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Chemically amplified resists based on poly(1,4-dioxaspiro[4.4]nonane-2-methyl methacrylate)

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Abstract

The present paper describes a novel class of ketal-protected chemically amplified photoresists. Poly(1,4-dioxaspiro[4.4]nonane-2-methyl methacrylate) (poly(DNMMA)) was synthesized and evaluated as a matrix polymer. The ketal group of the polymer hydrolyzes under acid catalysis to give two alcohol functionalities and a cyclopentanone. The ketal polymer is insoluble in an aqueous developer, while the hydrolyzed products are soluble. The decomposition temperature in the presence of acid was below room temperature. The polymer has high transparency in the deep UV region and its absorbances were 0.015 μm^{-1} at 248 nm and 0.163 μm^{-1} at 193 nm. The existence of the generated cyclopentanone after deprotection improves sensitivity by increasing acid diffusion. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Chemically amplified resist; Poly(1,4-dioxaspiro[4.4]nonane-2-methyl methacrylate); Ketal-protected polymer

1. Introduction

Deep-UV lithography is one of the most promising technologies for the sub-0.5 μm feature delineation [1]. It is well recognized that to accomplish this goal, exposure tools which operate in the deep UV region (190–300 nm) of the spectrum will have to be used. New resist materials based on the principle of chemical amplification have been developed to meet the need for very sensitive and transparent resist materials for deep-UV tools that in general have a low energy output at the wafer plane. The concept of chemical amplification in microlithography [2,3] has long been applied to the resist systems susceptible to cationic process. This concept was first demonstrated in the development of the poly(4-butoxycarbonyloxystyrene) resist [4,5] that operated on the basis of acid catalyzed thermolysis to poly(4-hydroxystyrene) with the evolution of carbon dioxide and isobutylene.

Our goal in this investigation was to apply a new type of ketal-protected polymers for a deep UV chemically amplified resist system. We used the substituent, 1,4-dioxaspiro[4.4]nonane-2-methyl ester, as an acid labile protective group which generates cyclopentanone in the exposed region. In this article, we discuss the synthetic method of the polymer, acid catalyzed deprotection mechanism, and the effect of generated cyclopentanone after deprotection on the resist sensitivity.

2. Experimental

2.1. Materials

Cyclopentanone, glycerol, and methacryloyl chloride purchased from Aldrich Chemical Company were purified by distillatioin under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) purchased from TCI Chemical Company was purified by recrystallization in diethyl ether. Triethylamine (TEA) and tetrahydrofuran (THF) purchased from Junsei Chemical Company were refluxed for a day over sodium metal and distilled prior to use. Triphenylsulfonium triflate (TPSTf) as a photoacid generator (PAG) was synthesized according to the literature [6].

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 measured with a Bio-Rad FTS-165 spectrometer. UV

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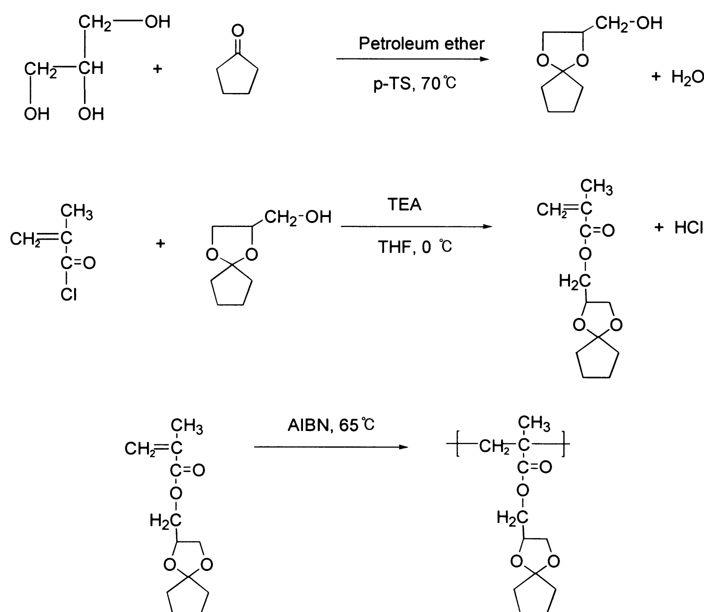

Fig. 1. Synthesis of DNMMA and polymerization.

spectra were recorded as spin-coated films on quartz plates with a Hewlett-Packard Model 8453 spectrophotometer. The number-average molecular weights and molecular weight distributions were determined on a Waters GPC-150C in THF using a calibration curve for polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained on a Perkin–Elmer TA 7 series system at a heating rate of 10 and 20°C min^{-1}, respectively. The etch rates were obtained by measuring the thickness of the polymer films on silicon substrates before and after reactive ion etching for CF_4/CHF_3 mixed gas.

2.3. Synthesis of 1,4-dioxaspiro[4.4]nonane-2-methanol

In a 250 ml three-necked flask equipped with a condenser with Dean-Stark trap are placed 23.9 g (0.26 mol) of glycerol, 16.8 g (0.2 mol) of cyclopentanone, 60 ml of petroleum ether, and 0.1 g of *p*-toluenesulfonic acid monohydrate (*p*-TS). The mixture was refluxed for 6–8 h with azeotropic removal of water until no more water collects in the Dean-Stark trap. The organic layer was separated and the aqueous layer was extracted twice with ethyl ether. The organic layer and the extracts were combined and concentrated to give a pale yellow syrup, which was purified by column chromatography on a silica gel with ethyl acetate/*n*-hexane (1:3 v/v) as eluent. The desired fractions were combined and dried under reduced pressure. 1,4-dioxaspiro[4.4]nonane-2-methanol was obtained in a yield of 25.6 g (81%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 4.0–4.1 (1H, m), 3.8–3.9 (1H, m), 3.7 (1H, m), 3.5–3.6 (2H, m), 2.6 (1H, t), 1.6–2.0 (8H, m). FT-IR (cm^{-1}): 3454 (–OH), 2939 (cyclic CH), 1336, 1108 (C–O of ether).

2.4. Synthesis of 1,4-dioxaspiro[4.4]nonane-2-methyl methacrylate (DNMMA)

To a well dried 250 ml three-necked flask fitted with a dropping funnel, a nitrogen gas inlet, and a drying tube filled with $CaCl_2$ were added 21.2 g (0.134 mol) of 1,4-dioxaspiro[4.4]nonane-2-methanol, 14.9 g (0.147 mol) of triethylamine, and 40 ml of dry THF under a dry nitrogen atmosphere. The mixture was stirred at 0°C. To this mixture, 14.0 g (0.134 mol) of methacryloyl chloride was added dropwise through the dropping funnel for 1 h and stirred vigorously. Then the reaction mixture was kept cold in an ice-water bath and was stirred for 8 h. The triethylamine salt was removed by filtration and the reaction mixture was washed twice with 100 ml of distilled water. The organic layer was separated and the aqueous layer was extracted twice with ethyl ether. The organic layer was dried with anhydrous magnesium sulfate. After filtration, the organic layer and the extracts were combined and concentrated to give a pale yellow syrup, which was purified by column chromatography on a silica gel with ethyl acetate/*n*-hexane (1:3 v/v) as eluent. The desired fractions were combined and dried under reduced pressure. DNMMA was obtained as a pale yellow oil with a yield of 21.8 g (72%). ^{1}H NMR ($CDCl_3$): δ 6.1 (1H, s), 5.6 (1H, s), 4.3 (1H, m), 4.2 (2H, d), 3.7 (1H, m), 4.0 (1H, m), 1.9 (3H, s), 1.4–1.8 (8H, m). FT-IR (cm^{-1}): 2960 (cyclic CH), 1719 (C=O of ester), 1638 (vinyl), 1336, 1108 (C–O of ether).

2.5. Synthesis of poly(1,4-dioxaspiro[4.4]nonane-2-methyl methacrylate) (poly(DNMMA))

Polymerization was run using AIBN as an initiator in 1,4-dioxane at 65°C under vacuum in a sealed ampoule for 10 h.

Table 1
Polymerization of 1,4-dioxaspiro[4.4]nonane-2-methyl methacrylate

AIBN[a] (mol%)	S/M[b]	Time (h)	Yield (%)	M_n[c]	MWD[c]	T_g (°C)
1	8	5	gel	–	–	–
5	8	10	64	13,500	2.15	135
10	8	10	68	8,900	2.24	135

[a] Mol% of the initiator to the amount of monomer.
[b] S/M is the ratio of the weight of 1,4-dioxane to the weight of monomer.
[c] Molecular weights and molecular weight distribution were determined by GPC with polystyrene standards.

The polymers were precipitated three times into a large amount of *n*-hexane. The resultant precipitate was filtered and dried under reduced pressure.

2.6. Lithographic evaluation

A resist solution was prepared by dissolving 10 g of poly(DNMMA) ($M_n = 8900$) in 80 g of propylene glycol methyl ether acetate (PGMEA). TPSTf (7 wt.% of matrix polymer) was also dissolved in the solution as a photoacid generator. This solution was filtered through a 0.1 μm filter, spin-coated onto 1,1,1,3,3,3-hexamethyldisilazane-primed silicon wafers, and baked at 140°C for 2 min on a hot plate to form about 1.0 μm thick films. Exposures were carried out on a deep UV exposure system (Oriel corporation model 82531) with a filter transmitting light between 220 and 260 nm. The sensitivity of the resist was determined by plotting the film thickness remaining on the substrate against the exposure dose. The exposed films were baked at 80°C for 1 min and developed in a 2.38 wt.% tetramethylammonium hydroxide aqueous solution for 1 min.

3. Results and discussion

3.1. Synthesis and polymerization of DNMMA

The synthetic scheme to poly(DNMMA) is summarized in Fig. 1. 1,4-Dioxaspiro[4.4]nonane-2-methanol was prepared by the reaction of cyclopentanone and glycerol in refluxing petroleum ether at 70°C using *p*-toluenesulfonic acid monohydrate as a catalyst. Polymerization of DNMMA was carried out using AIBN as a radical initiator. The results are summarized in Table 1.

3.2. Acid catalyzed deprotection mechanism

On the basis of the experimental results, deprotection mechanism is shown in Fig. 2. Poly(DNMMA) is insoluble in an aqueous base; however, when it is exposed in the presence of a photosensitive onium salt, the acid which is produced decomposes the 1,4-dioxaspiro[4.4]nonane groups catalytically. Heterolysis of an *O*,*O*-ketal is induced by acid resulting in the formation of a resonance stabilized intermediate, an oxonium ion. In the presence of water, the highly electrophilic oxonium ion reacts further to produce a hemiketal, which can then collapse to give an alcohol, a cyclopentanone, and a proton. Discrimination between the exposed and unexposed portions of the resist to produce a pattern in a positive tone can now be made since poly(2,3-dihydroxypropyl methacrylate) is very soluble in a dilute aqueous base. Key to the chemical amplification feature of this resist is the fact that the proton that initiates the overall reaction sequence is not lost, which then becomes available for additional deprotection reactions. The acid-catalyzed cleavage of the protecting groups was studied by FT-IR. A FT-IR spectrum of the unexposed film was recorded as

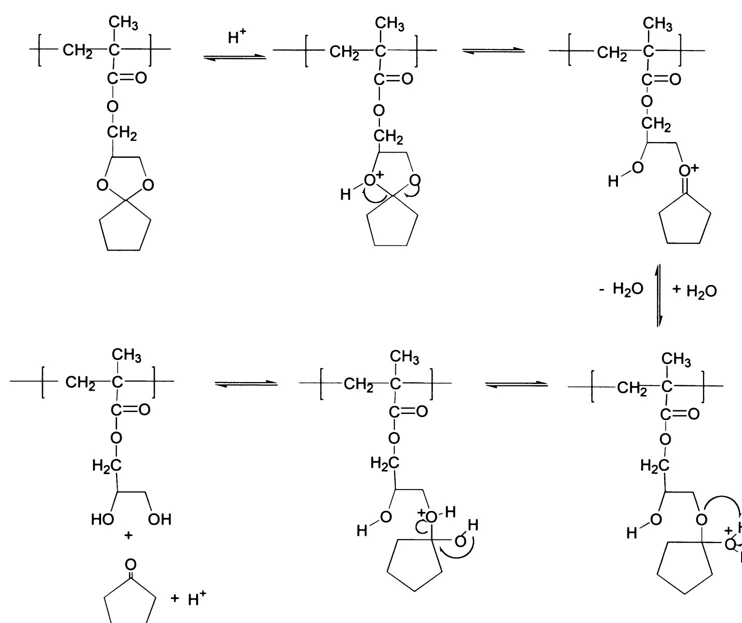

Fig. 2. Acid catalyzed deprotection mechanism of poly(DNMMA).

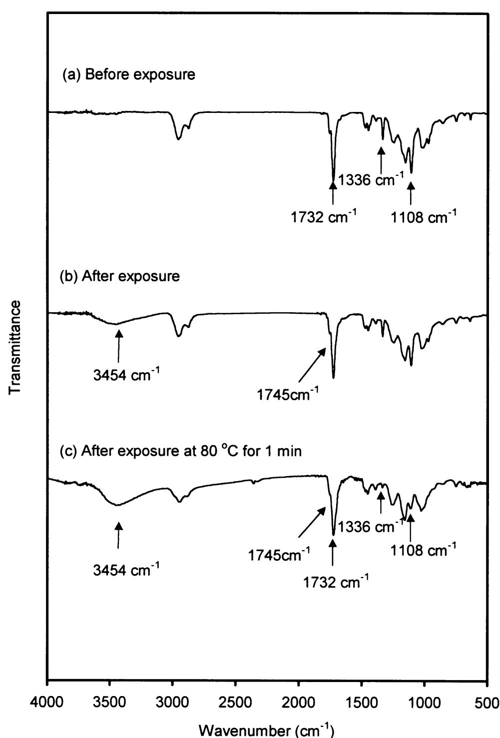

Fig. 3. Infrared spectral change of poly(DNMMA) before exposure (a), after exposure (b), and after exposure and PEB at 80°C for 1 min (c).

shown in Fig. 3(a). Prior to exposure, the absorption at 1732 cm^{-1} characteristic of the ester carbonyl and the ether absorption (1336 and 1108 cm^{-1}) are apparent. After exposure (50 mJ cm^{-2}), the C–O–C bands of the ether group at 1108 and 1336 cm^{-1} shrink after cleavage with the formation of a new broad band corresponding to the alcoholic O–H band at about 3454 cm^{-1} (Fig. 3(b)). The peak around 1745 cm^{-1} is due to the remaining cyclopentanone (boiling point; 135°C) after deprotection (Fig. 3(c)). Heating of the film 80°C for 1 min after exposure brought about the almost complete decomposition of the ether structure and elimination of the volatile products. This is confirmed by an FT-IR spectrum of the film showing the disappearance of the ether bands (1108 and 1336 cm^{-1}) and appearance of hydroxyl band (3454 cm^{-1}) from the resulting polymer (Fig. 3(c)). The radiation induced catalytic reaction of the ketal into alcohol and ketone starts immediately after exposure at room temperature. The process is almost completed by the application of post-exposure bake (PEB) at 80°C. When PEB temperature is above 90°C, some concurrent cross-linking reactions are observed, which may deteriorate the image quality.

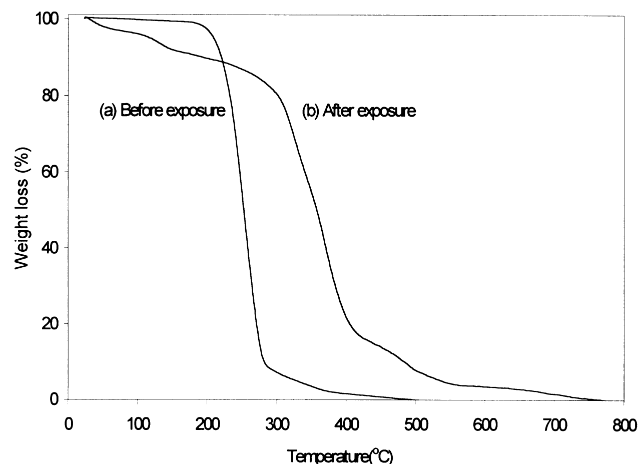

Fig. 4. Comparison of TGA thermograms of (a) polymer (poly(DNMMA)) and (b) resist containing 7 wt.% of TPSTf after deep UV exposure.

3.3. Thermal analysis

Fig. 4 shows the TGA curves of the resist before (a) and after (b) exposure with a dose of 50 mJ cm^{-2}. In Fig. 4(a), poly(DNMMA) was found to be stable up to 200°C. At that temperature, a rapid weight loss took place due to decomposition of the polymer. In Fig. 4(b), the cleavage of the dioxaspiro group of poly(DNMMA) is found to begin around 32°C, and then the cyclopentanone was evolved subsequently. If the polymer would decompose into

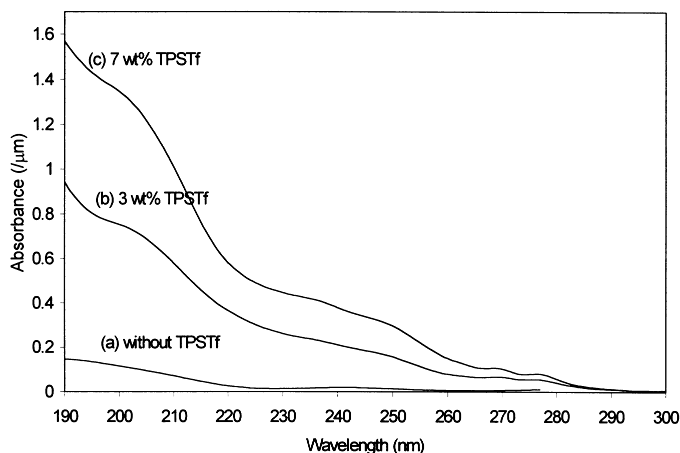

Fig. 5. Deep UV absorption spectra of poly(DNMMA) film without PAG (a), with 3 wt.% TPSTf (b), and with 7 wt.% TPSTf (c).

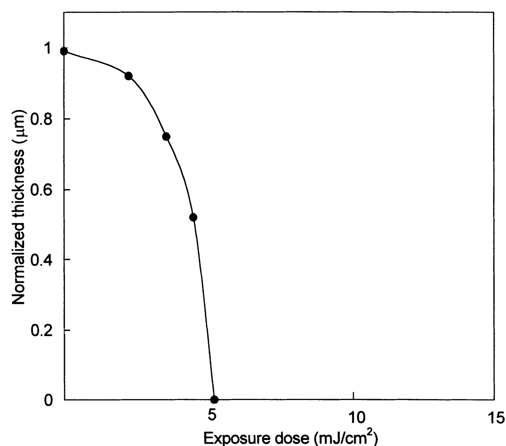

Fig. 6. Plot of the normalized thickness versus dose for 248 nm exposure of poly(DNMMA) containing 7 wt.% of TPSTf; development with 2.38 wt.% TMAH aqueous solution for 1 min, PEB temperature: 80°C for 1 min.

poly(2,3-dihydroxypropyl methacrylate) and cyclopentanone, the theoretical weight loss for this polymer should be 38%. However, the weight loss below 200°C looks much smaller than this value because the radiation induced catalytic reaction starts immediately after exposure at room temperature to a large extent.

3.4. UV absorbance

Poly(DNMMA) exhibits excellent transparency at 248 and 193 nm. The absorbances of the polymer in the solid state were determined to be 0.015 μm^{-1} at 248 nm and 0.163 μm^{-1} at 193 nm (Fig. 5(a)) and therefore it can be used in resists for ArF excimer laser steppers as well as KrF excimer laser steppers. A 1.00 μm thick film, containing 7 wt.% triphenylsulfonium triflate, shows an absorbance of 0.316 μm^{-1} at 248 nm (Fig. 5(c)). The major contributor to the absorption of the photoresist at this wavelength is the PAG.

3.5. Dry-etching resistance

The etch rates of poly(DNMMA), polymethyl methacrylate (PMMA), and the novolac resist were investigated for a CF_4/CHF_3 gas mixture. Table 2 shows the etch rates of the polymers normalized to that of the novolac-based resist (TOK, IP-3300). The etch rate of poly(DNMMA) is 1.63 times that of the novolac-based resist, while PMMA has less dry-etching resistance (1.85 times the rate of the novolac). It was considered that high carbon content of poly(DNMMA) gives better etching resistance than PMMA.

Table 2
Etching rate of polymers (CF_4:CHF_3 = 20:35 standard cubic centimeters per minute gas flow, 60 mTorr, 650 W, 100 s)

Polymer	Etching rate
Poly(DNMMA)	1.63
PMMA	1.85
Novolac resin (TOK, IP-3300)	1.0

3.6. Resist sensitivity

The sensitivity curve of poly(DNMMA) gives the sensitivity of 5 mJ cm^{-2} as shown in Fig. 6. Asakawa et al. reported that the diffusion of acid could be described as a function of the sum of excess free volume originating from the remaining solvent and the intrinsic free volume of the polymer [7]. The generated cyclopentanone creates the diffusion channels for acid molecules within the resist film. Therefore, the deprotection reaction can take place at relatively low temperatures since the acid diffuses more easily through these channels and has a greater probability of encountering the protecting groups.

4. Conclusions

A novel polymer, poly(DNMMA), has high transparency in the deep UV region and can induce a polarity change effectively in the presence of a photogenerated acid. It can be applied to a chemically amplified resist with a PAG. The 1,4-dioxaspiro[4.4]nonane group of the polymer hydrolyzes under acid catalysis to give two alcohol functionalities and a cyclopentanone. The generated cyclopentanone after deprotection can increase the acid diffusion.

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