Silicon-containing Bilayer Resist Based on a Single Component Nonchemically Amplified Resist System

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A photobleachable bilayer resist material based on a nonchemically amplified resist system was synthesized by copolymerization of 3-methacryloxypropyl trimethoxysilane, 2-(2-diazo-3-oxobutyryloxy)ethyl methacrylate, and γ-butyrolactonyl methacrylate. Upon UV irradiation, the resist film in the exposed region become insoluble in organic solvent by the reaction of methoxysilanes with carboxylic acids generated by photoinduced reaction of diazoketo groups. The initial lithographic evaluation of the resist showed the potential of this system for the next generation resist.

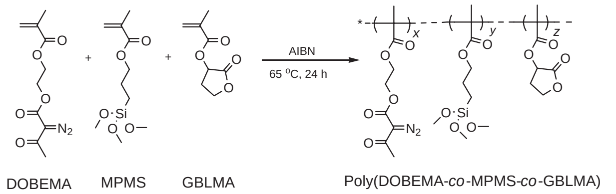

Figure 1. The synthetic scheme of poly(DOBEMA-*co*-MPMS-*co*-GBLMA).

In conventional microlithography, positive and negative photoresist systems based on chemical amplification (CA) are well established for various industrial fields including the production of integrated circuits. However, common CA resists suffer from serious problems such as T-top and line width shift caused by air-borne contamination and acid diffusion in the resist films when the post-exposure bake is delayed.[1,2] To solve these PED problems, positive-tone of nonchemically amplified resists containing photoactive diazoketo groups showed potential solutions to the PED problems,[3–5] though their sensitivities were relatively low. Therefore, new type of highly sensitive nonchemically amplified resist system should be developed.

Silicon-containing photolithographic materials are gaining increasing interests to be used as an imaging layer of a bilayer system.[4–7] Here we synthesized a new silicon-containing resist material which is processable without photoacid generator and induces both photobleaching in the deep UV regions and solubility change upon exposure. Acid-sensitive trimethoxysilanes and photoactive diazoketo groups which produce carboxy groups photochemically were selected to provide desired solvent resistance upon exposure.

All polymers were prepared by free radical polymerization in sealed ampoules. 3-Methacryloxypropyl trimethoxysilane (MPMS), 2-(2-diazo-3-oxobutyryloxy)ethyl methacrylate (DOBEMA),[3] γ-butyrolactonyl methacrylate (GBLMA), and 2 mol % AIBN were dissolved in THF, and the resulting mixture was heated at 65 °C for 6 h. After the polymerization, the solutions were diluted with THF and poured into petroleum ether to separate the product. The precipitated polymers were collected by filtration and washed with the precipitating solvent. After drying under vacuum for 24 h, white powdery materials were obtained. The overall scheme for the synthesis of the polymer is given in Figure 1. The results of copolymerization of MPMS, DOBEMA, and GBLMA with various compositions are summarized in Table 1. The number-average molecular weights of polymers were in the range of 3818–4247 and the polydispersity indices were 3.1–3.4. The polymerization yields were 66–72%.

First of all, the photoinduced reaction of resist material was studied using ^{1}H NMR spectroscopy of the corresponding active monomers, DOBEMA and MPMS. Upon exposure, the methyl proton peaks of the diazoketo groups at 2.3 ppm and the proton peak of methoxysilane groups at 3.4 ppm were reduced as shown in Figure 2. On the other hand, the protons neighboring the ester and carboxy groups newly appeared at 3.3 and 1.3 ppm. From these results, the solubility change of the resist film in the exposed region is attributed to the reaction of methoxysilanes with carboxy groups generated by photoinduced reaction of diazoketo groups in the presence of moisture, since the methoxysilanes can form covalent Si–O–CO links with COOH groups.[8]

The photobleaching degree of the polymer was calculated by measuring the absorbance coefficient values of spin-coated polymer film on quartz disk before and after UV irradiation. Figure 3 shows the UV absorption spectra of polymer B, measured on a 1-μm thick film before and after 200 and 400 mJ cm^{-2} irradiation. The absorbance decreased by 90.1% at 248 nm and 65.8% at 193 nm after 400 mJ cm^{-2} irradiation.

The oxygen reactive ion etching (O$_2$-RIE) rate was obtained by measuring the remaining thickness of polymer film after a certain time of the reactive ion etching process,[9] which is essential for a resist material to be used as a bilayer resist.

Table 1. Radical polymerization of DOBEMA, MPMS, and GBLMA

Polymer	Monomer feed ratio DOBEMA:MPMS:GBLMA	Copolymer composition[a] DOBEMA:MPMS:GBLMA	Yield /%	M_n[b]	MWD[b]
A	50:0:50	52:0:48	69	4065	3.4
B	30:40:30	30:41:29	72	4247	3.1
C	30:50:20	29:49:23	66	3818	3.2

[a]Determined by integration of the corresponding peaks in the ^{1}H NMR spectra. [b]Measured by GPC using THF as eluent and polystyrene as standard.

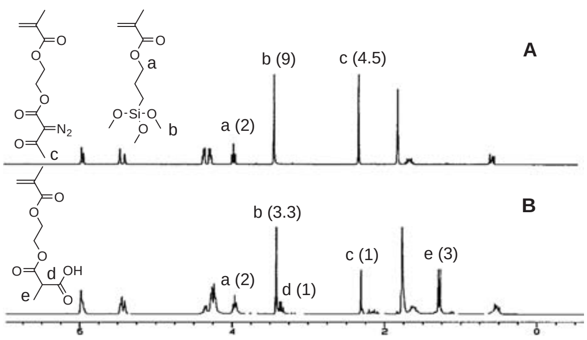

Figure 2. ^{1}H NMR spectral change of DOBEMA and MPMS (A) before exposure (B) after UV flood exposure (dose = 400 mJ cm^{-2}). Integrated values of assigned peaks are shown in brackets.

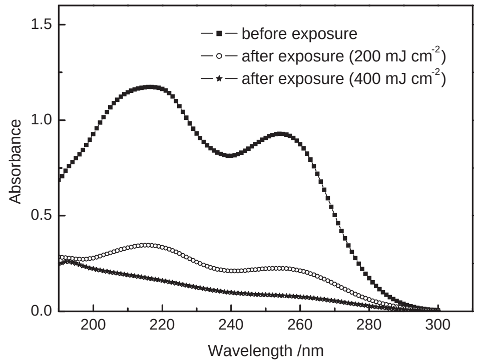

Figure 3. UV absorption spectra of polymer B before and after UV exposure.

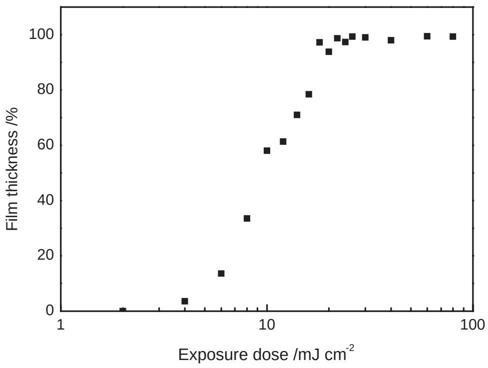

Figure 4. Film thickness of polymer B after development in cyclopentanone as a function of exposure dose.

Table 2. The results of oxygen reactive ion etching

Polymer	Before RIE /Å	After RIE /Å	Time /s
A	2574	0 (0.0%)	38
B	3519	597 (16.9%)	300
C	3418	643 (18.8%)	300
Novolac	6492	0 (0.0%)	113

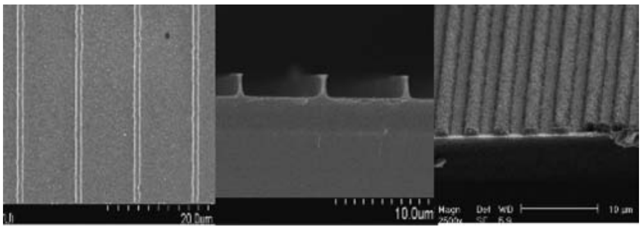

Figure 5. Scanning electron micrograph of line and space negative tone image formed with polymer B at a dose of 17 mJ cm^{-2} as a bilayer resist after O_2 plasma etching.

Table 2 shows the results of O_2-RIE of polymers and novolac resin (planarizing bottom layer). Polymer A and novolac resin that contain no silicon were completely etched, whereas the remaining thicknesses of B and C were 16.9 and 18.8% of their initial thicknesses after O_2-RIE for 300 s.

The film thickness of polymer B after development in cyclopentanone as a function of exposure dose is shown in Figure 4. The polymer film becomes insoluble in organic solvent after about 13 mJ cm^{-2} of irradiation. This result shows much improved sensitivity as a non-CA resist compared to the reported results.[3,4] For the lithographic evaluation, the planarizing layer was formed by spin coating of the novolac resist solution onto a silicon wafer. Flood exposure of deep UV light was carried out on a deep UV exposure system with a high-pressure mercury–xenon lamp over the planarizing layer, which was further hard baked at 200 °C for 10 min. Then, a film of 0.25-μm thickness was formed from 10 wt % resist solution of polymer B in cyclopentanone over a planarizing layer of 1.5-μm thickness. Exposure (dose = 17 mJ cm^{-2}) was carried out using a Hg-Xe lamp in a contact printing mode and the unexposed regions were developed with cyclopentanone. The wet-developed pattern of the imaging layer was anisotropically transferred to the underlying planarizing layer by O_2 plasma. Figure 5 shows the scanning electron micrograph of the line and space negative tone image formed with polymer B as an imaging layer in bilayer system after O_2 plasma etching.

In conclusion, a novel silicon-containing bilayer resist based on a non-CA system was successfully synthesized, which does not need the addition of photoacid generator and post-exposure baking, thereby eliminating post-exposure delay problems. The results show this new platform has the potential for the next generation resists, although further lithographic evaluation is necessary. The initial lithographic studies have shown the feasibility of this system to be used as a bilayer resist.

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References and Notes

1 P. I. Tattersall, D. Breslin, S. M. Grayson, W. H. Heath, K. Lou, C. L. McAdams, D. McKean, B. M. Rathsack, C. G. Willson, *Chem. Mater.* **2004**, *16*, 1770.
2 E. Reichmanis, L. Thompson, *Chem. Rev.* **1989**, *89*, 1273.
3 J.-B. Kim, K.-S. Kim, *Macromol. Rapid Commun.* **2005**, *26*, 1412.
4 J.-B. Kim, R. Ganesan, J.-H. Choi, H.-J. Yun, Y.-G. Kwon, K.-S. Kim, T.-H. Oh, *J. Mater. Chem.* **2006**, *16*, 3448.
5 R. Ganesan, S.-K. Youn, J.-B. Kim, *Macromol. Rapid Commun.* **2008**, *29*, 437.
6 E. Tegou, V. Bellas, E. Gogolides, P. Argitis, *Microelectron. Eng.* **2004**, *73–74*, 238.
7 H. Wu, Y. Hu, K. E. Gonsalves, M. Yakaman, *J. Vac. Sci. Technol., B* **2001**, *19*, 851.
8 D. Gan, S. Lu, Z. Wang, *J. Macromol. Sci., Pure Appl. Chem.* **2001**, *38*, 699.
9 The O_2 gas flow rate, RF power, and pressure in chamber were 30 sccm, 100 W, 200 mTorr, respectively.

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