Experimental details

Synthesis of HfO$_2$ nanoparticles

Hafnium isoproxide (6.0 g, 12.6 mmol) was dissolved in 30.0 ml acetic acid and stirred at 65 °C for 15 min to form a clear solution. Then 10.0 ml of a solution comprised of 9.0 ml acetic acid and 1.0 ml H$_2$O (1.0 g, 55.5 mmol) was added causing the formation of a white precipitate. The reaction mixture was stirred at 65 °C for 18 h before 10 ml of a similar acetic acid – water solution was added followed by stirring for 3 h at the same temperature. The white precipitate was centrifuged at 8,000 g for 10 min and then washed once with acetic acid and twice with acetone. The final product was dried overnight to give a fine white powder.

Synthesis of (s)-(+-)tetrahydrofurfuryl -O-O'-diacetyl-(2R,3R)-hydrogen tartrate (TDHT)

To a stirred mixture of racemic tetrahydrofurfuryl alcohol (4.7 g) and pyridine (0.4 g) solid diacetyltartaric anhydride (10 g) was added. Stirring was continued for 30 minutes at room temperature, then 5 ml of ethyl acetate was added, and the temperature was raised to 80 °C. After 2 hr heating, 10 ml of ethyl acetate was added, and the mixture was allowed to cool to room temperature, then kept for 10 hrs at 5 °C. The crystals were filtered off, washed with ethyl acetate (10 ml) and dried. 7 g of crude ester was obtained. The crude product was recrystallized three times from ethyl acetate to yield 1.8 g of pure TDHT. IR (KBr, cm$^{-1}$): $\nu$(C-O):1069, 1212; $\nu$(C=O): 1750, 1759; $\nu$(CH$_3$): 2605, 2944; $\nu$(OH): 3495. $^1$H NMR (Acetone-d$_6$): $\delta$ 5.74-5.68 (2H, m), 3.62-4.26 (5H, m), 2.09-2.17 (6H, s), 1.18-2.08 (4H, m) ppm.

Ligand exchange reaction and purification

HfO$_2$-acetate x (x=0.04~0.12 g) was mixed with ligand 0.2 g + 1 ml of PGMEA in 25 ml round flask. After ultra-sonication of the solution for 5 minutes, the cloudy solution was heated at 130 °C for 10 minutes. After ligand exchange, the solution became clear. To eliminate any residue of acetate or acetic acid, an excess of acetone/water/ether co-solvent was added to the solution. The solution was centrifuged at 10,000 rpm for 10 min, and then washed three times with a mixture of acetone/water/ether. The residual powder was redissolved in water/acetone (50/50) mixture. The solution was purified by dialysis using semipermeable membrane (molecular cut off, 500) for 3 days and vacuum dried at 50 °C.
**Film preparation**

193 nm photoresist powder poly(methyladamantane methacrylate-co-alpha-methacryloxy-gamma-butyrolactone) (PMAdMA-co-GBLMA) (Mitsubishi Rayon America, Inc.) 50 mg and photoacid generator (PAG) triphenylsulfonium triflate 2.5 mg were dissolved in 1 ml of PGMEA. A desired amount of HfO$_2$-TDHT is added to the photoresist solution. After sonication and heat treatment, the solution became transparent. After being filtered through 0.2 μm syringe filter, the solution was spin-coated onto 2 inch BARC-coated or HMDS primed Si wafers at 2000 rpm for 60 s. The film was baked at 130 °C for 60 s after spin coating to remove residual solvent in the film. The BARC-coated Si wafer (~90 nm thickness) was supplied by SEMATECH (ARC29A-8) and was baked at 120 °C for 60 s for the dehydration and was cooled to room temperature prior to resist coating. The film thickness and the roughness of each film are listed in table S1.

<table>
<thead>
<tr>
<th>HfO$_2$-TDHT content in PMAdMA-co-GBLMA</th>
<th>Film thickness (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>130±16</td>
<td>0.287±0.005</td>
</tr>
<tr>
<td>4%</td>
<td>180±10</td>
<td>0.276±0.004</td>
</tr>
<tr>
<td>8%</td>
<td>210±7</td>
<td>0.539±0.013</td>
</tr>
<tr>
<td>12%</td>
<td>220±8</td>
<td>0.485±0.022</td>
</tr>
</tbody>
</table>

**Table S1.** Film thickness and roughness of PMAdMa-co-GBLAMA + HfO$_2$-TDHT film after spin-coated at 2000 rpm for 60 s on BARC coated film.

**Lithographic Evaluation**

Deep-UV patterning was done by exposing films through a quartz mask using an ABM mask aligner at a wavelength of 254 nm (measured power 8.7 mW/cm$^2$). High-resolution patterning was done using a Leica VB6-HR electron-beam lithography system operating at 100 kV, followed by a post-exposure bake of 115 °C for 60 sec.
Supporting figures

Figure S1. $^1$H NMR spectrum of TDHT

Figure S2. FTIR spectra of (a) HfO$_2$-acetate, (b) TDHT, (c) HfO$_2$-TDHT
Figure S3. Optical micrograph of P(MAdMA-co-GBLMA)/ HfO$_2$–TDHT nanoparticles (8 wt%).

Figure S4. SEM images of (c) P(MAdMA-co-GBLMA)/ HfO$_2$–acetate (8wt%) and (f) P(MAdMA-co-GBLMA)/ HfO$_2$–TDHT (8wt%) and corresponding elemental maps (a), (d) C at K peak and (b), (e) Hf at M peak.
Figure S5. TGA thermogram for HfO$_2$-acetate and HfO$_2$-TDHT (left) and 1$^{st}$ derivative curve of the left graph (right). The peak a is attributed to the disconnection of crystal water and the shoulder next to the peak a is related with the reaction: CH$_3$COO $\rightarrow$ CO$_2$ + solid residue. The peak b is related with the dissociation of TDHT group. The Peak c and d are attributed to the decomposition of organic residue.
Figure S6. Optical microscopy images of (a) P(MAdMA-co-GBLMA), (b) P(MAdMA-co-GBLMA)/HfO₂–TDHT nanoparticles (8 wt%) and (c) P(MAdMA-co-GBLMA)/HfO₂–TDHT nanoparticles (12 wt%), patterned by DUV contact aligner.

References