Novel Electron-Beam Molecular Resists with High Resolution and High Sensitivity for Nanometer Lithography

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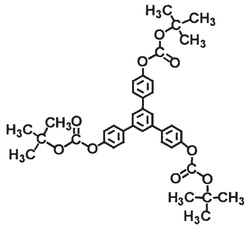
A novel class of chemically-amplified, electron-beam molecular resists for nanometer lithography were created. These molecular resists functioned as positive resists in the presence of an acid generator, exhibiting a high sensitivity of ≈2 μC cm^{-2} and enabling the fabrication of ≈25 nm line patterns.

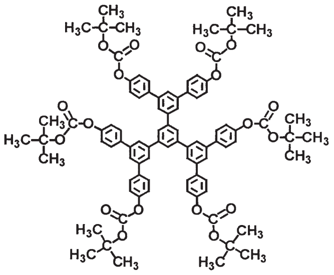
Electronic circuits density in semiconductor devices has become higher year by year, and the minimum feature size required for device fabrication has become smaller. While 1 Gbit DRAMs with a resolution of 130 nm have been produced at present, it is expected that 4 Gbit DRAM chips with a resolution of 65 nm will be fabricated in the near future. Both new lithographic processes and new resist materials for future nanolithography are under investigation. Electron-beam lithography, which enables direct writing of nanometer-scale high-resolution patterns without masks, is expected to be a promising nanolithographic process.

Polymers or composite polymer materials have been used as resist materials owing to their capability of uniform amorphous film formation.[1] Generally, low molecular-weight organic compounds tend to readily crystallize and do not form uniform amorphous films. Since the late 1980s, we have performed a series of studies on the creation of small organic molecules that readily form stable amorphous glasses, which are referred to as amorphous molecular materials.[2] Amorphous molecular materials, which are characterized by well-defined glass-transition temperatures ($T_{\rm gs}$) usually associated with polymers, readily form smooth, uniform amorphous films by themselves by vapor deposition or spin coating from solution. We have proposed a new concept for resist materials, "molecular resists."[3] Molecular resists, namely, amorphous molecular materials with resist properties have advantages over polymer materials in their smaller molecular size and the absence of any molecular-weight distribution. On the basis of this new concept, we have created a few electron-beam molecular resists, e.g., 1,3,5-tris[4-(4-toluenesulfonyloxy)phenyl]benzene (TsOTPB) and 4,4′,4″-tris(allylsuccinimido)triphenylamine (ASITPA). TsOTPB and ASITPA permitted the fabrication of 150–70 nm line patterns on exposure to 50-keV-electron beam; however, the sensitivity of these molecular resists were in the range of mCcm^{-2}.[3]

We report here the creation of a novel class of electron-beam molecular resists with high sensitivity and high resolution and show that molecular resists can be promising candidates for future nanolithography. The created molecular resists are chemically amplified, positive-type molecular resists, 1,3,5-tris(4-*tert*-butoxycarbonyloxyphenyl)benzene (*p*-BCOTPB) and 5′,5‴-bis(*tert*-butoxycarbonyloxy)phenyl-5″-[4,4″-bis(*tert*-butoxycarbonyloxy)-1,1′:3′,1″-terphenyl-5′-yl]-1,1′:3′,1″:3″,1‴:3‴,1⁗-quinquephenyl (BCOQP).



p-BCOTPB



BCOQP

p-BCOTPB and BCOQP were synthesized by the reaction of pyrocarbonic acid di-*tert*-butyl dicarbonate with 1,3,5-tris(4-hydroxyphenyl)benzene (HOTPB) and 5′,5‴-dihydroxyphenyl-5″-(4,4″-dihydroxy-1,1′:3′,1″-terphenyl-5′-yl)-1,1′:3′,1″:3″,1‴:3‴,1⁗-quinquephenyl (HOQP), respectively, in the presence of K_2CO_3 and 18-crown-6 in tetrahydrofuran (THF). HOTPB and HOQP were synthesized by the hydrolysis of the corresponding methoxy-substituted compounds, 1,3,5-tris(4-methoxyphenyl)benzene (*p*-MeOTPB) and 5′,5‴-dimethoxyphenyl-5″-(4,4″-dimethoxy-1,1′:3′,1″-terphenyl-5′-yl)-1,1′:3′,1″-3″,1‴:3‴,1⁗-quinquephenyl (MeOQP), with hydrobromic acid in acetic acid. *p*-MeOTPB was prepared by the acid-catalyzed condensation reaction of 4-methoxyacetophenone in the presence of trifluoromethanesulfonic acid in toluene. MeOQP was synthesized by the Suzuki coupling reaction of 1,3,5-tris(3,5-dibromophenyl)benzene with 4-methoxyphenylbononic acid in the presence of tetrakis(triphenylphosphine)palladium(0) catalyst in THF/2N K_2CO_3 (aq). These new compounds were identified by mass spectrometry, FT-IR, ^{1}H and ^{13}C NMR spectroscopic methods, and elemental analysis.[4]

While *p*-BCOTPB was obtained as polycrystals by recrystallization from mixed solvents of THF/ethanol, BCOQP was obtained as an amorphous glass despite attempted recrystallization from solution. *p*-BCOTPB readily formed an amorphous glass when the melt sample was cooled on standing in air. The formation of the amorphous glasses was confirmed by differential scanning calorimetry (DSC), polarizing light microscopy and X-ray diffraction. The $T_{\rm gs}$ of *p*-BCOTPB and BCOQP were 67 and 139 °C, respectively, as determined by DSC.

p-BCOTPB and BCOQP readily formed uniform, amorphous films by spin coating from solution. The films of *p*-BCOTPB and BCOQP containing a 5 wt % acid generator, diphenyliodonium triflate (DPI), were prepared by spin coating from THF solution onto a silicon wafer. Thickness of the films was ca. 0.2 μm. These spin-coated films were prebaked at 30–55 °C for 2 min for *p*-BCOTPB and at 60–100 °C for 1 min for BCOQP, and then irradiated with a focussed electron-beam by the use of a scanning electron microscope (SEM) at 50 keV. The irradiated *p*-BCOTPB film was developed with mixed solvents of tetramethylammonium hydroxide (TMAH):isopropyl alcohol (IPA) = 30:7 (v/v) for 120 s, rinsed with deionized water, and air-dried. The irradiated film of BCOQP was post-baked at 100–120 °C for 0–120 s, and then developed with mixed solvents of TMAH:IPA = 30:6 (v/v) for 60 s, rinsed with deionized water, and air-dried.

The synthesized materials functioned as positive-type resists. That is, the exposed area of the resist films became soluble in the developer solvent described above. It is thought that the solubility change caused by electron-beam irradiation in the presence of DPI resulted from the transformation of the *tert*-butoxycarbonyloxy group in *p*-BCOTPB and BCOQP to the hydroxy group. The resulting hydroxy-substituted compounds are soluble in the developer solvent. The transformation of the *tert*-butoxycarbonyloxy group to the OH group in *p*-BCOTPB was confirmed by FT-IR spectroscopy.

The *p*-BCOTPB resist film exhibited a sensitivity of 4.4 μCcm^{-2} on exposure to 50-keV-electron beam. BCOQP with a higher T_g than that of *p*-BCOTPB permitted post-exposure bake at 100 °C, and showed higher sensitivity and higher resolution than *p*-BCOTPB. While the sensitivity without any post-exposure bake process was ca. 10 μC cm^{-2}, the sensitivity increased with the increasing post-exposure bake time, giving 2 μC cm^{-2} after the bake treatment for 120 s, as shown in Figure 1. It has been reported that the post-exposure bake process usually enhances sensitivity, since the diffusion of Brønsted acid generated by the chemical transformation of the *tert*-butoxycarbonyloxy group to the hydroxy group, which is accompanied by the formation of isobutene, carbon dioxide, and proton, is thermally assisted.[5] The sensitivities obtained for the present chemically-amplified molecular resists, *p*-BCOTPB and BCOQP, well meet the requirements of practical use as electron-beam resist materials.

Figure 2 shows the SEM image of a positive-tone line pattern obtained for the BCOQP resist film containing DPI as an acid generator on exposure to a 50-keV-electron beam. *p*-BCOTPB and BCOQP permitted the fabrication of line patterns of 40 and 25 nm, respectively. These sensitivity and resolution results show that molecular resists can be promising candidates for electron-beam resist materials for future nanolithography.

In summary, a novel class of chemically amplified, electron-beam molecular resists for nanometer lithography, *p*-BCOTPB, and BCOQP, were designed and synthesized. They were found to readily form stable amorphous glasses with well-defined T_{gs} and to form uniform amorphous films by themselves by spin coating from solution. They functioned as positive-type electron-beam resists in the presence of an acid generator such as DPI. The BCOQP molecular resist was found to exhibit a high sensitivity of 2 μC cm^{-2}, enabling the fabrication of 25 nm line patterns on exposure to 50-keV-electron beam. The present study shows a new paradigm for resist materials for future nanolithography, paving the way for further development of molecular resists.

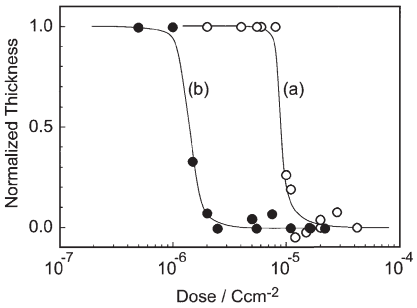


Figure 1. Sensitivity curves of BCOQP resist films containing 5 wt % of DPI. (a) without the post-exposure bake process. (b) with the post-exposure bake process at 100 °C for 120 s.

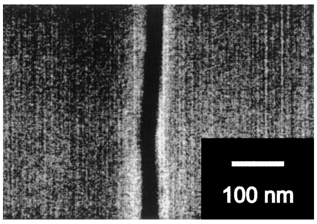


Figure 2. SEM image of a positive tone line pattern obtained for BCOQP resist film containing 5 wt % of DPI on exposure to a 50-keV-electron beam at 66 μCcm^{-2}. Post-exposure bake treatment was carried out at 100 °C for 90 s.

References and Notes

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4 ***p*-BCOTPB**: Yield: 18%. mp: 100 °C. Mass (FAB): *m/z* 655 (MH^+). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.70 (3H, s), 7.66 (6H, d), 7.28 (6H, d), 1.59 (27H, s). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 151.9, 150.8, 141.6, 138.6, 128.3, 125.1, 121.7, 83.7, 27.7. FT-IR (KBr, cm^{-1}): 3033, 2981, 2934, 1759, 1606, 1509, 1371, 1279, 1221, 1147, 1014, 885, 834. Anal. Calcd for $C_{39}H_{42}O_9$: C, 71.54; H, 6.47; O, 21.99. Found: C, 71.52; H, 6.47%. **BCOQP**: Yield: 54%. Mass (FAB): *m/z* 1460 (MH^+) ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.95 (3H, s), 7.85 (6H, d), 7.76 (3H, t), 7.70 (12H, d), 7.28 (12H, d), 1.58 (54H, s). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 152.3, 151.3, 143.1, 142.7, 142.3, 139.1, 128.9, 128.8, 126.4, 126.0, 125.4, 122.2, 84.2, 28.2. FT-IR (KBr, cm^{-1}): 3033, 2980, 2931, 1760, 1592, 1510, 1371, 1279, 1224, 1149, 1016, 891, 836. Anal. Calcd for $C_{90}H_{90}O_{18}$: C, 74.06; H, 6.21; O, 19.73. Found: C, 73.96; H, 6.33%.

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