Supporting Information

Towards Novel non-Chemically Amplified (n-CARS) Negative Resists for Electron Beam Lithography Applications

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The chemical syntheses of monomer and copolymer are outlined as follows:
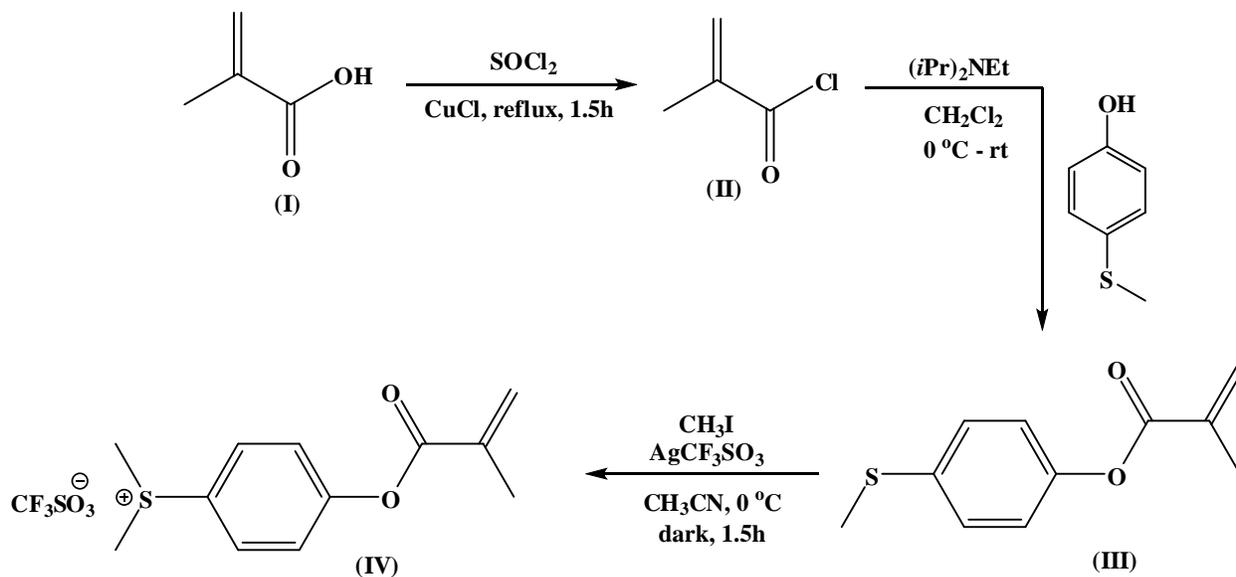
Scheme S1: Synthesis of MAPDST monomer (**IV**).
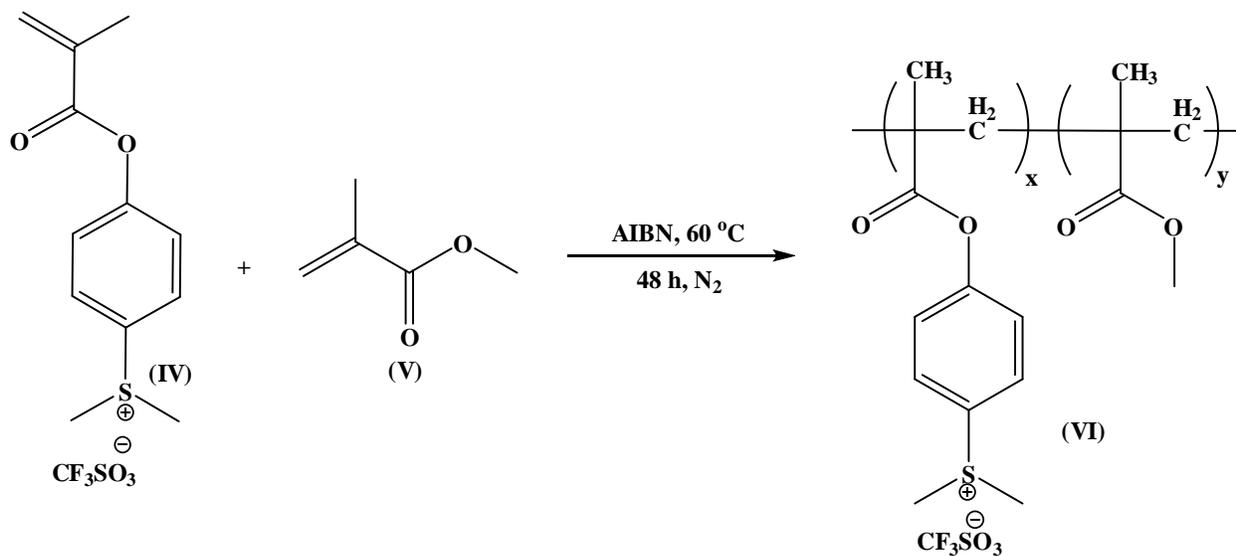
Scheme S2: Synthesis of MAPDST-MMA Copolymer.

Materials and methods:

All the chemicals and solvents were purchased from commercial sources and used as received. Tetrahydrofuran (THF) was dried using Na wire/benzophenone and acetonitrile (CH_3CN) was dried using Calcium hydride (CaH_2). AIBN (Azobisisobutryronitrile) was recrystallized two times before using for polymerizations. FT-IR spectra were recorded on a Perkin Elmer Spectrum 2 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Jeol JNM ECX 400 MHz spectrometer in DMSO-d_6. TGA/DSC measurements were done on NETZSCH STA 449 F1 JUPITER Series instrument. The heating range was 10 °C/min in N_2 atmosphere over temperature range from 20 °C to 800 °C. Molecular weights were determined at the maximum displacement of curve by performing GPC analysis with PL gel MIXED B 10 μm column using Agilent Technologies, 1260 Infinity Series instrument. Methacryloyl chloride (**II**), 4-(methylthio)phenyl methacrylate (**III**) and MAPDST [(4-(methacryloyloxy)phenyl)dimethylsulfonium triflate] Monomer (**IV**) were prepared following literature reported procedures and the spectral data were in agreement with the literature data.[1-3]

*Procedure for the synthesis of MAPDST-MMA Copolymer (**VI**):*

MAPDST Monomer (**IV**) (0.8 g, 2.15 mmol) and AIBN (Azobisisobutryronitrile) (1% by weight, relative to both the monomers) were dissolved under N_2 in a mixture of THF-CH_3CN (80:20) in a vial with a side arm and the resulting solution was siphoned to the polymerization flask equipped with a silicone septum and a Teflon stirring bar. To this solution, MMA (methyl methacrylate) monomer (**V**) (0.23 cm^3, 2.15 mmol) was added through a microsyringe. The mixture, after 1 h N_2 purging, was left under magnetic stirring at 60 °C for 48 hours under N_2 atmosphere. After completion, the reaction mixture was poured slowly into dry hexane and the separated solid was washed with CH_2Cl_2. The resulting crude product was dissolved in methanol and then re-precipitated using less polar diethylether. The separated white pure product was filtered and dried in a temperature controlled hot air oven at 50 °C for 1 day. Yield: 500 mg (49.27%). FT-IR: ν_{max}/cm^{-1} 3029 and 2939 (CH), 1755 (C=O), 1638 and 1587 (C=C), 1262 (CF), 1172 (OCH$_3$). ^1H NMR (400 MHz, DMSO-d_6) δ_H 8.12 (2H, br s, *m,m′*-ArH), 7.51 (2H, br s, *o,o′*-ArH), 3.5-3.6 (3H, split peak, OCH$_3$), 3.29 (6H, s, S(CH$_3$)$_2$), 2.1-2.4 (2H, br peak, CH$_2$ polymeric), 0.9-1.5 (3H, br peak, CH$_3$ aliphatic); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 176 (C=O), 156.27, 132.93, 132.77, 132.69, 126.64, 125.31, 125.05, 124.40, 123.42, 120.31, 118.92, 117.34 (aromatic, CF$_3$), 54.88 (OCH$_3$), 29.54 (SCH$_3$), 23.00 (CH$_3$).

^{1}H NMR Spectrum of MAPDST-MMA Copolymer (**VI**):
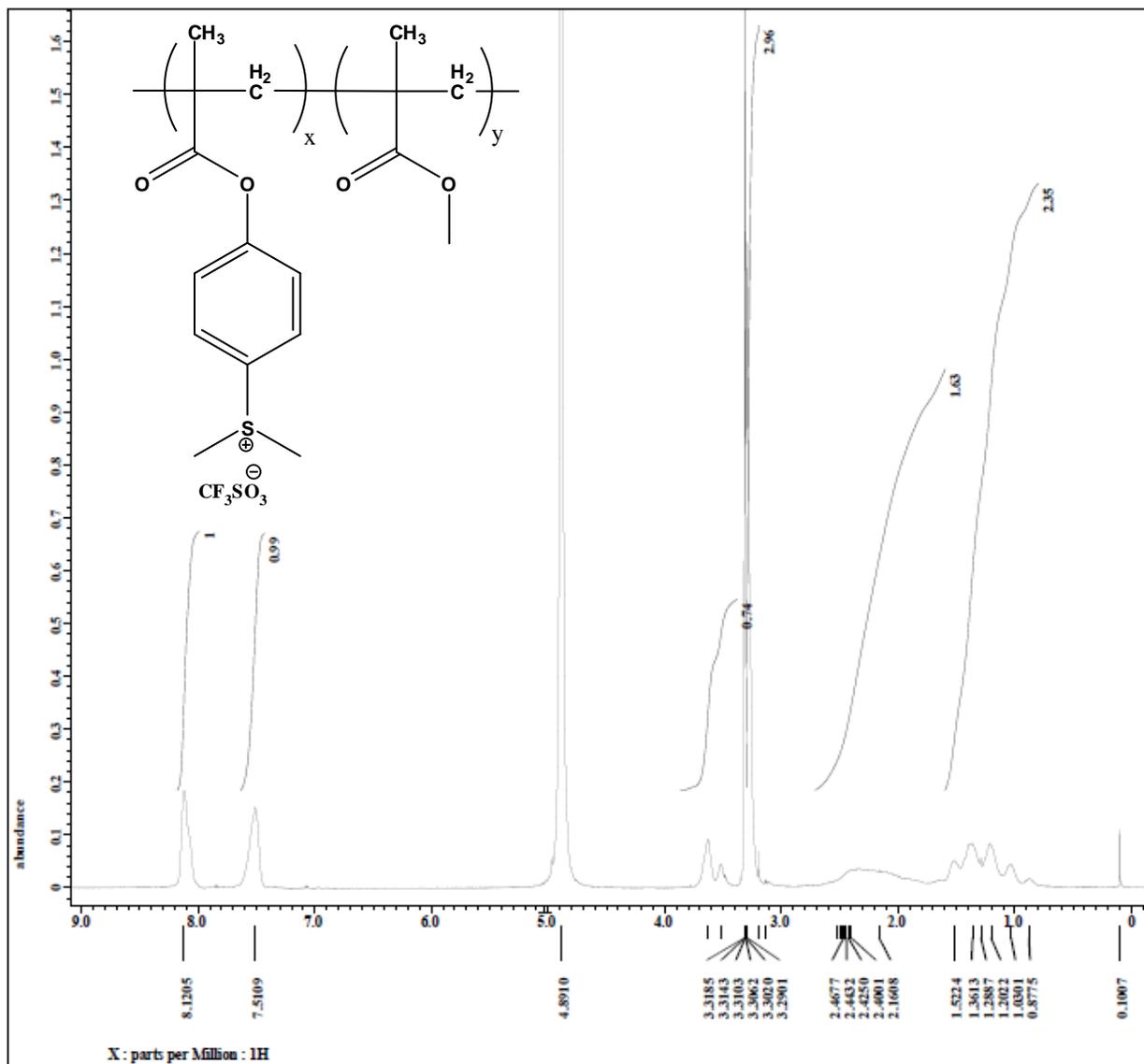
^{13}C NMR Spectrum of MAPDST-MMA Copolymer (**VI**):
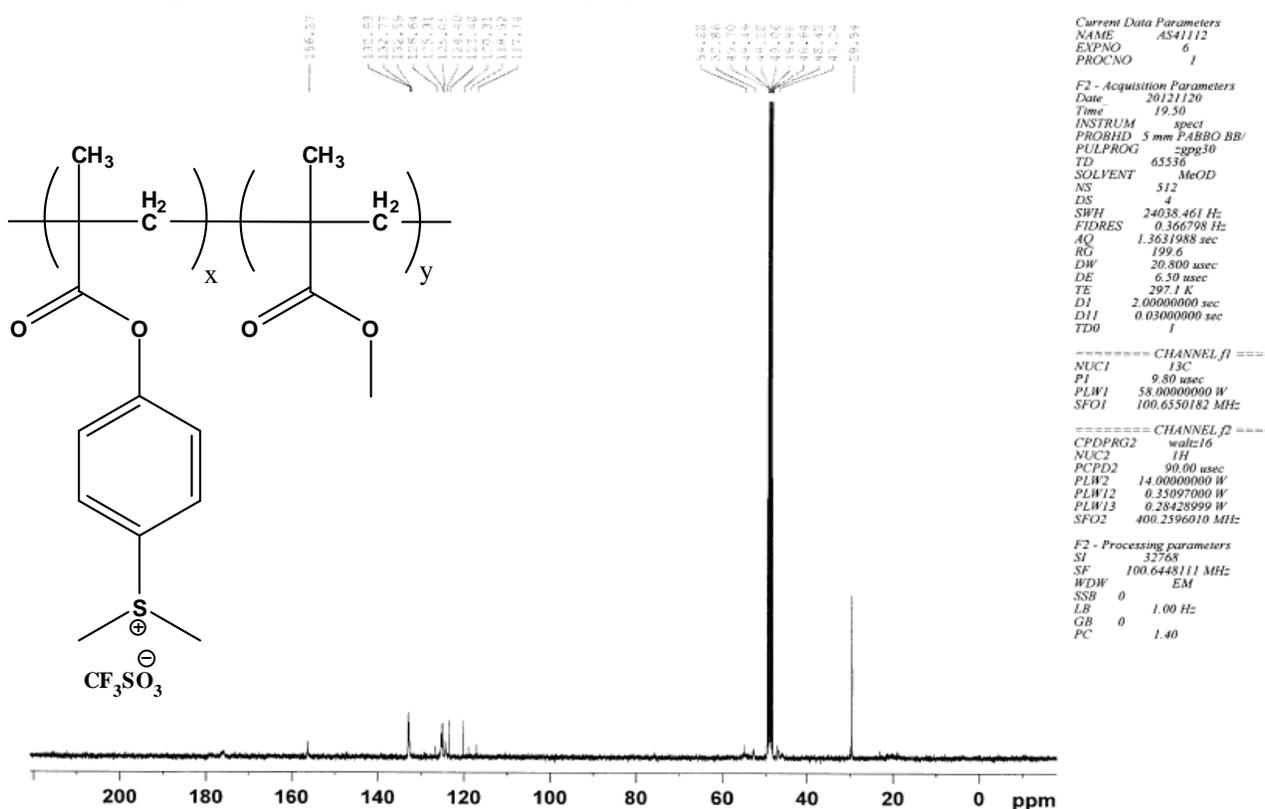
Table S1. Polymerization results of MAPDST-MMA Copolymer.

| Monomer | Polymer compositions | | Yield (%) | M_w (PD)[b] | T_g^c (°C) |
	Molar feed ratio (mol%)	Copolymer composition[a] (mol%)			
MAPDST	50	75	49.27	4300 (2.02)	165
MMA	50	25			

[a]Copolymer compositions were calculated by ^{1}H NMR spectrum.
[b]M_w and polydispersity (PD) were calculated with PEO and PEG standards using DMF solvent.
[c]The glass transition temperature (T_g) was measured at a heating rate 10 °C/min in N_2.

RESIST PROCESSING - LITHOGRAPHY

Substrate Coating:

Resist solution was prepared using MAPDST-MMA copolymer 3% by weight in methanol by subsequent filtration through a 0.2 µm Teflon$^®$ filter and was used in all experiments. The substrates were 2″ diameter p-type Si (100) wafers purchased from Wafer world, Inc. Prior to spinning, silicon wafers were cleaned by RCA cleaning method to remove organic contaminants and given a dehydration bake at 200 ℃ for 10 min and finally cooled to room temperature. Single stage spinning for duration of 60 sec at 5000 rpm gave us the desired thickness. The resulted film was baked at 90 ℃ for 2 min on a hotplate to yield a good quality film of ~50 nm thickness.

Softbake:

The soft-bake was done at 90 ℃ on a hotplate and the soft-bake was given for 2 min. At this temperature the resist did not appear to be sensitive to this soft-bake time. However, in order to dry out the solvent completely we had to apply soft-bake for 2 min.

Exposure Parameters:

Exposures were performed using Raith GmbH, 150-Two model machine (e-beam) at the INUP, IIT Bombay, India. It has TFE filament with beam size ≤ 2 nm at 20 keV and the minimum line width is < 20 nm with a stitching accuracy of ≤ 40 nm and overlay accuracy of ≤ 40 nm. The Electrons beam current is measured by using the Faraday cup and the line patterns were written in a single pass at 20 KeV e-beam with an aperture of 20 µm.

Moreover, in order to achieve the high resolution 20nm EBL feature of isolated line/space pattern, the non-chemically amplified resist (~50nm) was exposed by beam current (I) ~196.8pA, step size 15nm at 20 KeV. The base dose for this exposure was 10µC/cm^2, followed by multiples of dose factors upto 100µC/cm^2. The line width (γ) and single pass line dose (D_t), defined in units of C/cm is linear at lower doses and saturates at higher doses. Therefore, the optimal area dose is computed from the following relation and the subsequent parameters in consideration for proximity effect:

$$Area.dose = \frac{Dwell.time \times BeamCurrent}{\left(StepSize\right)^2}$$

Where, $D_{well\ time}$ is the beam is still at each location, Beam current is the current reaching to the resist sample surface and Step size is the length of beam moved between each $D_{well\ time}$, when the beam is still making the exposure

Post-exposure bake:

To obtain good resist mask edges we followed post-exposure bake (PEB) method. The substrate was put on the hot plate set to 120 ºC for 2 min. The glass transition temperature (T_g = 165 ºC) of MAPDST-MMA copolymer suggest that post-exposure bake temperature may be increased up to 160 ºC without risk of unexposed cross-linking.

Development:

Development was completed using standard concentration TMAH (tetramethylammonium hydroxide), 0.022 N aqueous solution by maintaining pH = 11.54 at room temperature for 20 sec, rinsed with de-ionized water about 15 sec and finally dried by passing pure nitrogen gas over the films.

0.022 N TMAH developer solution was prepared by adding 0.1 gram of TMAH in 50 mL DI water (pH = 5.56) and the pH of the developer solution was maintained at 11.54.

Imaging and Thickness measurements:

Resolution and image quality were determined by examining the developed resist profiles with SEM attached to Raith 150 lithography system at INUP, IIT Bombay. The exposed features were evaluated at energy of 5 keV.

The resist thickness was determined using ZETA 150 optical profilometer. The thickness of the resist material coated on Si wafer was ~50 nm.

Table S2. Comparison of MAPDST-MMA Copolymer with literature values in terms of sensitivity and contrast.

Resist	Sensitivity $\mu C/cm^2$	Contrast (γ)	CAR/n-CAR
MF03-04[4] (2006)	8-550	1.22-1.33	CAR
C5/Epoxide:C5/C0[4] (2006)	7.5	1.58	CAR
MF07-01[5] (2007)	8-550	0.5-2.21	CAR
Fullerol[6] (2008)	3600-15000	2.3-4.8	n-CAR
HSQ[7] (2009)	5500-25000	2.2	n-CAR
maN2400[8] (2012)	60-160	1.7-2.8	n-CAR
MR-EBL6000[8] (2012)	2-20	0.7	CAR
AR-N7720[9] (2012)	50	~1	CAR
AR-N7500[9] (2012)	25-50	>5	n-CAR
AR-N7700[9] (2012)	8	>5	CAR
SU-8[10] (2012)	1-20	0.7-1.7	CAR
MAPDST-MMA Copolymer	2.06	1.8	n-CAR

RIE-Experiment

STRIE-320PC system was used for etch resistance investigation experiments for MAPDST-MMA Copolymer at CEN-lab IIT-Mumbai, India. Two different etch chemistries (like SF_6 and CHF_3/O_2) were used to characterize the resist material, and thickness were measured before and after RIE by Bruker's DektakXT™ Stylus Profilometer, which has the **Key Features:** 2.0 μm diamond-tip stylus. Z-Resolution as low as 5 Å, x-y scan sizes up to 22 mm x 22 mm. Linear step height scans, and 3D stitching inbuilt capability:

RIE results of MAPDST-MMA Copolymer:-

1. The etchant was SF6 at a flow rate of 5 sccm at pressure of 10 mTorr with RF power of 20 W for 1min. The etch ratio of MAPDST-copolymer to the silicon substrate was 8.335.

2. The etchant was CHF_3/O_2 a flow rate of 22.5/2.5 sccm at pressure of 80 mTorr with RF power of 150 W for 1min. The etch ratio of MAPDST-copolymer to the silicon dioxide was 0.36.

Thickness measurements before and after RIE etching

MAPDST-MMA Copolymer thickness before RIE etching

Analytical Results		
Label	Value	Units
M Cursor Pos	0.386	Millimeter
M Cursor Width	-0.015	Millimeter
R Cursor Pos	0.026	Millimeter
R Cursor Width	0.017	Millimeter
Type	Two-Points Cursors	

Plot Legend
☑ Height Data

Cursor Status

Label	Position (mm)	Height Data (nm) ▼	Width (mm)
R	0.0259	-4.2964	0.0169
M	0.3509	90.4024	-0.0063
Δ	0.3250	94.6988	

Watch List

Label	Value
Total_ASH	90.88 nm
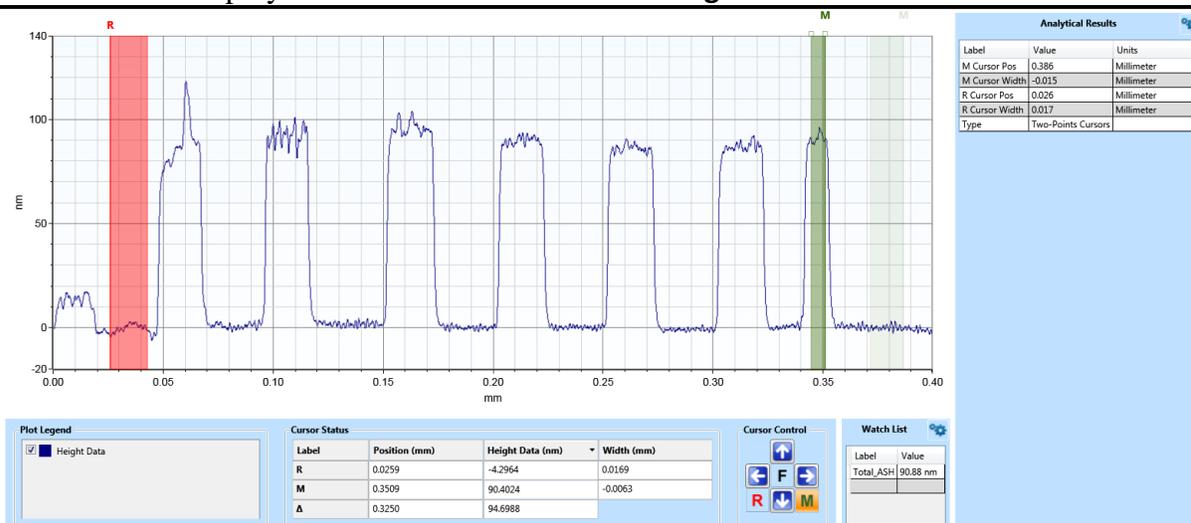
MAPDST-MMA Copolymer thickness After RIE etching

Analytical Results		
Label	Value	Units
M Cursor Pos	0.257	Millimeter
M Cursor Width	0.012	Millimeter
R Cursor Pos	0.659	Millimeter
R Cursor Width	-0.019	Millimeter
Type	Two-Points Cursors	

Plot Legend
☑ Height Data

Cursor Status

Label	Position (mm)	Height Data (nm) ▼	Width (mm)
R	0.6585	-0.4067	-0.0188
M	0.6202	110.2099	0.0056
Δ	-0.0383	110.6166	

Watch List

Label	Value
Total_ASH	114.19 nm
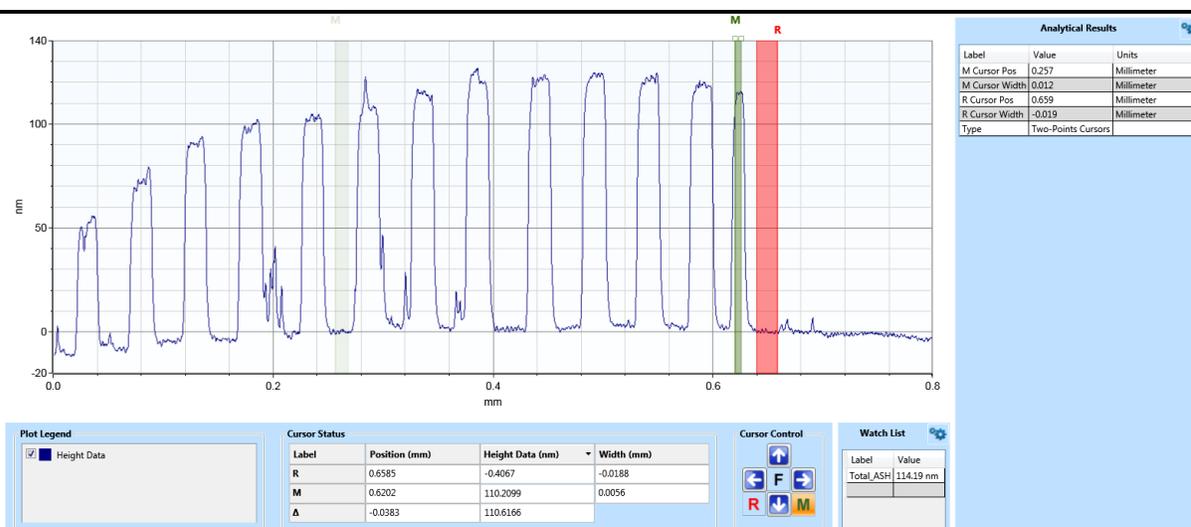
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