

## High Performance Molecular Resists Based on $\beta$ -Cyclodextrin

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Typical polymeric resist materials are used with pendant functional groups that undergo a polarity change when the resist film is exposed to an appropriate wavelength of light, altering the solubility of the exposed regions.<sup>1–3</sup> An important problem encountered with these polymeric resist materials in small-scale pattern fabrication is that the bulkiness of the molecular size together with the large molecular weight distribution causes fluctuation of line patterns. So the amorphous molecular resist materials comprised of smaller building blocks are gaining more attention. The amorphous low-molecular-weight materials have several advantages over conventional polymeric systems such as higher resolution and smaller line edge roughness due to smaller molecular size with defined molecular weight, uniform properties because of uniform molecular structure, and the absence of molecular chain entanglements.<sup>4–6</sup> There are many reports on molecular resists based on calixarene and other aromatic compounds.<sup>7–18</sup> These materials, however, are not suitable for 193 nm lithography due to their high absorption. An interesting study has been carried out with cyclodextrin derivatives containing fluorine atoms as molecular resists by T. Nishikubo and coworkers.<sup>19</sup>

In this paper we propose new chemically amplified molecular resists based on cyclodextrins. Cyclodextrins are well known materials that have polar outside rim and non-polar inside cavity. They have well-defined structure and discrete molecular weight. The synthesis, physical properties, and lithographic performance of the newly designed molecular resist will be discussed.

## EXPERIMENTAL

### Materials

$\beta$ -Cyclodextrin ( $\beta$ -CD), pyridine, *N,N*-dimethylacetamide (DMAc), and di-*t*-butyldicarbonate (DtBDC) were purchased from Aldrich Chemical Company and used without further purification. Triphenylsulfonium triflate (TPSTf) was supplied by Seoul Fine Tech.

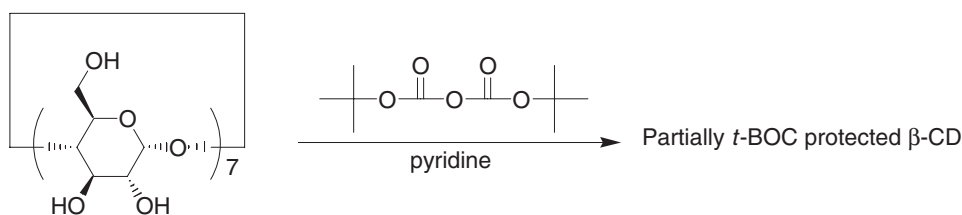
### Synthesis of *t*-Butoxycarbonyl (*t*-BOC) Protected $\beta$ -CD

The protection of  $\beta$ -CD with *t*-BOC group was synthesized according to the similar method in the literature.<sup>20,21</sup>  $\beta$ -CD (2.27 g) and pyridine were dissolved in 20 mL of DMAc and the resulting solution was cooled to 0 °C. Calculated amount of DtBDC was added dropwise into this solution. Then the reaction mixture was allowed to warm to room temperature and stirred for 10 h. The reaction mixture was precipitated into warm water. The white precipitate was filtered, washed with warm water, and dried under reduced pressure.

### Lithographic Evaluation

A resist solution was prepared by dissolving 1.0 g of *t*-BOC-protected  $\beta$ -CD and 0.02 g of TPSTf in 5.0 g of propylene glycol methyl ether acetate (PGMEA). The solution was filtered through a 0.2  $\mu$ m Teflon filter prior to the application on the substrate. The resist film was prepared by spin-coating of the resist solution on a hexamethyldisilazane-treated silicon wafer and baking at 110 °C for 90 s. Exposure was carried out with a KrF exposure tool (Nikon S203B, 0.68 NA, 2/3 Annular). The exposed wafer was baked at 110 °C for 90 s on

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**Figure 1.** The synthesis of *t*-BOC protected  $\beta$ -CD.

**Table I.** The results of *t*-BOC protection

Materials	Feed Ratio of DtBDC (mol %)	<i>t</i> -BOC protection ratio <sup>a</sup> (mol %)
A	50	31
B	65	34
C	70	37
D	80	40

<sup>a</sup>Data calculated from the TGA.

a hot plate and developed in a 2.38 wt % tetramethylammonium hydroxide (TMAH) aqueous solution for 60 s.

## RESULTS AND DISCUSSION

### Synthesis of *t*-BOC Protected $\beta$ -CD

New molecular resist materials based on  $\beta$ -CD were synthesized as shown in Figure 1. *t*-BOC protected  $\beta$ -CDs with various protection ratios were obtained by varying the amount of the DtBDC in the reaction and the results are summarized in Table I. The *t*-BOC protection ratios were calculated from the thermogravimetric analysis (TGA). The *t*-BOC protection ratio (34%) of the material B approximately corresponds to the 7 *t*-BOC protecting groups on the upper rim of  $\beta$ -CD. The 7 primary hydroxyl groups on the upper rim of the  $\beta$ -CD were protected with *t*-BOC groups, since the reactivity of the primary alcohol is higher than that of secondary one on the lower rim of the  $\beta$ -CD.<sup>23–26</sup> The UV absorbances of *t*-BOC protected  $\beta$ -CDs at 193 nm were 0.22 to 0.24/ $\mu\text{m}$ .

### Adhesion Property

The adhesion properties of the resist materials were evaluated from the work of adhesion between a resist film and a silicon substrate. The work of adhesion was calculated according to Owen's and Wendt's, Young's, and Dupré's equations.<sup>22</sup> The work of adhesion ( $W_{\text{ps}}$ ) of the resist materials on silicon substrates are summarized in Table II. The work of adhesion of *t*-BOC-protected  $\beta$ -CD is as high as that of the Novolac resist because poly-hydroxyl groups on the surface contribute the multivalent interaction between the resist and the substrate. The work of adhesion of the resist materials decreased linearly as the *t*-BOC

**Table II.** The work of adhesion

Materials	Contact Angle (°)		$W_{\text{ps}}$ (dyne/cm)
	H <sub>2</sub> O	CH <sub>2</sub> I <sub>2</sub>	
A	70.0	44.9	73.3
B	73.5	47.6	71.8
C	73.6	47.1	70.7
D	74.7	49.0	69.7
Novolac	80.8	38.5	73.5

**Table III.** The dry-etching resistances

Materials	The relative dry-etching resistance
<i>t</i> -BOC-protected $\beta$ -CD (B)	1.25
Poly( <i>t</i> -BMA)	1.42
Partially <i>t</i> -BOC protected poly(4-hydroxystyrene)	1.00

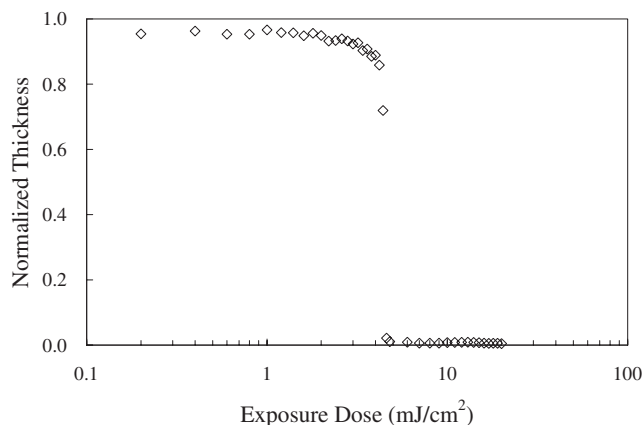
protection ratios of  $\beta$ -CD increased due to hydrophobic nature of *t*-BOC groups.

### Dry-Etching Resistance

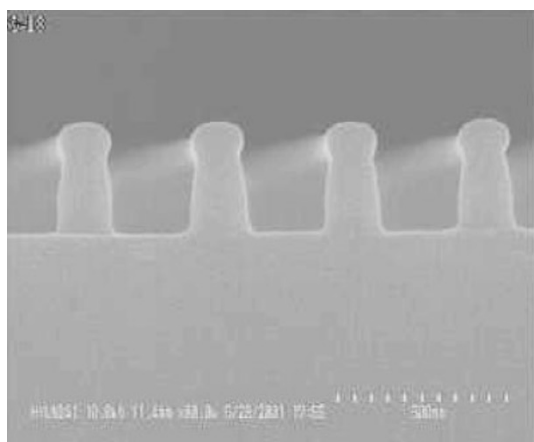
The dry-etching rates of the resist materials formulated with *t*-BOC-protected  $\beta$ -CD, poly(*t*-butyl methacrylate), and partially *t*-BOC protected poly(4-hydroxystyrene) were obtained by measuring the time needed for etching the resist film completely during a CF<sub>4</sub> reactive ion etching process. The CF<sub>4</sub> gas flow rate, RF power, and pressure in the chamber were 30 sccm, 100 W, and 200 mTorr, respectively. Table III shows the relative etching resistances of the resist materials normalized to that of partially *t*-BOC protected poly(4-hydroxystyrene). The dry-etching resistance of the resist material B is better than that of poly(*t*-butyl methacrylate) and comparable to that of partially *t*-BOC protected poly(4-hydroxystyrene). Since  $\beta$ -CD has lot of oxygen in its structure, the dry etching resistance of  $\beta$ -CD was thought to be poor. But in case of *t*-BOC-protected  $\beta$ -CD, owing to its highly compact conical cylindrical structure, the dry-etching resistance was reasonably high.<sup>23–26</sup>

### Lithographic Evaluation

The resist consisting of *t*-BOC-protected  $\beta$ -CD (B) showed high sensitivity of 5.0 mJ/cm<sup>2</sup> and contrast value of 21.0 (Figure 2). The scanning electron micro-



**Figure 2.** The sensitivity curve of *t*-BOC-protected  $\beta$ -CD (B).



**Figure 3.** Scanning electron micrograph of the resist formulated with the material B (Scale bar = 500 nm).

graph of the line and space patterns for the resist, formulated with the material B was shown in Figure 3. The resist patterns of 180 nm feature size were obtained at a dose of 14 mJ/cm<sup>2</sup> with the conventional 2.38 wt % TMAH developer using a KrF excimer laser stepper.

### CONCLUSION

A positive tone molecular resist based on  $\beta$ -CD has been developed. *t*-BOC-protected  $\beta$ -CD has low absorbance at Deep UV region and good film forming property. Using *t*-BOC-protected  $\beta$ -CD, 180 nm patterns were obtained using KrF excimer laser stepper and the conventional TMAH developer. Additional work is underway to obtain sub-100 nm resolution using an ArF lithography tool.

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