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Synthesis of poly(2-trimethylsilyl-2-propyl methacrylate) and their application as a dry-developable chemically amplified photoresist

Jin-Baek Kim*, Hyunwoo Kim, Jae-Hak Choi

Department of Advanced Materials Engineering, Korea Advanced Institute of Science and Technology, PO Box. 201, Cheongryang, Seoul 130-650, South Korea

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Abstract

Poly(2-trimethylsilyl-2-propyl methacrylate) was synthesized and evaluated as a potential dry-developable chemically amplified photoresist. The deprotection of 2-trimethylsilyl-2-propyl group of the polymer takes place in the exposed region after post-exposure bake. The difference of silicon content between the unexposed region and exposed regions is large enough to form patterns using oxygen reactive-ion etching. The etching selectivity of the unexposed region to the exposed region was 142. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Dry-developable resist; Chemically amplified resist; Silicon containing polymer

1. Introduction

Today chemically amplified resists (CARs), operating at 248 nm and 193 nm, are accepted by microelectronics device manufacturers for the production of 256 Mbit and 1 Gbit DRAMs, because of their high transparency and sensitivity [1]–[4]. However, there is a problem in the conventional CAR systems: resist pattern collapse during the resist development process. Resist pattern collapse occurs while the rinse liquid is being dried off [5]. The source of resist pattern collapse is the surface tension of the rinse liquid. The force increases with decreasing space width between resist patterns [5], [6]. To avoid the resist pattern collapse problem, dry-developable resist systems, such as trilayer resists, silicon-containing resists, and top surface imaging process were proposed, which were developed anisotropically with oxygen plasma. However, the trilayer resists process and the top surface imaging process are cumbersome. There are a significant number of processing steps, and large capital investment is required. Conventional silicon-containing resists that require wet developing of imaging layer have poor sensitivities and resolutions.

Here, we propose a new photoresist system, which can be developed only by reactive-ion etching, without any wet development or silylation step. 2-Trimethylsilyl-2-propyl groups were introduced as acid labile protective groups into the methacrylate polymer, which is transparent in the deep ultra-violet (u.v.) region. Upon exposure and post-exposure bake (PEB), the silicon-containing labile groups will be removed. Therefore, the resist can be dry-developed utilizing the silicon content difference between the exposed and unexposed regions.

2. Experimental

2.1. Materials

Acetyl trimethylsilane, methyllithium, and *n*-butyllithium were purchased from Aldrich Chemical Company and used without further purification. Methacryloyl chloride was purchased from Aldrich Chemical Company and distilled prior to use. The onium salt, triphenylsulfonium trifluoromethanesulfonate (TPSTFMS), was prepared as described in several publications [7]–[9]. 2,2′-Azobisisobutyronitrile (AIBN), which was purchased from TCI Co., was recrystallized in ethanol.

2.2. Measurements

Proton and carbon nuclear magnetic resonance (n.m.r.) spectra were recorded in deuterated chloroform using a Varian model 2000 spectrometer equipped with a Fourier transform accessory. Chemical shifts were measured relative to the residual proton signal of the deuterated solvent and were reported in parts per million from tetramethylsilane. Infra-red

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* Corresponding author. Tel.: +82-2-958-3514; Fax: +82-2-958-3504

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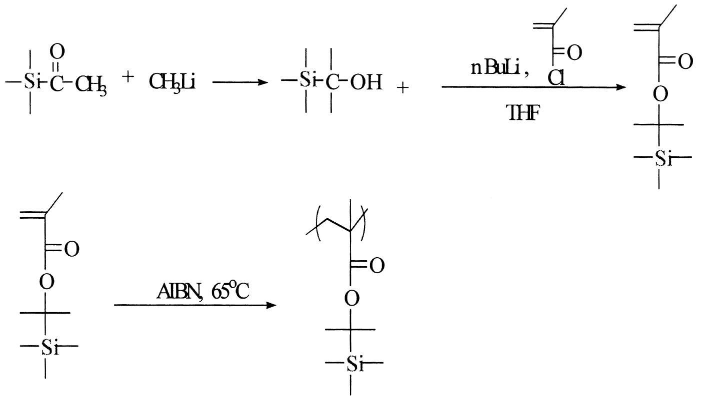

Fig. 1. Synthesis of 2-trimethylsilyl-2-propyl methacrylate and polymerization.

(i.r.) spectra were recorded on a Bio-Rad FTS-165 spectrometer. U.v. spectra were recorded on a Shimadzu UV-240 spectrophotometer. The number-average molecular weights and polydispersities were determined in tetrahydrofuran (THF) by a Waters GPC-150C calibrated with polystyrene standards. Thermogravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.) data were obtained on a Perkin Elmer 7 series thermal analysis system. T.g.a. and d.s.c. measurements were made at heating rates of 10°C min^{-1} and 20°C min^{-1}, respectively, under nitrogen. A Headway photoresist spinner was employed for applying the photoresist solutions to silicon wafers. Deep u.v. exposures were performed by contact printing using a 1000 W DUV illuminator (model 82531) from Oriel corperation comprising of a high pressure Hg (Xe) lamp with a shutter system, an intensity controller, and an exposure timer. Power density was measured using a radiant power energy meter (model 70260) from Oriel corperation. Film thickness was measured with a P-10 surface profiler from Tencor instruments. Oxygen reactive-ion etching (RIE) was carried out using a RIE-80 system from Plasma Technology.

2.3. Preparation of 2-trimethylsilyl-2-propyl methacrylate (TMSPMA)

2-Trimethylsilyl-2-propanol was prepared as described in several publications [10], [11]. To a solution of 2-trimethylsilyl-2-propanol (93 mmol) in 100 ml THF was added *n*-butyllithium (*n*-BuLi) (1.5 M, 102.3 mmol) at 0°C, and the reaction mixture was allowed to warm to room temperature. After being stirred for 30 min, it was cooled again to 0°C. Methacryloyl chloride (111.6 mmol) was added slowly, and then the mixture was warmed up to room temperature. After being stirred for 10 min, it was heated to 50°C and stirred for 1 h. THF was removed in a rotary evaporator. After being quenched with aqueous NH_4Cl solution, the aqueous phase was extracted with ether and the combined ethereal solution was washed with water. The organic layer was dried over magnesium sulfate and concentrated. The crude product was purified by distillation under reduced pressure. Yield: 84% b.p. 200°C. ^1H n.m.r. ($CDCl_3$): $\delta = 0.06$ (9H, s, $Si(CH_3)_3$), 1.4 (6H, s, O–$C(CH_3)_2$–Si), 1.88 (3H, s, CH_3) and 5.44, 5.98 (2H, s, CH_2=).

2.4. Preparation of poly(TMSPMA)

A solution of TMSPMA in benzene or dioxane that contained AIBN was heated at 65°C in vacuo in a sealed ampoule. The polymer was precipitated in fresh methyl alcohol and dried under reduced pressure.

2.5. Lithographic evaluation

Resist solutions were prepared by dissolving poly(TMSPMA) (~15 wt%) in propylene glycol methyl ether acetate (PGMEA). TPSTFMS (5 wt% of matrix polymer) was also mixed with the solutions as a photoacid generator. The resist solutions were filtered through a 0.2 or 0.1 μm Millipore filter. Resist solutions were spin-coated at 2500–3000 rpm to obtain about 1 μm-thick films on silicon wafers for lithographic evaluation, on NaCl plates for i.r. spectroscopy, and on quartz cells for u.v. spectroscopy. The resist films were prebaked at 130°C for 2 min to remove residual solvent. The deep u.v. exposure system consisted

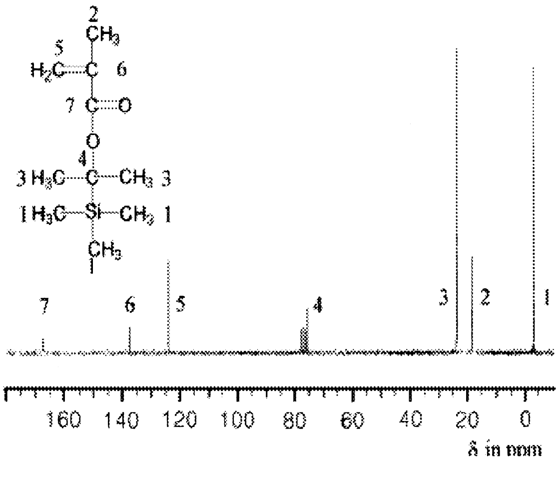

Fig. 2. ^{13}C n.m.r. ($CDCl_3$) spectrum of TMSPMA.

Table 1
Radical polymerization of TMSPMA

Solvent	AIBN[a] (mol%)	M/S[b] (g ml^{-1})	Time (h)	Conversion (%)	M_n (°C)	M_w/M_n	T_g (°C)
Dioxane	5	1	24	85	15 000	2.01	110
Dioxane	3	1	24	80	17 000	1.97	110
Dioxane	1	1	24	75	22 000	2.02	114
Dioxane	0.5	1	20	65	29 841	1.92	117
Benzene	0.5	1	43	70	25 774	2.04	115

Polymerizations were carried out at 65°C.

[a] Mol% of initiator AIBN to the amount of monomer.

[b] M/S is the ratio of the weight of monomer to the volume of solvent.

of a high-pressure Hg (Xe) lamp. After exposure, the wafers were hard-baked at 115°C for 4 min. The exposed and hard-baked region was etched by oxygen RIE in a parallel plate reactor at 50 mtorr pressure and with a power density of 50 mW cm^{-2} and an oxygen flow of 50 standard cubic centimetres per minute, and the etch rate was compared with that of the unexposed region.

3. Results and discussion

The synthetic route of TMSPMA and poly(TMSPMA) is shown in Fig. 1. 2-Trimethylsilyl-2-propanol was prepared by reacting acetyl trimethylsilane with methyllithium. The synthesis of TMSPMA involves conversion of 2-trimethylsilyl-2-propanol into its lithium alkoxide salts by means of *n*-BuLi in THF, followed by the addition of an equivalent of methacryloyl chloride. The ^{13}C n.m.r. spectrum of TMSPMA is depicted in Fig. 2. The characteristic Si–CH$_3$ peak of TMSPMA was shown at $-$ 2.7 ppm and the C=O peak is shown at 167 ppm, which is the characteristic peak of an ester. The polymerization results are shown in Table 1. The number-average molecular weights of the poly(TMSPMA) were in the range of 15 000–30 000, the polydispersities were 1.90–2.05 in 70–85% conversion, and the glass transition temperatures (T_gs) of the polymers were 110–117°C.

The acid catalysed cleavage of the protected polymer was studied using t.g.a. and Fourier transform i.r. (*FT*i.r.). The t.g.a. curve of poly(TMSPMA), shown in Fig. 3A, indicates that poly(TMSPMA) possesses good thermal stability up to 200°C. At that temperature, a rapid weight loss takes place due to evolution of 2,2,3-trimethyl-2-silabut-3-ene resulting from thermolysis of 2-trimethylsilyl-2-propyl groups, as shown in Fig. 4. In the presence of a photogenerated acid, deprotection of 2-trimethylsilyl-2-propyl groups occurrs, as indicated in Fig. 3B. The cleavage of the 2-trimethylsilyl-2-propyl groups is found to begin around 100°C. By comparing the curves in Fig. 3, the thermal deprotection of the 2-trimethylsilyl-2-propyl groups resulted in almost the same weight loss of 40 wt% with or without acid, which corresponds to the theoretically calculated weight loss due to the evolution of 2,2,3-trimethyl-2-silabut-3-ene.

Fig. 5 shows that the cleavage reaction results in the disappearance of 2-trimethylsily-2-propyl group the and formation of the carboxylic acid functionality in the polymer. The Si–C stretching band at 840 cm^{-1} and the C–O–C band of TMSPMA unit at 1110 cm^{-1} disappears, the carboxylic O–H stretching band appears at 3000–3400 cm^{-1}, and the C=O stretching band shifts from 1720 to 1703 cm^{-1} after exposure (dose = 20 mJ cm^{-2}) and post-exposure bake. Fig. 6 shows the u.v. spectrum of poly(TMSPMA) in the deep u.v. region. The polymer has relatively low absorbances at 193 nm and 248 nm, and therefore it can be used in resists for ArF eximer lasers as well as KrF eximer lasers.

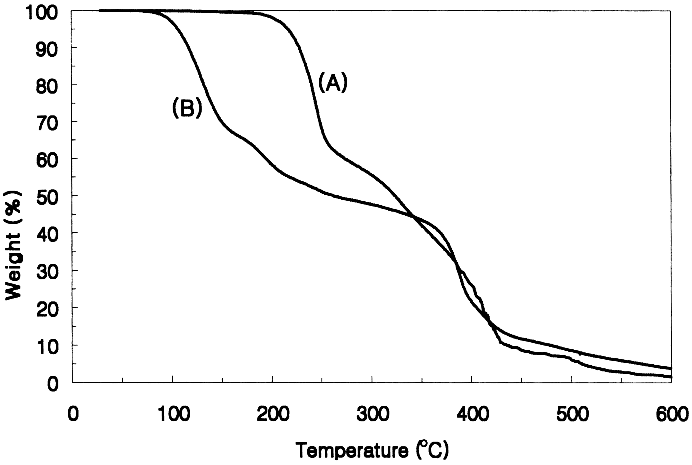

Fig. 3. Comparison of t.g.a. thermograms of poly(TMSPMA) containing 5 wt% of TPSTFMS before (A) and after (B) u.v. exposure.

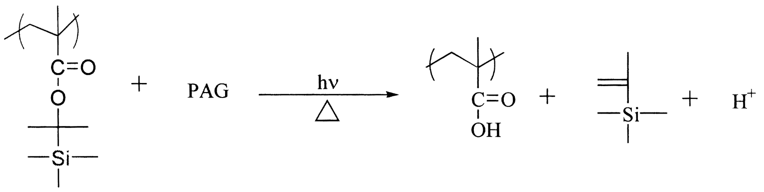

Fig. 4. Acid catalysed deprotection of 2-trimethylsilyl-2-propyl group.

O_2 RIE rates of the photoresists were also measured. The unexposed region which has 14 wt% of silicon content generates both volatile and nonvolatile products (i.e. SiO_2) upon oxygen reactive ion etching treatment. The silicon oxide layer over the remaining resist inhibits further erosion. On the other hand, the exposed and hard-baked region which has little silicon content forms only volatile etching products and will erode rapidly. The etching rate of the unexposed region was 18 Å min^{-1}, and that of the exposed region was 2560 Å min^{-1}. This indicates that this polymer can be used for a dry-developable photoresist.

The resist system based on poly(TMSPMA) and TPSTFMS has the following advantages over conventional resist systems. The polymer has low absorbances at 248 nm and 193 nm and has a good thermal stability up to 200°C. In this resist system, the acid catalysed reaction product, 2,2,3-trimethyl-2-silabut-3-ene, is readily evaporated by PEB. Therefore, additional processes such as silylation or wet developing of the top layer in a bilayer system are not necessary.

The experiments are being continued, to improve the adhesion property of the homopolymer by copolymerization with appropriate hydrophilic monomers. Detailed lithographic evaluation (patterning experiment) of this resist system is in progress, and a full account of the results will be published.

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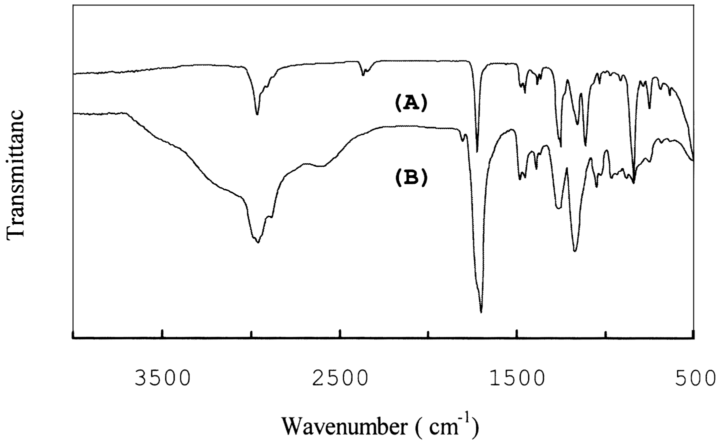

Fig. 5. I.r. spectral change of poly(TMSPMA) before (A) and after (B) acidolysis with post-exposure bake at 110°C for 5 min.

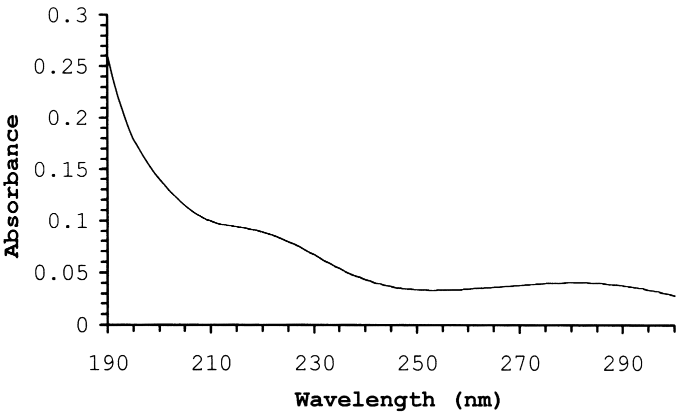

Fig. 6. U.v. absorbance spectrum of a 0.5 mm thick film of poly(TMSPMA).

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