Novel Molecular Resist Based on Derivative of Cholic Acid

Jin-Baek Kim,* Hyo-Jin Yun, and Young-Gil Kwon
Department of Chemistry, School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea

(Received May 13, 2002; CL-020407)

Glycerol tris(glutarate 3-(*tert*-butyl cholate) ester) was synthesized as a low molecular weight amorphous resist material for 193-nm lithography, and it has good transmittance at 193 nm and good dry etch resistance to CF_4 reactive ion etching. The resist formulated with this material forms well defined line and space patterns at a dose of 12 mJ cm^{-2} using a mercury-xenone lamp in a contact printing mode.

Amorphous materials are attractive for their excellent processability, flexibility, transparency, inexistence of grain boundaries, etc. Many amorphous polymers are known and have received attention from both fundamental and practical viewpoints. However, little attention has been paid to low molecular weight materials that form stable amorphous glasses above room temperature.

To meet the upcoming demand of next generation lithography, new chemically amplified resist materials should be developed that can perform at the limit where the image feature size is on the order of molecular dimensions. Most of the commercial resists make use of linear polymers as the matrix resins. However, the low molecular weight materials have the advantages over the linear polymers. First, higher resolution is expected due to the smaller molecular size of the low molecular weight resist materials relative to that of linear polymers. Second, since the low molecular weight materials are free of intermolecular chain entanglement, less internal stress will be developed during the lithographic process. Therefore, image distortion due to the stress and entanglement will be reduced during development. And third, since the low molecular weight materials have the exact molecular weights, the segments in all the molecules have the same dissolution property in a developer.[1–3]

We synthesized a flexible core from glycerol and glutaric anhydride.[4] Dry glycerol (0.1 mol), freshly distilled glutaric anhydride (0.3 mol), and a catalytic amount of pyridine were dissolved in dry dioxane (150 ml) and refluxed for 24 h. The product was isolated by evaporation of dioxane and pyridine and was identified spectroscopically as glycerol trisglutarate.[3] The product was then dissolved in an excess amount of thionyl chloride and stirred at room temperature for 2 h. After evaporation of thionyl chloride, the product was flash evaporated three times with dry toluene to remove the remaining thionyl chloride. Glycerol tris(4-chlorocarbonyl-butyrate) (GTCCB) was obtained and was identified spectroscopically.[6] Glycerol tris(glutarate 3-(*tert*-butyl cholate) ester) (GTGTBC) was prepared by the reaction between GTCCB and *tert*-butyl cholate in the presence of triethylamine under a nitrogen atmosphere. *tert*-Butyl cholate was employed because it has good etch resistance and transparency at 193 nm due to its alicyclic structure. The triethylamine salt was removed by filtration and the final product was obtained as a white powder after evaporation of the filtrate.[7]

The synthetic scheme for the preparation of GTGTBC is shown in Figure 1. GTGTBC is confirmd to be amorphous from the X-ray powder diffractions.

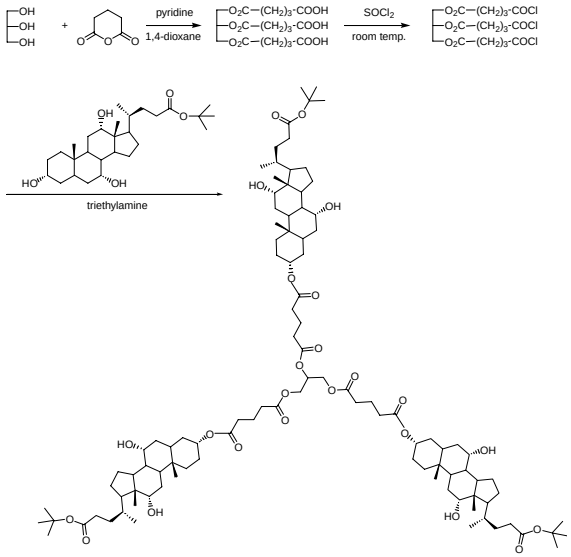

Figure 1. The synthetic scheme for preparation of GTGTBC.

The UV-Vis spectrum of the film of GTGTBC is shown in Figure 2. The absorbance is 0.26 μm^{-1} at 193 nm and this indicates that it is relatively transparent comparing with other polymeric materials used for 193-nm resists.

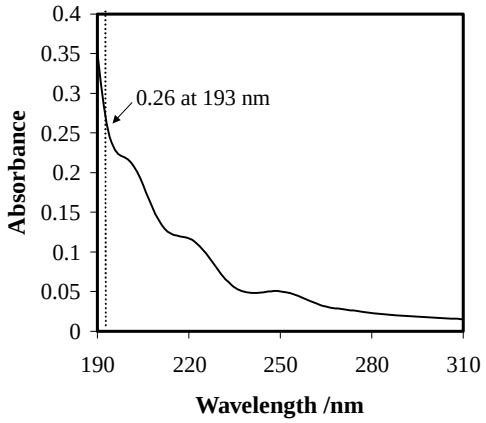

Figure 2. UV-Vis spectrum of GTGTBC.

The dry-etching rate of GTGTBC was obtained by measuring the time needed for etching the resist film completely.[8] As shown in Table 1, the dry etching rate of GTGTBC relative to poly(4-hydroxystyrene) was 1.07 for CF_4 gas and this shows that

Table 1. Etch rate of GTGTBC relative to poly(4-hydroxystyrene)

Run	Materials	Etch Resistance (Å s^{-1})	Etch Rate
1	GTGTBC	11.1	1.07
2	Poly(4-hydroxystyrene)	10.4	1.00

GTGTBC has good dry etching resistance comparable with that of the commercial 248-nm resist.

The sensitivity curve of GTGTBC is shown in Figure 3. The resist solution consists of 1 g of GTGTBC, 0.02 g of triphenylsulfonium triflate (TPSTf) as a photoacid generator (PAG), and 5 g of propylene glycol methyl ether acetate. The solution was filtered through a 0.2 μm filter and spin-coated onto silicon wafers at 1,500 rpm to obtain about 0.5 μm-thick films. The wafers were then cut into small pieces and subsequently exposed to obtain sensitivity curves. Exposures were taken using a Hg-Xe lamp with a contact printing method. The exposed films were baked at 110 °C for 90 s and developed in a 4.1×10^{-3} N tetramethylammonium hydroxide (TMAH) aqueous solution. The photoresist showed a sensitivity of 9.8 mJ cm^{-2} and a contrast of 22.0.

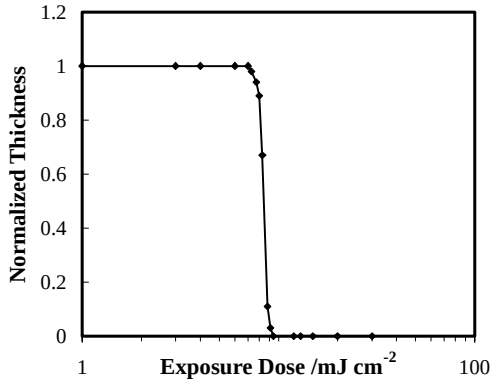

Figure 3. Sensitivity curve of the resist formulated with GTGTBC.

To evaluate the lithographic properties, exposure was carried out with a Hg-Xe lamp at a dose of 12 mJ cm^{-2}. Imagewise exposure through a mask was carried out in a contact-printing mode. The top view profiles were obtained by Hitachi S-8840 SEM (Figure 4).

In conclusion, a new type of chemically amplified photoresist for 193-nm lithography has been prepared based on a novel amorphous organic compound. GTGTBC was synthesized as a low molecular weight amorphous resist material, and it has good transmittance at 193 nm and possesses good dry etch resistance to CF_4 reactive ion etching. The resist formulated with this compound was exposed using Hg-Xe lamp in a contact printing mode, and a well defined line and space patterns were obtained at a dose of 12 mJ cm^{-2}.

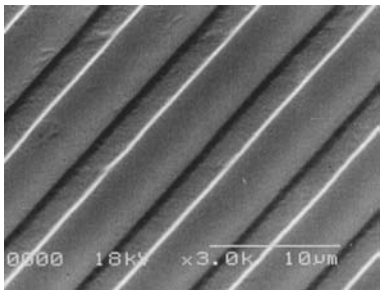

Figure 4. Scanning electron micrograph of positive line and space features with a thickness of 0.5 μm printed with GTGTBC at a dose of 12 mJ cm^{-2}.

The authors would like to acknowledge the financial support of Ministry of Commerce, Industry & Energy, the Center for Advanced Functional Polymers at Korea Advanced Institute of Science and Technology, and Brain Korea 21 (BK21) project.

References and Notes

1 Y. Shirota, *J. Mater. Chem.*, **10**, 1 (2002).
2 Y. G. Kwon, J. B. Kim, T. Fujigaya, Y. Shibasaki, and M. Ueda, *J. Mater. Chem.*, **12**, 53 (2002).
3 K. Takeshi, R. Nakayama, and M. Ueda, *Chem. Lett.*, **1998**, 865.
4 H. R. Kricheldorf and B. Fechner, *Macromolecules*, **34**, 3517 (2001).
5 Glycerol trisglutarate was obtained in a yield of 92% as a viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): 1.95 (6H, m), 2.41 (12H, m), 4.30 (4H, m), 5.27 (1H, m), 10.5 (3H, br. s, -COOH). FT-IR (cm^{-1}): 1739 (C=O of ester), 1711 (C=O of acid).
6 GTCCB was obtained in a yield of 90.5% as a viscous liquid. FT-IR (cm^{-1}): 2952 (aliphatic CH), 1797 (C=O of acyl chloride), 1740 (C=O of ester).
7 GTGTBC was obtained in a yield of 84% as a white powder. ^{1}H-NMR ($CDCl_3$, 300 MHz, TMS): 0.65 (3H, s, 18-methyl), 0.88 (3H, s, 19-methyl), 0.96 (3H, d, $J = 6$ Hz, 21-methyl), 1.01–2.02 (26H, m), 1.41 (9H, s, *tert*-butyl), 3.86 (1H, m), 3.96 (1H, m). FT-IR (cm^{-1}): 3444 (OH), 2938 (aliphatic and alicyclic CH), 1730 (C=O of ester). The glass transition temperature (T_g) of GTGTBC is 84.0 °C. The most conclusive molecular weight of GTGTBC was determined by MALDI-TOF MS spectrometry. The m/z value of GTGTBC appears as a main peak at 1773.57 which corresponds to the calculated value of 1773.83.
8 The dry-etching resistance was determined using a etcher under CF_4 plasma. The CF_4 gas flow rate, RF power, and pressure in chamber were 30 sccm, 100 W and 200mTorr, respectively. The dry-etching rate of resists formulated with GTGTBC and poly(4-hydroxystyrene) were obtained respectively by measuring the time needed for etching the resist film completely during reactive ion etching process.