

# Photobleachable silicon-containing molecular resist for deep UV lithography

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A novel molecular resist material based on polyhedral oligomeric silsesquioxane, possessing diazoketo groups, was successfully synthesized for deep UV lithography. The initial lithographic evaluation of the molecular resist shows the potential of the new platform for the next generation resists.

Chemically amplified resists utilizing acid-catalyzed reactions have been widely used for the production of integrated circuits. Despite their high photosensitivity, the chemically amplified resists suffer from serious problems such as the appearance of an anomalous insoluble skin layer and line-width shift caused by air-borne contamination and acid diffusion in the resist films when the post-exposure bake is delayed. These post-exposure delay problems make it difficult to fabricate fine patterns.<sup>1</sup> Moreover, photoacid generators are used almost exclusively in their monomeric forms and have limited compatibility with the polymeric photoresist material. The resulting problems include phase separation and non-uniform acid diffusion and thereby limit the resolution.<sup>2</sup> Furthermore, most of the commonly used photoacid generators contain aromatic rings in their structure and present potential environmental hazards.

As the feature size of patterns keeps on shrinking to molecular dimensions, molecular resists, which utilize smaller building blocks compared to the polymeric resists, are gaining more attention due to their high resolution capability and reduced line edge roughness.<sup>3,4</sup> Photoresists containing silicon have been studied for use as an imaging layer of a bilayer resist.<sup>5</sup> Bilayer resists have several advantages. Because the top imaging layer is very thin, resist materials of relatively high absorbance can also be used. The anti-reflective bottom planarizing layer diminishes defects like the standing wave effect, which causes irregular line edge profiles. Furthermore, bilayer resists need only a small depth of focus and high aspect ratio patterns can be obtained.

Our goal in this investigation is to find a proper silicon-containing molecular resist that is processable without a photoacid generator and induces both photobleaching in the deep UV regions and polarity change upon exposure. We thought diazoketo groups could give such effects. There is no necessity for the post-exposure bake step that is the cause of acid diffusion. Polyhedral oligomeric silsesquioxane (POSS) was chosen as the

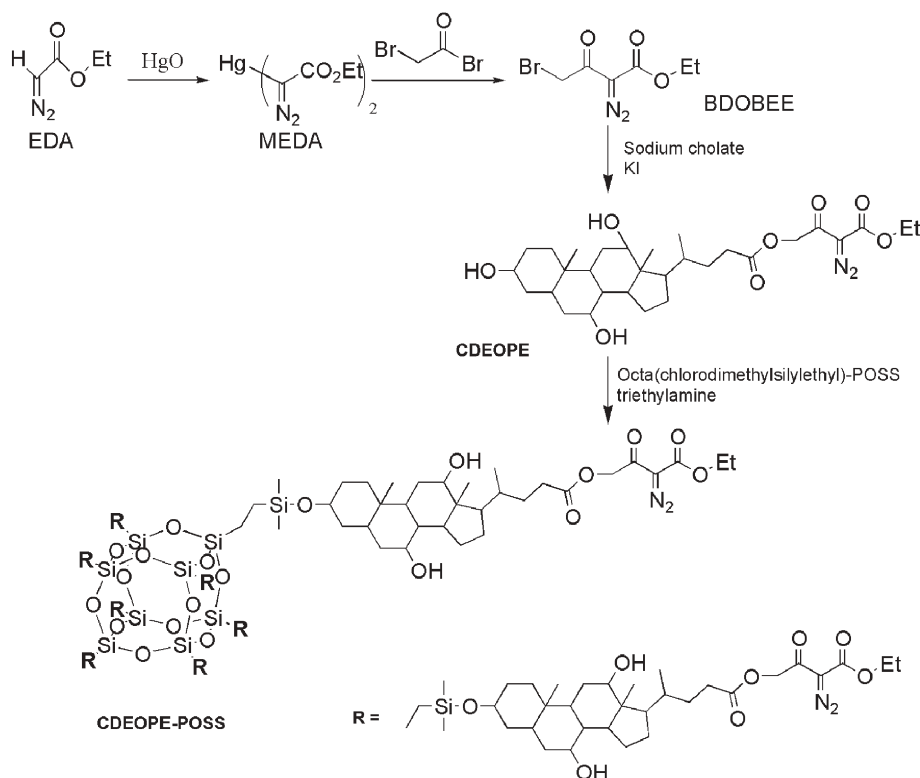
silicon-containing component because POSS molecules are thermally and physically more robust than silicones and are easy to functionalize.<sup>6</sup> In this communication, we report the synthesis of a novel silicon-containing molecular resist that incorporates diazoketo functional groups into its molecular structure.<sup>7</sup> To the best of the authors' knowledge, there is no previous report of molecular resists having diazoketo groups. POSS was used as the core and diazoketo-functionalized cholate derivatives were used as the shell part. Cholate derivatives, which are amphiphilic in nature, give good film formability. Moreover, alicyclic-rich cholate moieties give good dry-etch resistance, which is an essential requirement to transfer the formed pattern to the underlying silicon substrate.<sup>8</sup> The cholate moiety was functionalized with a diazoketo group that upon irradiation with deep UV light undergoes Wolff rearrangement to generate a carboxylic group and thereby offers a solubility change.<sup>9</sup> As the solubility change can be made merely by irradiation with UV light, post-exposure delay problems can be eliminated.

The overall scheme for the synthesis of the molecular resist material is given in Scheme 1. Ethyl diazoacetate (EDA) was treated with yellow mercuric oxide to obtain mercuryl ethyl diazoacetate (MEDA), which was further reacted with bromoacetyl bromide to yield 4-bromo-2-diazo-3-oxobutyric acid ethyl ester (BDOBEE).<sup>10</sup> BDOBEE was further reacted with sodium salt of cholic acid in the presence of KI catalyst to obtain cholic acid 3-diazo-3-ethoxycarbonyl-2-oxopropyl ester (CDEOPE).<sup>11</sup> To obtain the molecular resist material, CDEOPE was then reacted with octa(chlorodimethylsilylethyl)-POSS in the presence of triethylamine to give CDEOPE-POSS in 93% yield. After purification by precipitation in petroleum ether, the molecular resist material, CDEOPE-POSS, was isolated as a pale yellow solid. The structure was determined from its <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR spectra. Thermogravimetric analysis of CDEOPE-POSS shows it possesses good thermal stability with the thermal degradation beginning at 130 °C, which is higher than normal process temperatures (70–100 °C).

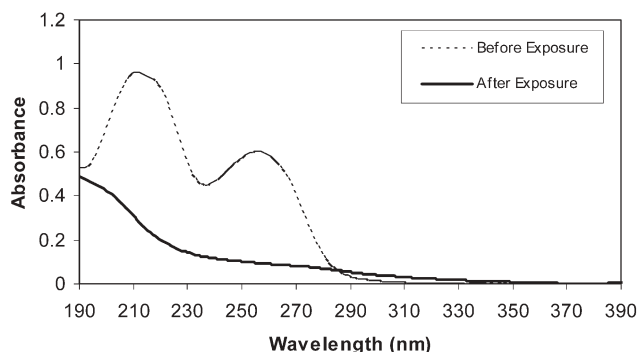
The photobleaching degree of CDEOPE-POSS was calculated by measuring the absorbance coefficient values before and after UV light irradiation. CDEOPE-POSS was spin-coated over a quartz disk and the UV absorbance was measured before and after the flood exposure of 1000 mJ cm<sup>-2</sup> to ensure completion of the photochemical reaction. Fig. 1 shows the UV absorbance spectra of CDEOPE-POSS, measured on a 0.51 μm thick film, before and after UV light exposure. The absorbance coefficient values before and after exposure at 193 nm were 1.06 and 0.92 μm<sup>-1</sup> respectively with a photobleaching degree of 13.2%. The absorbance coefficient

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**Scheme 1** Overall synthetic procedure of CDEOPE-POSS.



**Fig. 1** UV absorbance spectra of CDEOPE-POSS before and after UV light irradiation.

values before and after exposure at 248 nm were 1.09 and  $0.203 \mu\text{m}^{-1}$  respectively with a photobleaching degree of 81.4%.

Oxygen reactive ion etching ( $\text{O}_2$ -RIE) resistance is an essential criterion for a resist material to be used as a bilayer resist. Table 1 shows the  $\text{O}_2$ -RIE resistance values of CDEOPE-POSS, novolac

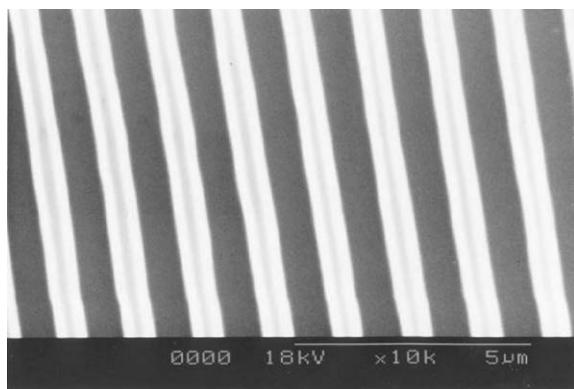
**Table 1** The results of oxygen reactive ion etching

Materials	Before RIE/ $\text{\AA}$	After RIE/ $\text{\AA}$	Etching time/s
CDEOPE-POSS	4876	4692	900
Novolac	6110	0	140 <sup>a</sup>
PTBMA	5586	0	100 <sup>a</sup>

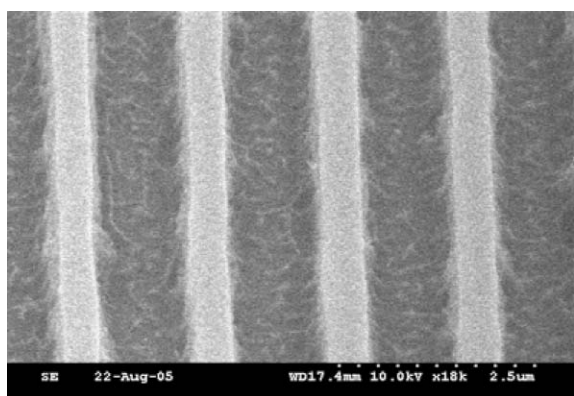
<sup>a</sup> The time needed for etching the film completely.

resin (planarizing layer) and poly(*tert*-butyl methacrylate) (PTBMA). Novolac resin and PTBMA which contain no silicon were fully etched within 140 and 100 s respectively, whereas CDEOPE-POSS showed a thickness loss of less than 200  $\text{\AA}$  even after 15 min of  $\text{O}_2$ -RIE using a parallel plate reactor at 200 mTorr pressure, an oxygen flow rate of 30 sccm and RF power of 100 W. These results show that CDEOPE-POSS has excellent  $\text{O}_2$ -RIE resistance due to the formation of a  $\text{SiO}_2$  layer on the top of the imaging layer.

The lithographic evaluation of CDEOPE-POSS was carried out both as single layer and bilayer resists. A high quality, uniform film was obtained from a 14 wt% solution of CDEOPE-POSS in propylene glycol methyl ether by spin coating on a hexamethyl-disilazane-treated silicon wafer that was further soft-baked at 80  $^\circ\text{C}$  for 90 s. Using the industrial standard 2.38 wt% tetramethylammonium hydroxide solution, homogeneous development was observed in the exposed regions of the resist film. For a film of 0.4  $\mu\text{m}$  thickness, a  $300 \text{ mJ cm}^{-2}$  dose was used. Fig. 2 shows the scanning electron micrograph of the 0.7  $\mu\text{m}$  line and space positive tone image formed with CDEOPE-POSS as a single layer resist. For the lithographic evaluation as an imaging layer of the bilayer resist system, a film of 0.25  $\mu\text{m}$  thickness was formed from a 11 wt% solution of CDEOPE-POSS in propylene glycol methyl ether on top of a planarizing novolac film of 0.5  $\mu\text{m}$ . Lithographic evaluation was carried out with a  $250 \text{ mJ cm}^{-2}$  dose and the exposed regions were developed with the standard tetramethylammonium hydroxide developer. The wet-developed pattern of the imaging layer was anisotropically transferred to the underlying planarizing layer by  $\text{O}_2$  plasma. Fig. 3 shows the scanning electron micrograph of the 0.7  $\mu\text{m}$  line and space positive tone image



**Fig. 2** Scanning electron micrograph of the 0.7  $\mu\text{m}$  line and space positive tone image, formed with CDEOPE-POSS as a single layer resist.



**Fig. 3** Scanning electron micrograph of the 0.7  $\mu\text{m}$  line and space positive tone image, formed with CDEOPE-POSS and novolac as a bilayer resist after  $\text{O}_2$  plasma etching.

formed with CDEOPE-POSS and novolac as a bilayer resist. The results show the potential of the new platform for next generation resists, although further optimization is necessary. The initial lithographic studies have shown the feasibility of CDEOPE-POSS to be used as both single layer and bilayer resists.

In summary, a novel silicon-containing molecular resist material (CDEOPE-POSS) having photobleachable and solubility changing groups was successfully synthesized for deep UV lithography without the need for the addition of a photoacid generator, thereby eliminating post-exposure delay problems, phase separation and non-uniform acid diffusion. Irradiation of the UV light induces the photobleaching and solubility change by the photo-reaction in the exposed regions of the resist film, which was developed using the industrial standard 2.38 wt% tetramethylammonium hydroxide solution, thereby creating positive-tone images. The core POSS enables the molecular resist to be used as a bilayer resist.

Cholic acid 3-diazo-3-ethoxycarbonyl-2-oxo-propyl ester (CDEOPE) was synthesized as follows. A solution of BDOBE (4.76 g, 25 mmol) in 75 mL of dimethyl sulfoxide was added to a solution of the sodium salt of cholic acid (10.76 g, 25 mmol) in 250 mL of dimethyl sulfoxide containing 0.42 g of potassium iodide (2.5 mmol). The reaction mixture was stirred for 24 h at

room temperature and then partitioned between 300 mL of diethyl ether and 200 mL of water. Diethyl ether was then concentrated and the pure CDEOPE was obtained as a pale yellow solid by column chromatography (diethyl ether–ethyl acetate, 1 : 3) in 67% yield (9.4 g). IR (film),  $\nu_{\text{max}}$  3511, 2935, 2868, 2142, 1749, 1716, 1675  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.64 (s, 3H), 0.95 (s, 3H), 3.40 (s, 1H), 3.79 (s, 1H), 3.93 (s, 1H), 4.23–4.31 (m, 2H), 5.06 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 12.46, 14.2, 61.8, 68.37, 161.01, 173.5, 185.45.

Cholic acid 3-diazo-3-ethoxycarbonyl-2-oxo-propyl ester-POSS (CDEOPE-POSS) was synthesized as follows. A solution of octa(chlorodimethylsilylethyl)-POSS (1.4 g, 1 mmol) in 150 mL of dry tetrahydrofuran was added dropwise to a solution of CDEOPE (4.73 g, 8.4 mmol) and triethylamine (0.85 g, 8.4 mmol) in 250 mL of dry tetrahydrofuran at 0  $^\circ\text{C}$ . The resulting solution was stirred under nitrogen atmosphere at room temperature for 6 h, filtered and evaporated to obtain a pale yellow solid, which was purified by precipitation in petroleum ether to give CDEOPE-POSS (5.2 g, 93%). IR (film),  $\nu_{\text{max}}$  3420, 2935, 2871, 2143, 1748, 1716, 1675  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.06 (s, 6H), 0.95 (s, 3H), 3.42 (s, 1H), 3.80 (s, 1H), 3.90 (s, 1H), 4.24–4.30 (m, 2H), 5.05 (s, 2H).  $^{29}\text{Si}$  NMR  $\delta$  (ppm): –66.7, 12.97.

Samples for lithographic evaluation were prepared by spin coating a 14 wt% resist solution of CDEOPE-POSS in propylene glycol methyl ether on a hexamethyldisilazane-treated silicon wafer that was further soft-baked at 80  $^\circ\text{C}$  for 90 s. For bilayer evaluation, the planarizing layer was formed by spin coating of the novolac resist solution onto the silicon wafer. Flood exposure of deep UV light was carried out over the planarizing layer which was further hard baked at 200  $^\circ\text{C}$  for 10 min. A 11 wt% resist solution of CDEOPE-POSS in propylene glycol methyl ether was spin coated over this planarizing layer and soft baked at 80  $^\circ\text{C}$  for 90 s. Exposures were carried out on a deep UV exposure system (Oriel corporation Model 82531) with a high-pressure mercury–xenon lamp and a filter transmitting light between 220 and 260 nm.

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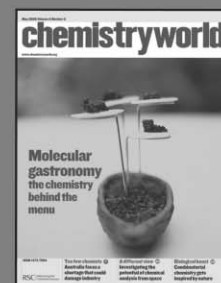
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