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Si-containing copolymer of 2,3-epoxypropyl-1-methacrylate

Photoresist sensitivity and plasma-etching behaviour

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Summary

Poly-p-trimethylsilylphenylmethacrylate(75)-co-glycidylmethacrylate (25) containing aromatic bisazides exhibits uv sensitivity as a negative type photoresist. Sensitometric data have been evaluated. The pressure-dependant reactivity under the conditions of oxygen reactive ion etching was determined.

Introduction

The most widely used photoresists consist of solid solutions of 2,1-diazonaphthoquinone-5-sulfonic acid esters in novolak resins (DNN resists) Microstructures are usually realized in these photoresist layers by transforming a mask pattern by irradiation systems into the resist and developing the carboxyl group containing latent pattern by means of organic bases. Two-layer resists are composed of a DNN bottom layer of about 2 µm thickness, planarizing the stepped surface and a thin imaging layer. The upper layer is used as mask for anisotropic etching Organosilicon polymers (1), polysiloxanes (2), and silicon-containing polymers (3) of different structures exhibit a strong resistance to O_2 reactive ion etching and are therefore preferred as top layers.

We synthesized a copolymer of 2,3-epoxypropyl-1-methacrylate and investigated its sensitivity to network formation by aromatic nitrenes. Nitrene formation was initiated in spin-coated layers of polymer/bisazide composites by uv irradiation. Poly-GMA and its copolymers are highly sensitive to nitrenes formed by irradiation of bisazides (4,5). Furthermore, GMA-polymers are preferable top layers as they adhere very strongly to any kind of bottom material.

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Experimental

Monomers, Azides

Glycidyl methacrylate (GMA) was purchased from Aldrich Co. purified by extraction of the stabilizer and destilled twice prior to use. The synthesis of 4-trimethylsilylphenyl methacrylate (SiPMA) was realized according to (6) starting from p-chlorophenol. $C_{13}H_{18}O_2Si$ (234.3), calc. C 66.62, H 7.74, Si 11.97; found C 66.50, H 7.67, Si 11.19; b.p.(0.1 mm) 110 ^oC.
4,4'-Bisazidodiphenyl (m.p. 128 ^oC) was obtained by diazotization of benzidine and reaction with sodium azide (7). 2,6-Bis(4-azidobenzylidene)-4-methyl cyclohexanone (BABC) from Aldrich Co. was used after drying.

Polymers

Polymerizations were carried out in dried degassed methylethylketone containing 15 % monomer under N_2 and stirring at temperatures in the range of 60 - 70 ^oC with 2,2'-azobisisobutyronitrile (AIBN) as initiator (Table 1). The polymers were precipitated in methanol. The Si-content of the copolymers is slightly lower (9.5%) than the value calculated for the monomer mixture (9.95%).

Table 1. Polymerization conditions and polymer data

Monomers mole%	AIBN mole%	Temp. ^oC	Time h	Conv. %	M_w	M_w/M_n	T_g ^oC
SiPMA (100)	0.30	70	12	50	110 000 A	3.0	123
SiPMA (75)	1.0	70	11	75	81 000 B	2.7	
	0.42	70	11	70	90 000 C	2.9	
GMA (25)	0.12	70	12	60	195 000 D	3.5	
	0.24	70	11	75	153 000 E	2.2	106
	0.24	65	13	55	178 000 F	2.5	
	0.24	60	13	15	196 000 G	2.1	

Resist sensitivity, plasma etching

15% w/v of copolymer E and 1.2% w/v of a bisazide were dissolved in purified chlorobenzene. The solutions were spin-coated (3000rpm) onto chromium-covered glass disks to form 0.6 µm films. After prebaking 20 min at 80 ^oC the resist composite was irradiated by a high-pressure Hg lamp through a mask. Methylisobutylketone(2)/isopro-

panol(3) v/v was used as developer. The patterned negative layer was postbaked for 20 min at 120 °C, coated with Al by vapour deposition and the time (energy) dependent increase of layer thickness determined by interferometry.
Oxygen reactive ion etching (O_2-RIE) was performed in a parallel plate stainless steel RIE equipment (ZWG Berlin) with 5-inch Al-electrodes. The etching experiments were conducted at a flow rate of 16 sccm oxygen, power density of 0.68 W/cm^2 and pressures of 1 - 8 Pa. The layer thickness was determined continuously by ellipsometry.

Results and Discussion

Under the influence of RIE-O_2 thin layers of silicon-containing polymers are transformed into a continuous layer of SiO_2(1,2,3). Its thickness is governed by the percentage of Si in the starting polymer and decreases in the course of the etching process. A minimum Si content of about 10% w/w Si is necessary. The homopolymer poly(4-tri-methylsilylphenyl)-methacrylate(11.9% Si) could thus advantageously be applied as a protecting layer. But it was to be expected and proved by preliminary experiments that its reactivity to nitrenes is much too low for resist application. In this respect poly-GMA is a highly reactive material as the formation of a stable network layer to an extent of 60% (cf. Fig.1, d/d_o=0.6) requires an irradiation dose $D_o^{0.6}$ of only 5 mJ/cm^2 (5) compared to more than 2500 mJ/cm^2 for poly-phenylmethacrylate and poly-SiPMA. From further preliminary experiments we chose copolymers containing 9.5% Si, synthesized from monomer mixtures of 75 mole% SiPMA and 25 mole% GMA. As sensitivity and etch resistance proved to be independent of the molecular weight in the investigated range (cf. Table 1) we applied copolymer E (M_w 153 000) for the irradiation and etching experiments.
The sensitivity of resist layers consisting of copolymer E and 8% w/w of BADP (λ_{max} 293 nm) or BABC (λ_{max} 353 nm) amounts to $D_o^{0,6}$ = 60 mJ/cm^2, irrespective of absorption region and extinction coefficient of the bisazides, thus permitting an effective patterning of resists (Fig. 1). A 1 µm line and space pattern is sharply resolved.

The etch results (Fig. 2) demonstrate that the etch rate of the copolymer E at 1.7 Pa (70 nm/min) is sufficiently lower than the according value for a conventional DNN resist (360 nm/min).
An application of the copolymer/bisazide compound for pattern transfer into DNN resists by RIE-O_2 seems to be possible.
With increasing pressure the ion energy of RIE-O_2 systems decreases (8). Hence the slightly decreasing rate of the DNN resist seems to be a consequence of these relations. Surprisingly the Si containing copolymer exhibits an inverse behaviour (Fig.2). This might be explained by a quite different oxidation mechanism of polymethacrylates under RIE-O_2 conditions compared with phenolic resins. The latter may form condensed rings as the pressure increases.

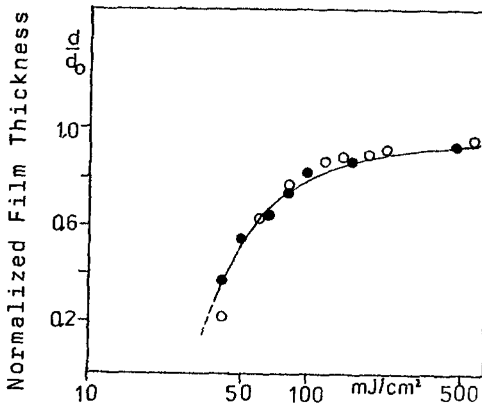

Fig. 1. Contrast Curves of 0,6 µm Films of Copolymer E/ 8% w/w Bisazide exposed to UV

(o) 4,4'-Bisazidodiphenyl
(●) 2,6-Bis(4-azidobenzylidene)-4-methylcyclohexanone

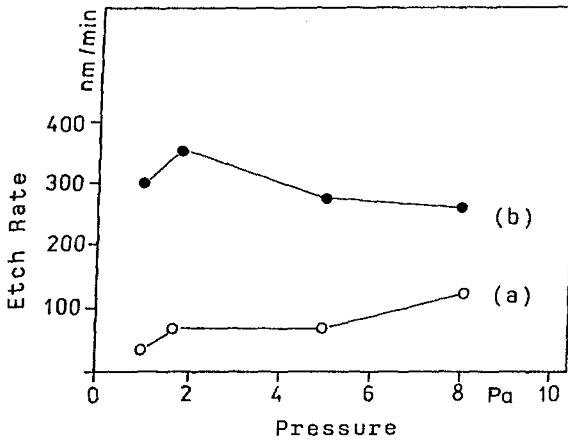

Fig. 2. Reactive Ion Etch Rate as a Function of Pressure

(a) Copolymer E
(b) DNN Resist ORWO

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