Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Design, Development, EUVL Applications and Nano Mechanical Properties of a New HfO_2 Based Hybrid Non-Chemically Amplified Resist†

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Experimental Section

1) Synthesis of HfO_2-acetate (HA)

Hafnium (IV) *tert*-butoxide (0.500 g) was dissolved in 2.5 ml of acetic acid and stirred at 65 ^oC for 15 min to form a white turbid solution. Then, 0.83 mL of 9:1 acetic acid-water mixture was added and stirring was continued for 5 minutes. During this process, a white precipitate is formed from the white turbid solution. This reaction mixture was stirred again for 18 h at the same temperature. After that, 0.83 mL of 9:1 acetic acid-water mixture was added again and stirring was continued for 3 h at the same temperature. Finally, the white precipitate was centrifuged at 8,000 rpm for 10 min and then washed once with acetic acid and twice with acetone. The product thus obtained was dried in an oven at 50 ^oC overnight to give a fine white powder of HA. Yield: 0.398 gm (83%). FT-IR: ν_{max}/cm^{-1} 1542.61 (C-O asymmetric), 1453.29 (C-O symmetric), 1411.09, 1346.16, 1256.90, 1203.60, 1029.31, 957.58, 924.79, 805.87, 649.08, 614.02, 473.60 (HfO_2). ^1H NMR (500 MHz,$CDCl_3$) δ_H 1.92 (3H, multiple singlets, $-CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 178.24 (C=O) and 24.27($-CH_3$).

2) Synthesis of HfO_2-methacrylate (HM)

To a stirred solution of methacrylic acid (0.1321 g) in 1 ml of PGMEA, HA (0.100 g) was added at room temperature and the reaction mixture was ultra-sonicated for 5 minutes. The resultant cloudy solution was stirred vigorously at 130 ^oC for 10 minutes. The solution becomes clear after the ligand exchange process. An excess of acetone/water/ether co-solvent mixture was added to the clear solution in order to remove acetate or methacrylic acid residues present in the reaction mixture and centrifuged at 10,000 rpm for 10 min. After centrifugation, the co-solvent mixture layer was separated out from the PGMEA reaction mixture. The residual light brown powder of HM was achieved by evacuating the PGMEA-ethanol mixture, which was obtained by the addition of ethanol into the PGMEA reaction mixture. Yield: 0.0913 g (74%). FT-IR: ν_{max}/cm^{-1} 1573.21-1551.98 (C-O asymmetric), 1455.49-1419.51 (C-O symmetric), 1370.37, 1242.87, 1200.57, 1172.29, 1006.25, 934.27, 883.68, 824.63, 668.45, 616.86, 824.63, 668.45, 616.86, 421.70 (HfO_2). ^1H NMR (500 MHz, $CDCl_3$) δ_H 6.07 (1H, split peak, CH_2), 5.40 (1H, split peak, CH_2), 1.8 (3H, S, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 172.61(C=O), 140.00, 124.38 (CH_2), 18.48 (CH_3).

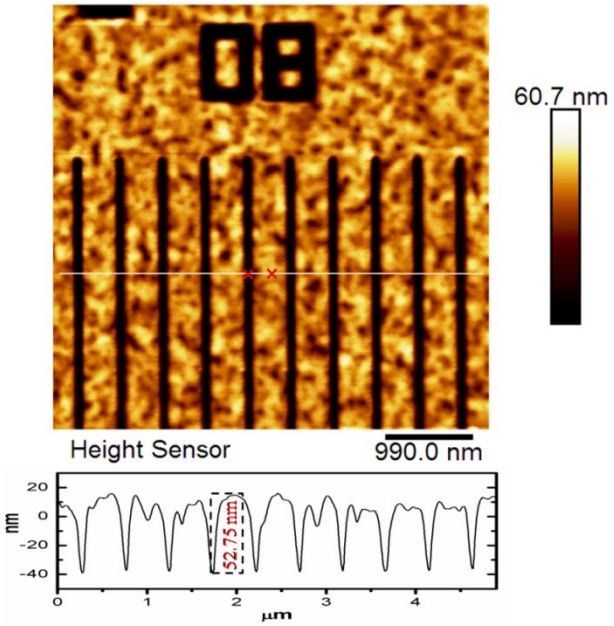

Figure S1. AFM line profile measurements for thickness analysis.

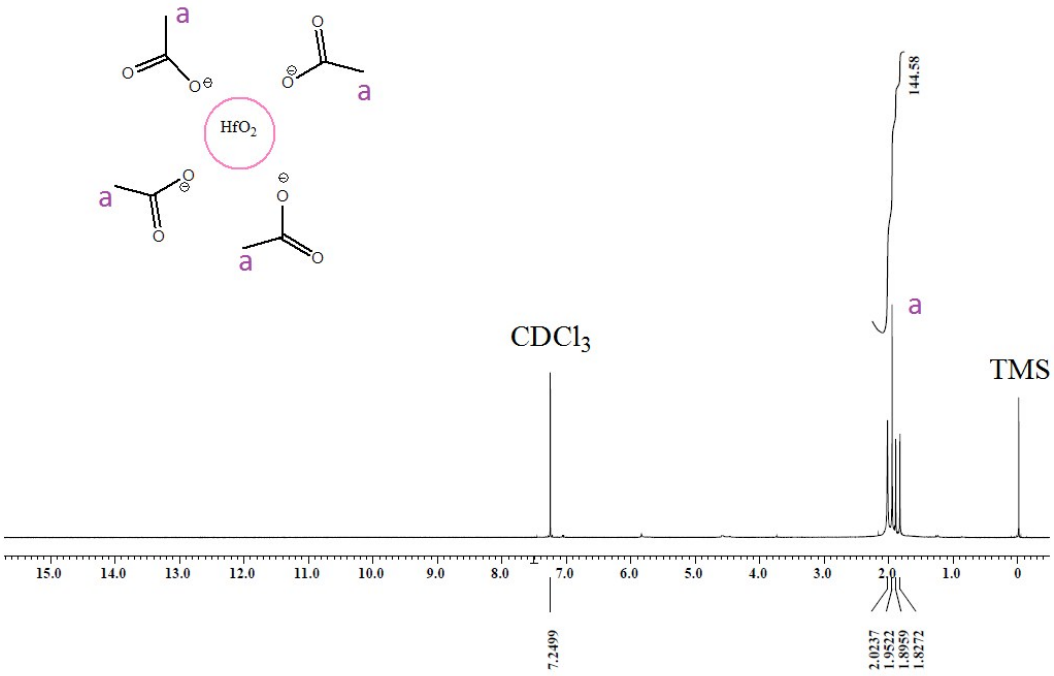

Figure S2. ^{1}H NMR of HfO_2-acetate (HA).

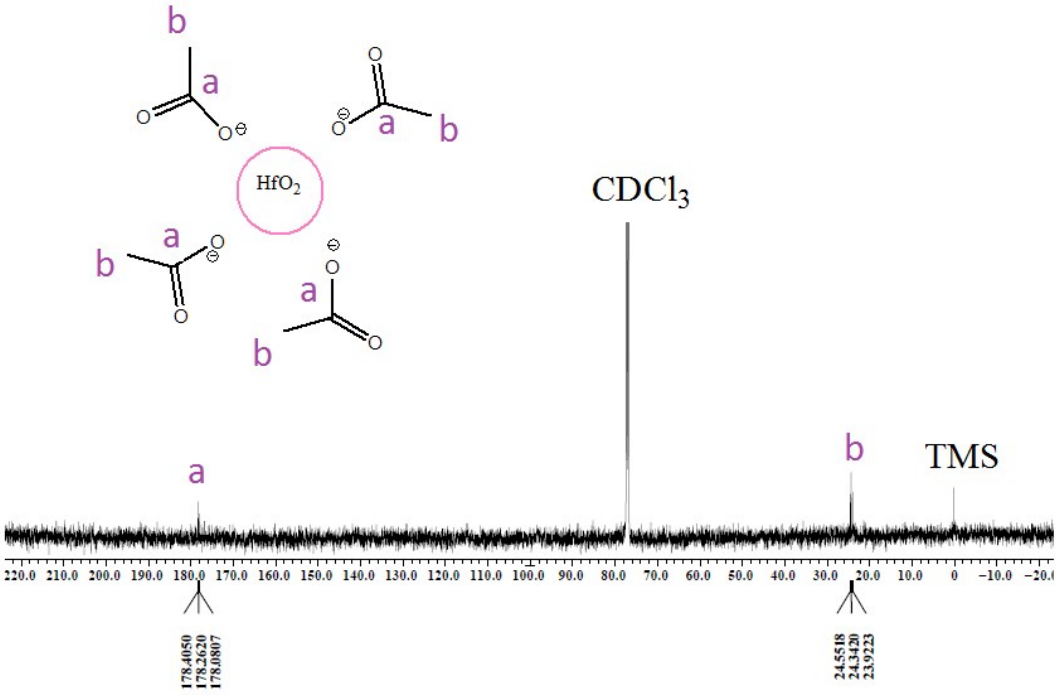

Figure S3. ^{13}C NMR of HfO_2-acetate (HA).

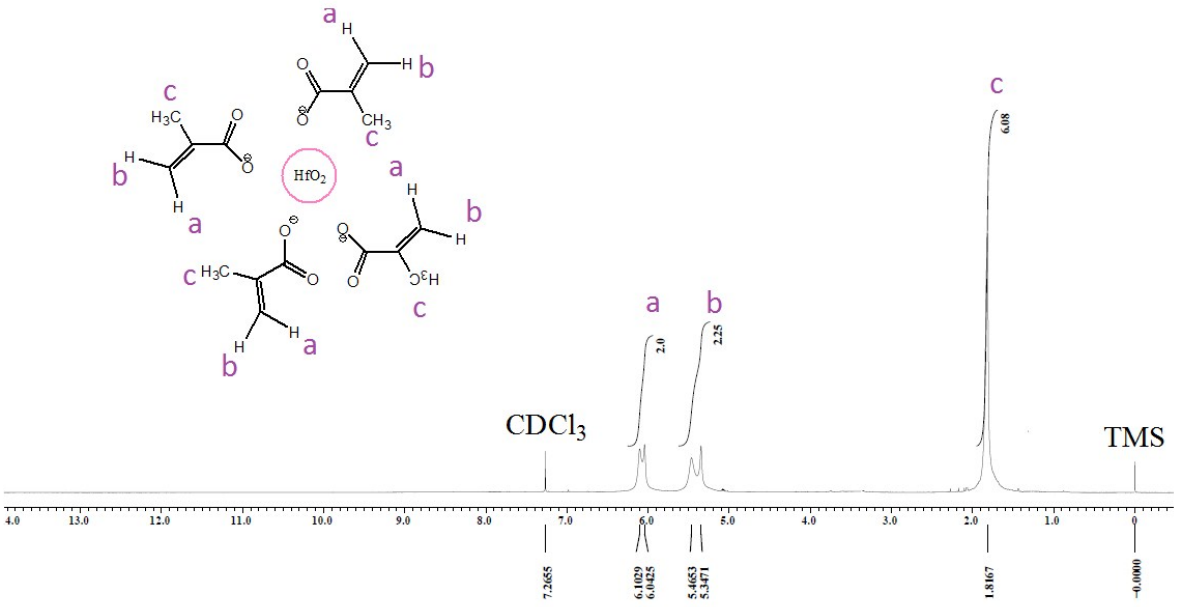

Figure S4. ^{1}H NMR of HfO_2-methacrylate (HM).

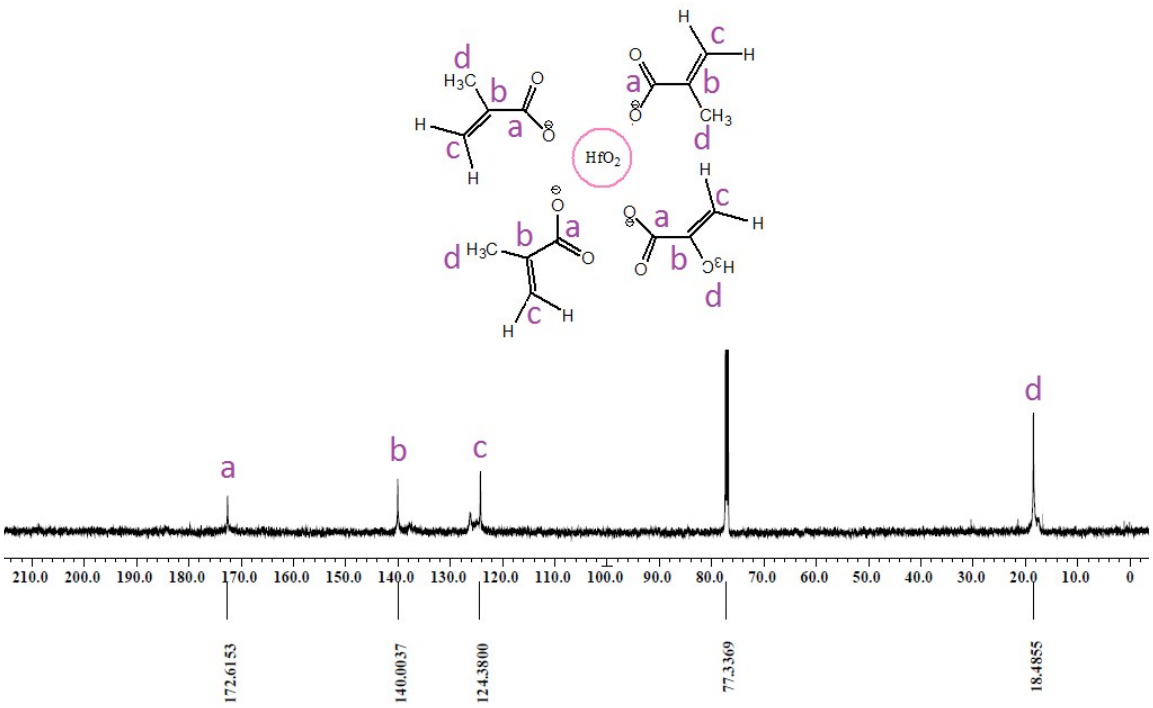

Figure S5. ^{13}C NMR of HfO_2-methacrylate (HM).

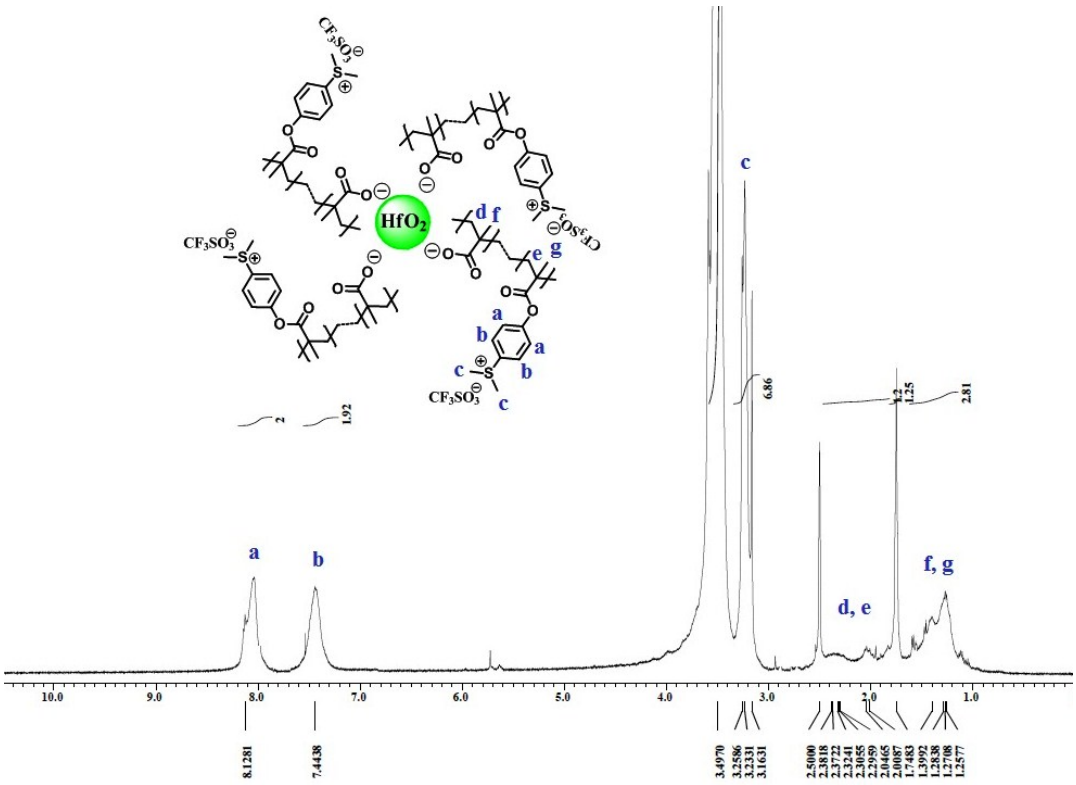

Figure S6. ^{1}H NMR of HfO_2-methacrylate-MAPDST (HMM).

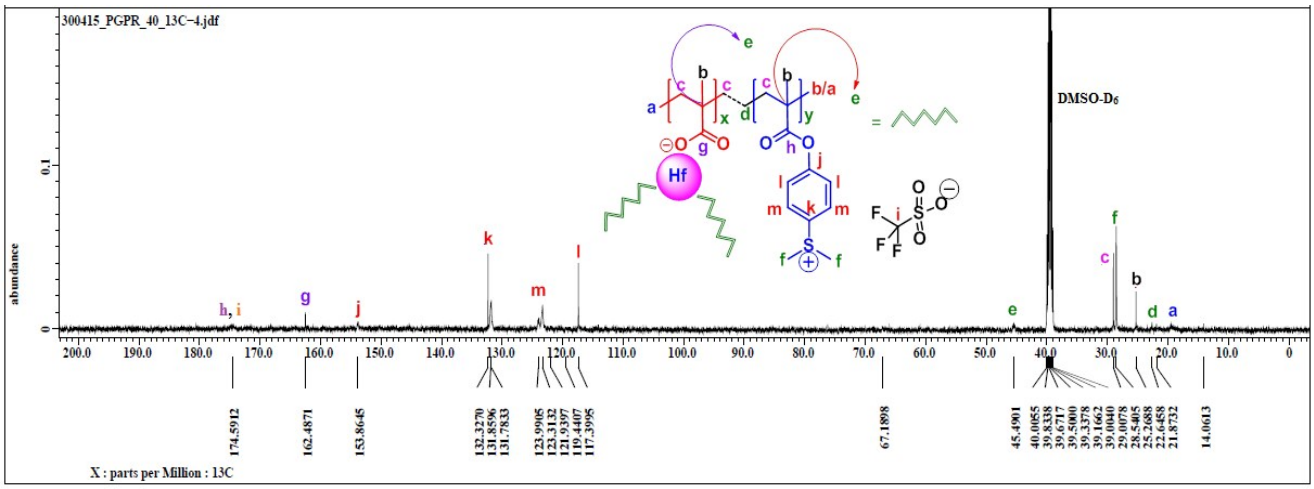

Figure S7. ^{13}C NMR of HfO_2-methacrylate-MAPDST (HMM).

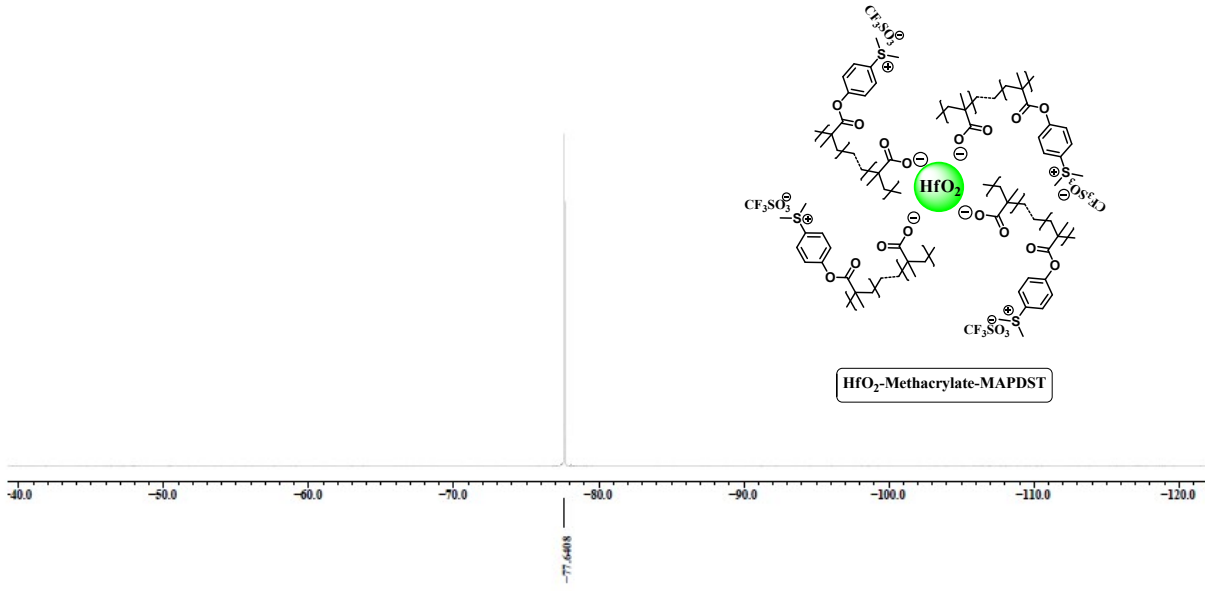

Figure S8. ^{19}F NMR of HfO_2-methacrylate-MAPDST (HMM)

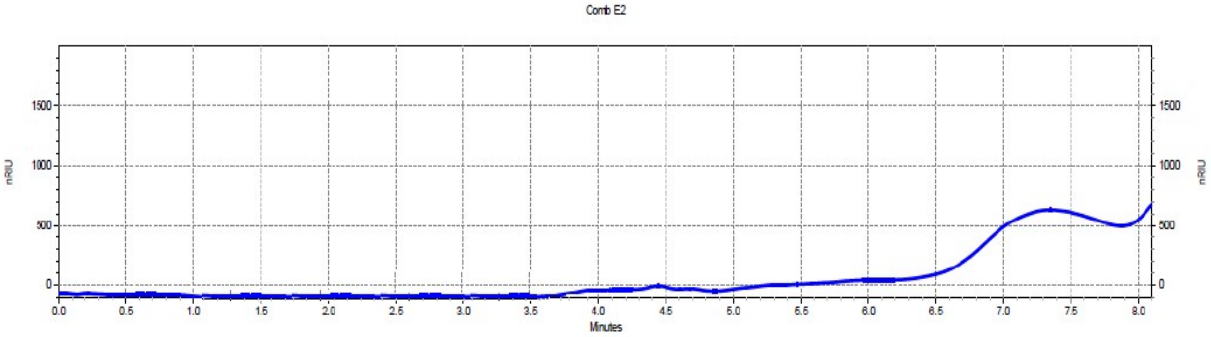

Figure S9. GPC data of HfO_2-methacrylate-MAPDST (HMM).

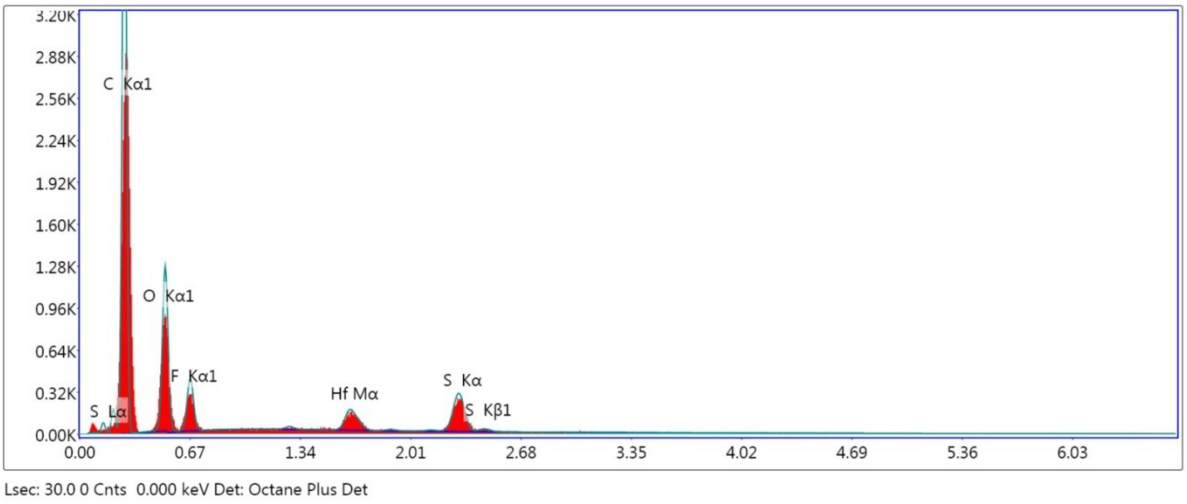

Figure S10. EDX of HfO_2-methacrylate-MAPDST (HMM).

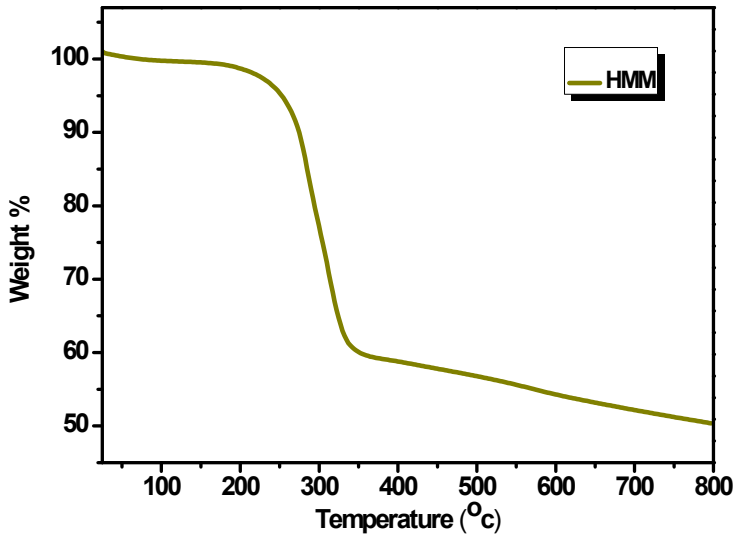

Figure S11. TGA profile of HfO_2-methacrylate-MAPDST (HMM).

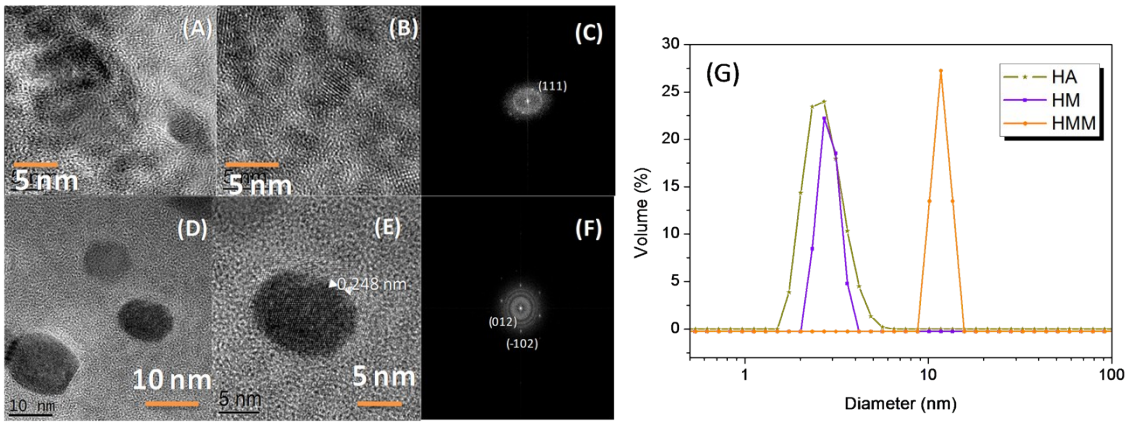

Figure S12. (Left) TEM images of HA (A), HM (B) and HMM (D, E); XRD profiles of HM (C) and HMM (F). (Right) DLS data of HA, HM and HMM (G).

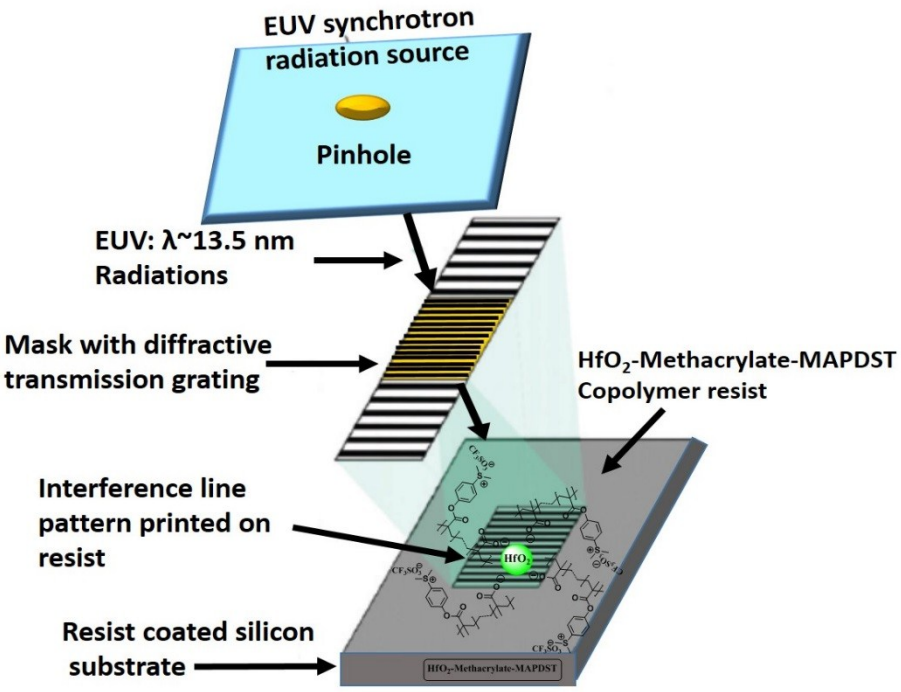

Figure S13. Schematic of EUV exposure process used for HMM n-CAR hybrid resist.