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Poly(2-trimethylsilyl-2-propyl methacrylate-co-γ-butyrolactone-2-yl methacrylate) for ArF lithography

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Abstract

Poly(2-trimethylsilyl-2-propyl methacrylate-co-γ-butyrolactone-2-yl methacrylate) was synthesized and evaluated as a chemically amplified resist for ArF lithography. The polymer has excellent transmittance at 248 nm and also has a good transmittance at 193 nm. In addition, the polymer possesses good thermal stability up to 200°C, whereas in the presence of an acid the cleavage of the 2-trimethylsilyl-2-propyl ester group begins at about 80°C in a catalytic manner. Patterns of 0.24 μm line/space were obtained with a conventional developer, 2.38 wt.% tetramethylammonium hydroxide aqueous solution, using an ArF excimer laser exposure system.

Keywords: ArF lithography; Chemically amplified resist; Silicon-containing polymer

1. Introduction

The design of positive 193 nm resists is a significant challenge. This emerging field has advanced remarkably in the past few years as a result of the efforts of resist designers around the world [1]. The majority of recently published works on 193 nm resists involves the design of new etch resistant polymers, focusing on the new backbone polymer chemistry [2], alicyclic pendant groups [3] and acid labile protecting groups [4,5]. There are various acid labile protecting groups of the matrix polymer for chemically amplified resists (CARs) [6]. *tert*-Butyl ester, tetrahydropyranyl ether, and tetrahydrofuranyl ether are well-known protecting groups of the matrix polymer for 193 nm CARs. We proposed a new silicon-containing protecting group, 2-trimethylsilyl-2-propyl (TMSP) ester, for a dry-developable CAR [7,8]. However, poly(TMSPMA) has a relatively low glass transition temperature and poor adhesion on a silicon wafer.

In this article, we synthesized a new matrix polymer, poly(2-trimethylsilyl-2-propyl methacrylate-co-γ-butyrolactone-2-yl methacrylate) (poly(TMSPMA-co-GBLMA)), for ArF lithography. TMSP ester groups were introduced as acid labile protecting groups into the methacrylate polymer, which is transparent in the deep ultra-violet (UV) region. γ-Butyrolactone-2-yl methacrylate (GBLMA) was introduced to increase the glass transition temperature and adhesion of the polymer. The work of adhesion of poly(TMSPMA-co-GBLMA) was measured. Upon exposure and post-exposure bake (PEB), the silicon-containing protective groups were effectively removed. The cleavage reaction resulted in disappearance of the TMSP group and formation of the carboxylic acid functionality in the copolymer. Therefore the resist could be developed by a conventional developer, 2.38 wt.% tetramethylammonium hydroxide (TMAH) solution. This article also describes the lithographic performance of the copolymer.

2. Experimental

2.1. Materials

2-Trimethylsilyl-2-propyl methacrylate (TMSPMA) was prepared using our previously published method [7]. GBLMA was synthesized as described in a publication [9]. Methacryloyl chloride and 2-hydroxy-γ-butyrolactone were purchased from Aldrich Chemical Company and used without further purification. The onium salt, di(4-*t*-butylphenyl)

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Fig. 1. Polymerization scheme.

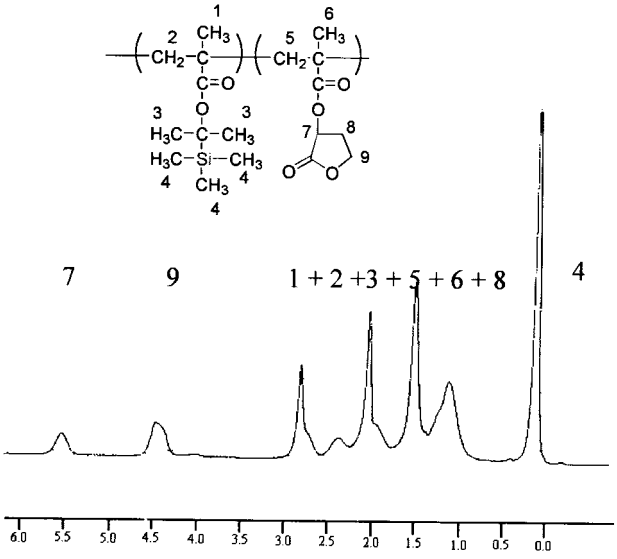


Fig. 2. ^{1}H NMR spectra of poly(TMSPMA$_{0.5}$-co-GBLMA$_{0.5}$).

iodonium perfluorobutanesulfonate (DTBPIPFBS), was given by Midori Kagaku Co., Ltd. 2,2′-Azobisisobutyronitrile (AIBN) which was purchased from TCI Co., was recrystallized in ethanol. APEX-E poly(vinyl phenol)-based resist (Shipley) and PFI-58B2 i-line resist (Sumitomo Chemical Company) were used as reference materials in measuring contact angles.

2.2. Measurements

Proton NMR spectra were recorded in deuterated chloroform using a Varian model 2000 spectrometer equipped with a Fourier transform accessory. Infrared spectra were recorded on a Bio-Rad FTS-165 spectrometer. UV spectra were recorded on a Shimadzu UV-240 spectrophotometer.

Table 1
Radical polymerization (carried out at 70°C).of TMSPMA and GBLMA

Molar feed ratio[a]	Composition[b]	AIBN[c] (mol%)	M/S[d]	Time (h)	Yield (%)	M_n	M_w/M_n	T_g (°C)
10/0	10.0/0.0	1	1	24	65	29 840	1.92	117
8/2	7.6/2.4	10	2	17	40	11 800	1.58	123
6/4	5.3/4.7	1	1	48	85	34 000	2.04	137
5/5	4.9/5.1	1	1	20	82	34 980	2.10	150
5/5	5.0/5.0	10	2	17	51	13 100	1.67	145
4/6	4.1/5.9	10	2	17	57	12 600	1.87	159
3/7	3.1/6.9	10	2	17	60	10 000	2.21	175
2/8	2.3/7.7	10	2	17	63	11 400	2.12	—[e]

[a] Mol% of TMSPMA/mol% of GBLMA in the feed mixture.
[b] Mol% of TMSPMA/mol% of GBLMA in the polymer.
[c] Mol% of AIBN based on the total amount of monomers.
[d] The ratio of the weight of monomer to the volume of solvent.
[e] was not measured below 200°C, onset temperature of TMSP cleavage.

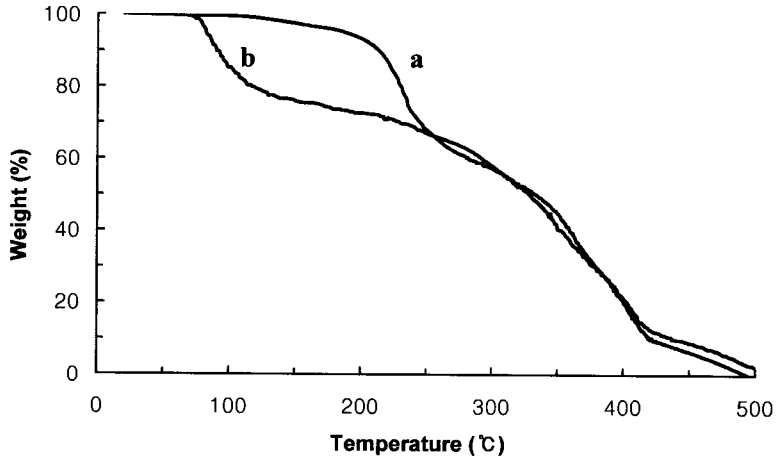


Fig. 3. Comparison of TGA thermograms of poly(TMSPMA$_{0.5}$-co-GBLMA$_{0.5}$) containing 1.5 wt.% of DTBPIPFS (a) before UV exposure of 20 mJ/cm^2 and (b).

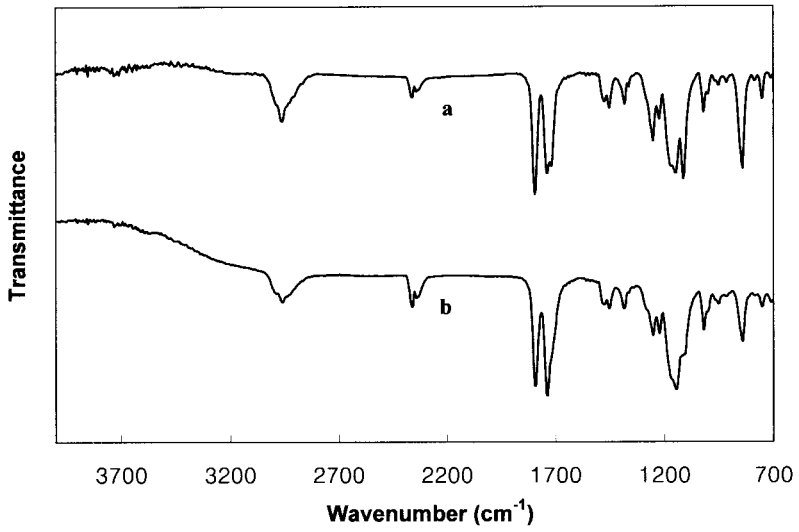


Fig. 4. IR spectral change of the resist containing poly(TMSPMA$_{0.5}$-co-GBLMA$_{0.5}$) and 1.5 wt.% of DTBPIPFS (a) before exposure and (b) after exposure and PEB (exposure and PEB conditions: 20 mJ/cm^2, 120°C for 90 s).

The number-average molecular weights and polydispersities were determined in tetrahydrofuran by a Waters GPC-150C calibrated with polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained on a Perkin–Elmer 7 series thermal analysis system. Contact angles were measured with the Krüss G2/G40 contact angle measuring system. Exposures were performed by a ArF stepper (ISI, NA = 0.6).

2.3. Preparation of poly(2-trimethylsilyl-2-propyl methacrylate-co-γ-butyrolactone-2-yl methacrylate) (poly(TMSPMA-co-GBLMA))

A solution of TMSPMA and GBLMA in benzene or dioxane that contained AIBN was heated at 70°C in vacuo in a sealed ampoule. The polymer was precipitated in fresh methyl alcohol and dried under reduced pressure at 40°C.

2.4. Optical density and work of adhesion

Resist solutions were prepared by dissolving each matrix polymer (14 wt.%) in propylene glycol methyl ether acetate (PGMEA) or cyclohexanone. The resist solutions were filtered through a 0.2 μm millipore filter and spin-coated at 2500–3500 rpm to obtain about 1 μm-thick films on quartz plates for UV spectroscopy.

The work of adhesion value of a polymer on a silicon substrate was calculated using formulas with contact angles of water and methylene iodide on the polymer film and the substrate as set forth by Owens' [10], Young's [11], and Dupré's equations.

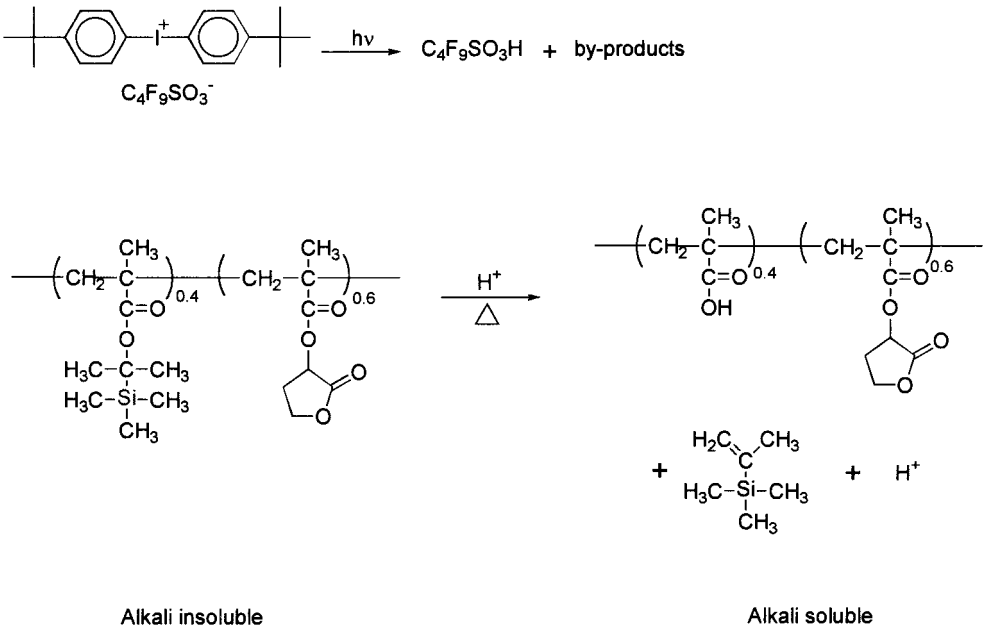


Fig. 5. Acid catalyzed deprotection of poly(TMSPMA-co-GBLMA).

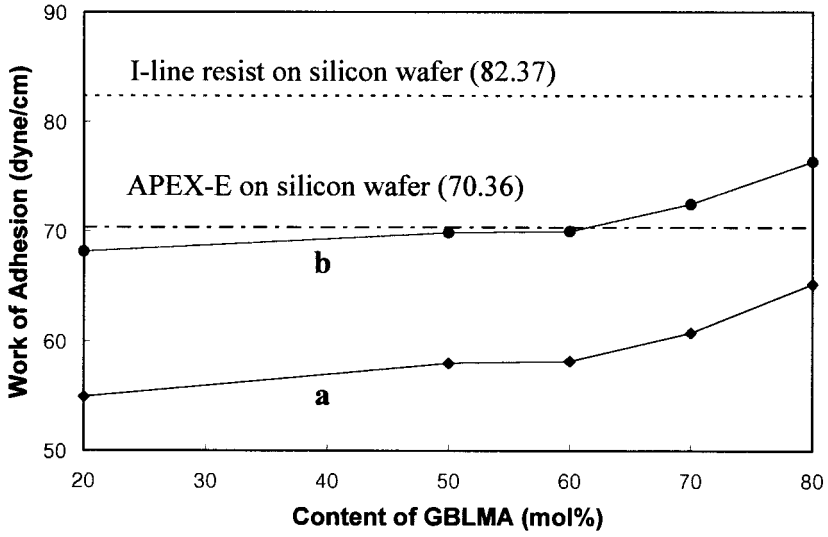


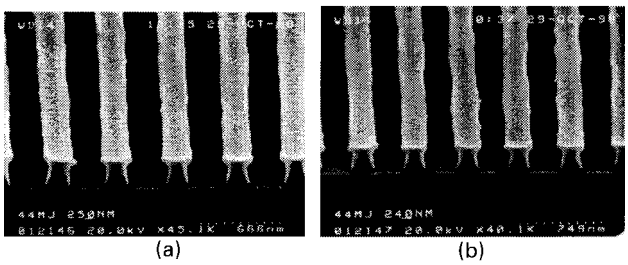
Fig. 6. Works of adhesion of poly(TMSPMA-co-GBLMA) (a) on a silicon wafer and (b) on a i-line resist film (PFI-58B2).

2.5. Lithographic evaluation

Resist solutions were prepared by dissolving poly(-TMSPMA$_{0.4}$-co-GBLMA$_{0.6}$) ($\sim$ 10 wt.%) in cyclohexanone. DTBPIPFBS (1.5 wt.% based on the polymer) was also mixed with the solutions as a photoacid generator. The resist solutions were filtered through a 0.2 μm millipore filter and spin-coated on silicon wafers for the lithographic evaluation. The resist films were prebaked at 120°C for 1 min to remove residual solvent, and exposed to deep UV by a ArF stepper (ISI, NA = 0.6). After exposure, the wafers were baked at 120°C for 90 s and developed in a 2.38 wt.% TMAH solution.

3. Results and discussion

Poly(TMSPMA-co-GBLMA) was prepared by free radical solution polymerization as shown in Fig. 1. The GBLMA was introduced to increase the adhesion property and glass transition temperature (T_g) of the matrix polymer. The polymerization results are shown in Table 1. The compositions in the copolymers were calculated from the proton NMR spectra of the copolymer. The protons of trimethylsilyl and γ-butyrolactone groups were clearly separated as shown in Fig. 2. The composition of the copolymer is almost the same as the feed ratio. The number average molecular weights of the poly(TMSPMA-co-GBLMA) were in the range of



(a) (b)

Fig. 7. SEM image of (a) 0.25 μm and (b) 0.24 μm line/space patterns printed with poly(TMSPMA$_{0.4}$-co-GBLMA$_{0.6}$) using a ArF exposure system (ISI, NA = 0.6) at 44 mJ/cm^2.

10 000–35 000 and the polydispersities were 1.58–2.21. The glass transition temperature (T_g) of the copolymer increases as the content of GBLMA increases.

The TGA curve of poly(TMSPMA$_{0.5}$-co-GBLMA$_{0.5}$) shown in Fig. 3(a) indicates that the polymer possesses good thermal stability up to 200°C. In the presence of photogenerated acid, cleavage of 2-trimethylsilyl-2-propyl groups is found to begin around 80°C as indicated in Fig. 3(b). The thermal deprotection of the 2-trimethylsilyl-2-propyl groups resulted in almost the same weight loss of 30 wt.% with or without acid, which corresponds to the theoretically calculated weight loss because of the evolution of 2,2,3-trimethyl-2-silabut-3-ene. Fig. 4 shows that the cleavage reaction resulted in disappearance of 2-trimethylsilyl-2-propyl groups and formation of the carboxylic acid functionality in the polymer. The Si–C stretching band at 840 cm^{-1} and the ester C–O–C band at 1110 cm^{-1} of TMSPMA moiety disappeared, and the O–H stretching band of carboxylic acid appeared at 3000–3600 cm^{-1} after exposure (dose = 20 mJ/cm^2) and post-exposure bake. The deprotection route is shown in Fig. 5. The solubility of the polymer in an alkaline aqueous developer changes significantly after exposure and bake.

UV absorbances of poly(TMSPMA-co-GBLMA) at 193 nm and 248 nm were shown in Table 2. The polymer has a relatively low absorbance at 193 nm and therefore it can be used in resists for ArF excimer laser lithography.

Works of adhesion of polymers on silicon substrates (W_{ps}) were calculated from the measured contact angles of water and CH_2I_2, and plotted in Fig. 6. Although the adhesion increased with the increase of GBLMA content, the work of adhesion of poly(TMSPMA-co-GBLMA) was somewhat lower than that of the APEX-E poly (vinyl phenol)-based resist. The work of adhesion of poly(TMSPMA$_{0.5}$-co-GBLMA$_{0.5}$) on the PFI-58B2 i-line resist film (Fig. 6(b)) was similar to that of the APEX-E resist on a silicon wafer. Therefore it is considered that poly(TMSPMA$_{0.5}$-co-GBLMA$_{0.5}$) has enough adhesion to be applied as an imaging layer of a bilayer resist system.

Table 2
UV absorbances of polymers

Polymer	Absorbance (μm^{-1})	
	At 193 nm	At 248 nm
Poly(TMSPMA)	0.41	0.069
Poly(TMSPMA$_{0.5}$-co-GBLMA$_{0.5}$)	0.44	0.043
Poly(TMSPMA$_{0.4}$-co-GBLMA$_{0.6}$)	0.46	0.041

Evaluation was performed on the poly(TMSPMA$_{0.4}$-co-GBLMA$_{0.6}$) based resist. The sensitivity of the resist was 15 mJ/cm^2 with PEB at 120°C for 90 s. Patterns of 0.24 μm line/space were resolved at 44 mJ/cm^2 exposure by a ArF stepper (ISI, NA = 0.6) using a conventional 2.38 wt.% TMAH solution (Fig. 7). As the silicon content difference is introduced by wet development, we expect that the resist be applicable to the imaging layer of the conventional bilayer resist system.

Lithographic evaluation of this polymer as a dry developable resist system is in progress, and the results will be published.

Acknowledgements

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