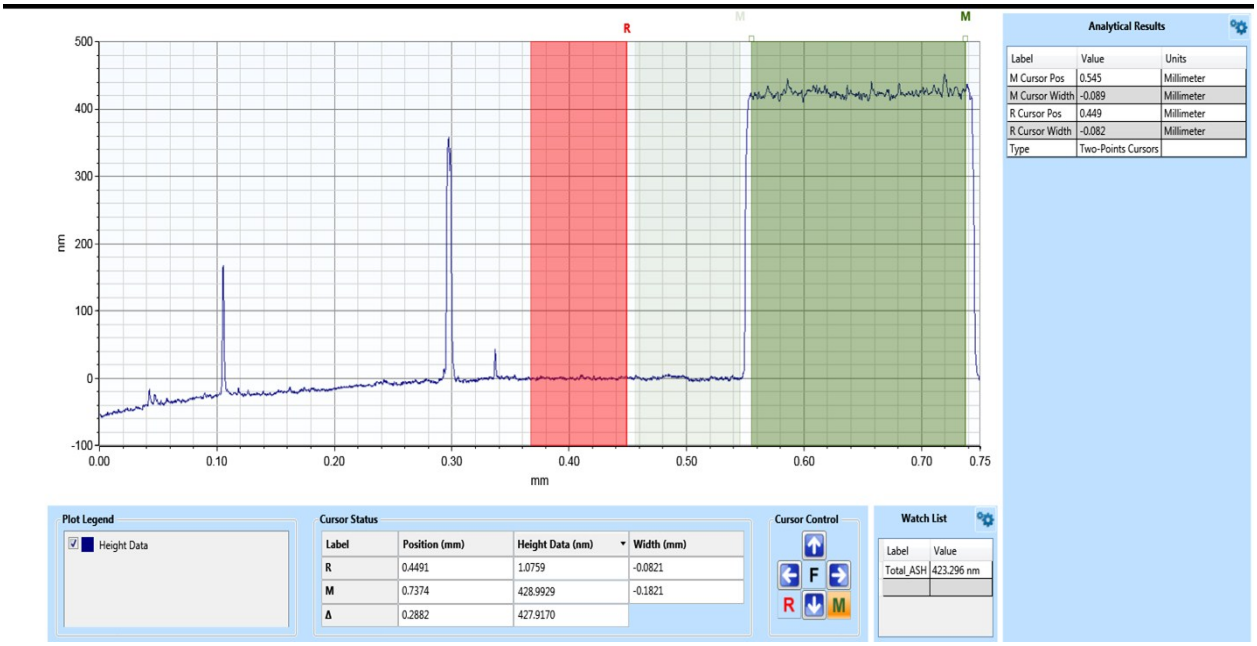


Figure S12. Thickness measurements of transferred line features on the silicon substrate at the etch time of 45 sec.

References

1) S. C. Kim, D. H. Nam, Y. H. Kim and B. K. Song, *Biotechnol. Bioprocess Eng.* 2010, **15**, 208-212.

2) M. Yamaguchi, H. Kikuchi and Y.Hirota, U. S Patent. 2004, Patent no: 6,770,777B2.

3) V. Singh, V. S. V. Satyanarayana, S. K. Sharma, S. Ghosh and K. E. Gonsalves, *J. Mater. Chem. C.* 2014, **2**, 2118.