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Synthesis of copolymers containing 3-hydroxycyclohexyl methacrylate and their application as ArF excimer laser resists

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Abstract

Copolymers containing 3-hydroxycyclohexyl methacrylate (HCMA) were synthesized as a base polymer for ArF excimer laser lithography. The dry-etching rates of these polymers for CF_4:CHF_3 mixed gas were 1.1–1.2 times that of a novolac-based resist. The adhesion properties of the polymers were also studied by estimating the work of adhesion. When the content of the HCMA unit in the polymer exceeds 60 mol%, the work of adhesion of the resist is similar to those of polyvinylphenol (PVP)-based photoresists. A 0.19 μm pattern profile was obtained using a resist based on the terpolymer containing HCMA and the conventional developer, 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: ArF photoresist; 3-Hydroxycyclohexyl methacrylate; Alicyclic methacrylate

1. Introduction

ArF excimer laser lithography has been investigated as one of the most promising technologies for producing patterns below 0.20 μm. Conventional phenolic resins cannot be used as a base polymer for the ArF excimer laser resist due to their strong absorption at 193 nm. In contrast, aliphatic polymers like poly(methyl methacrylate) show high transparency, but their dry-etching resistance is insufficient. Generally, single-layer resists require high optical transparency at 193 nm, good dry-etching resistance, thermal stability to withstand the temperature and conditions used in device manufacturing, and good adhesion to silicon substrate. In addition, alkaline development in a 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution is strongly recommended to utilize the established process for novolac and polyvinylphenol (PVP) resists.

Recently, methacrylate polymers containing alicyclic hydrocarbons, such as adamantyl [1,2], menthyl [3], isobornyl [4], and tricyclodecanyl [5,6] groups, have been proposed for their high transparency and good dry-etching resistance. However, the adhesion of these resists is poor due to the hydrophobic nature of the alicyclic group.

In this study, we synthesized a new monomer, 3-hydroxycyclohexyl methacrylate (HCMA), which has a polar and alicyclic group. Its copolymers with various alicyclic methacrylates were also synthesized and their physical properties and lithographic performance were evaluated.

2. Experimental

2.1. Materials

1,3-Cyclohexanediol, methacryloyl chloride, 1-adamantanol, and decahydro-2-naphthol were purchased from TCI company and used without further purification. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. Isobornyl methacrylate purchased from Aldrich was distilled under reduced pressure. The photoacid generator, triphenylsulfonium triflate, was prepared as described in several publications [7–9]. Triethylamine, tetrahydrofuran (THF), and 1,4-dioxane, purchased from Junsei were refluxed for a day over sodium metal and distilled prior to use.

2.2. Measurements

Proton n.m.r. spectra were recorded in deuterated chloroform using a Varian model 2000 spectrometer equipped with a Fourier transform accessory. Infrared spectra were obtained on a Bio-Rad FTS-165 spectrometer. U.v. spectra

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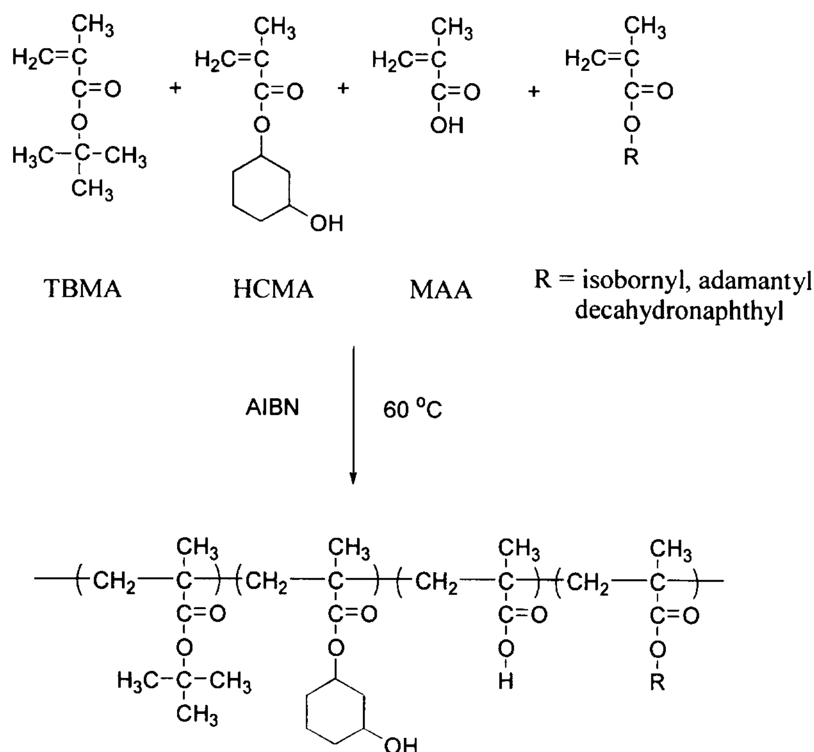

Fig. 1. Polymerization scheme.

were recorded as spin-coated films on quartz substrates with a Hewlett-Packard model 8453 spectrophotometer. Molecular weights were determined by gel permeation chromatography (g.p.c.) on a Tosoh HLC-8020 instrument equipped with a refractive index detector. Thermogravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.) data were obtained on a Perkin-Elmer TA 7 series system. Contact angles were measured with a Krüss G2/G40 contact angle measuring system. 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 and Wendt's [10], Young's [11], and Dupré's equations. Dry-etching resistance was measured with an Advanced Materials model P5000 RIE system. Exposures were carried out on an Oriel DUV exposure system or a ISI ArF small field exposure system (0.60 NA).

2.3. Preparation of alicyclic methacrylates

HCMA, adamantyl methacrylate (AdMA), and decahydronaphthyl methacrylate (DNMA) were synthesized in a one-step esterification using methacryloyl chloride and the corresponding alcohols in the presence of triethylamine. For example, HCMA was synthesized as follows: to a well dried 250 ml three-necked flask fitted with a dropping funnel, a nitrogen gas inlet, and a drying tube filled with $CaCl_2$, 25 g (0.215 mol) of 1,3-cyclohexanediol, 23.9 g (0.237 mol) of triethylamine, and 100 ml of dry THF under a dry nitrogen atmosphere were added. The mixture was stirred at 0°C. To this mixture, 21.47 g (0.215 mol) of methacryloyl chloride were added dropwise through the dropping funnel for 1 h and stirred vigorously. Then the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The resultant mixture was washed with 100 ml of water. The organic layer was separated and the water layer was extracted three times with ethyl ether. The organic layer and the extracts were combined and concentrated to give a pale yellowish syrup, which was purified by column chromatography on a silica gel with ethyl acetate/*n*-hexane (1:3) as eluent. The desired fractions were combined and dried at reduced pressure. HCMA was obtained in a yield of 16.76 g (42.3%) as a colourless oil. ^{1}H n.m.r. ($CDCl_3$, ppm): 5.9 (1H, s), 5.4 (1H, s), 4.5 (1H, m), 3.9 (2H, m), 1.0–2.1 (13H, m). *FT*i.r. (cm^{-1}): 3450 (–OH), 2936 (cyclic CH), 1716 (C=O of ester), 1637 (vinyl).

2.4. Polymerization

Copolymers of the methacrylates were obtained by free radical solution polymerization with AIBN at 60°C in a sealed ampoule. The polymer was precipitated in petroleum ether:ethyl ether (1:1) and dried at reduced pressure.

2.5. Lithographic evaluation

A resist solution was made by dissolving 3 g of the polymer and 0.06 g of triphenylsulfonium triflate as a photoacid generator in 22 g of cyclohexanone. The resist solution was filtered through a 0.2 μm Teflon membrane filter, spun

Table 1
Thermal and optical properties of polymers

Polymer	M_n^a	M_w/M_n^a	T_g^b (°C)	T_d^c (°C)	$T_d'^d$ (°C)	Absorbance at 193 nm (μm^{-1})
Poly(TBMA$_{0.3}$–HCMA$_{0.7}$)	13600	2.91	159	230	102	0.125
Poly(TBMA$_{0.3}$–HCMA$_{0.6}$–MAA$_{0.1}$)	9470	2.75	158	230	105	0.120
Poly(TBMA$_{0.3}$–HCMA$_{0.4}$–IBMA$_{0.2}$–MAA$_{0.1}$)	9550	2.31	171	231	103	0.160
Poly(TBMA$_{0.3}$–HCMA$_{0.4}$–AdMA$_{0.2}$–MAA$_{0.1}$)	9780	2.46	188	231	105	0.255
Poly(TBMA$_{0.3}$–HCMA$_{0.4}$–DNMA$_{0.2}$–MAA$_{0.1}$)	9880	2.55	158	230	105	0.255

[a] M_n and M_w were obtained by g.p.c. using a calibration curve for polystyrene standard
[b] T_g was measured by d.s.c. at a heating rate 10°C/min
[c] Onset deprotection temperature (T_d) was measured by t.g.a. at a heating rate 20°C/min
[d] Onset deprotection temperature (T_d') in presence of photogenerated acid was measured by t.g.a. at a heating rate 20°C/min

onto hexamethyldisilazane (HMDS)-primed silicon wafers, and baked at 120°C for 1 min to remove residual solvent. The resist was exposed with a DUV or ArF exposure system (ISI, NA 0.6). The exposed film was post-exposure baked at 140°C for 2 min and developed in 2.38 wt% TMAH aqueous solution.

3. Results and discussion

A terpolymer of *t*-butyl methacrylate (TBMA), HCMA, and methacrylic acid (MAA) was synthesized. Methacrylates with various alicyclic groups were also introduced to improve dry-etching resistance (Fig. 1). Each monomer serves a separate function in the terpolymer. TBMA is used to provide an acid-cleavable side group which is responsible for creating a radiation-induced solubility change. MAA is used to control dissolution rate and photospeed. HCMA is used as an adhesion promotor to silicon substrate and to improve dry-etching resistance.

The properties of methacrylate polymers are shown in Table 1. These polymers have high glass transition temperatures (T_g) and good thermal stability. The onset deprotection temperatures (T_d) of these polymers accomplished by loss of isobutene in TBMA are observed at ca. 230°C. However, in the presence of a photogenerated acid, the deprotection reaction occurred at 102–105°C; and the polymers have low absorbances (0.120–0.255) at 193 nm.

Table 2
Etching rate of polymers

Polymer	Etching rate
Poly(TBMA$_{0.3}$–HCMA$_{0.6}$–MAA$_{0.1}$)	1.20
Poly(TBMA$_{0.3}$–HCMA$_{0.4}$–IBMA$_{0.2}$–MAA$_{0.1}$)	1.18
Poly(TBMA$_{0.3}$–HCMA$_{0.4}$–AdMA$_{0.2}$–MAA$_{0.1}$)	1.15
Poly(TBMA$_{0.3}$–HCMA$_{0.4}$–DDMA$_{0.2}$–MAA$_{0.1}$)	1.11
PMMA	1.85
Novolac resin (TOK, IP-3300)	1.0

CF_4:CHF_3 = 20:35 sccm, 60 mTorr, 650 W, 100 s

The dry-etching rates of the polymers were investigated (Table 2). The etching rate of poly(TBMA-co-HCMA-co-MAA) is 1.2 times that of a novolac-based resin (TOK, IP-3300). Dry-etching rates of tetrapolymers containing various alicyclic methacrylates are lower than that of the terpolymer.

Works of adhesion of polymers on silicon substrates (W_{PS}), and the contact angles of water and CH_2I_2 are summarized in Table 3. Poly(TBMA$_{0.3}$–HCMA$_{0.6}$–MAA$_{0.1}$) and poly(TBMA$_{0.3}$–HCMA$_{0.7}$) show higher W_{PS} than those of conventional PVP-based resists (APEX-E, UVII-HS), even though W_{PS} values of these polymers are lower than that of novolac-based resist.

Table 3
Contact angles and works of adhesion of polymers (W_{PS})

Polymer	Contact angle (°)		W_{PS}^a (dyne/cm)
	H_2O	CH_2I_2	
Poly(TBMA$_{0.7}$–HCMA$_{0.3}$)	83.3	59.2	62.28
Poly(TBMA$_{0.6}$–HCMA$_{0.4}$)	82.3	58.9	63.01
Poly(TBMA$_{0.5}$–HCMA$_{0.5}$)	79.9	57.2	64.96
Poly(TBMA$_{0.4}$–HCMA$_{0.6}$)	78.1	56.6	66.29
Poly(TBMA$_{0.3}$–HCMA$_{0.7}$)	73.3	50.9	70.48
Poly(TBMA$_{0.3}$–HCMA$_{0.6}$–MAA$_{0.1}$)	73.0	53.8	70.22
Poly(TBMA$_{0.3}$–HCMA$_{0.4}$–DNMA$_{0.2}$–MAA$_{0.1}$)	77.5	53.8	67.17
Novolac-based resist	71.4	48.0	72.20
PVP-based resist (APEX-E)	76.4	56.9	67.42
PVP-based resist (UVII-HS)	74.8	61.1	67.78

[a] Work of adhesion of polymer on HMDS primed silicon substrate

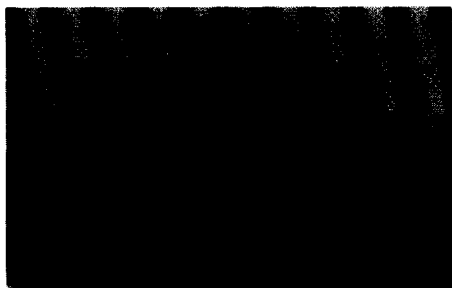

Fig. 2. SEM image of 0.19 μm L/S patterns printed with poly($TBMA_{0.3}$–$HCMA_{0.6}$–$MAA_{0.1}$) using ArF exposure system (ISI, NA = 0.6) at 19 mJ/cm^2.

The adhesion increased with an increase in the content of HCMA. When the HCMA content in the polymer exceeded 60 mol%, the work of adhesion was higher than that of the conventional PVP-based resist. However, poly($TBMA_{0.3}$–$HCMA_{0.4}$–$DNMA_{0.2}$–$MAA_{0.1}$) has lower work of adhesion than those of terpolymers.

Preliminary evaluations of the resists formulated with poly($TBMA_{0.3}$–$HCMA_{0.6}$–$MAA_{0.1}$) and poly($TBMA_{0.3}$–$HCMA_{0.4}$–$IBMA_{0.2}$–$MAA_{0.1}$) using DUV exposure system showed excellent sensitivities in the range of 10–30 mJ/cm^2. Lithographic performance of these polymers was also evaluated using an ArF exposure system (ISI, NA = 0.6). The resists formulated with poly($TBMA_{0.3}$–$HCMA_{0.6}$–$MAA_{0.1}$) exhibited a good resolution of 0.19 μm lines and spaces (Fig. 2) at 19 mJ/cm^2 using a conventional developer. However, for the resists formulated with poly($TBMA_{0.3}$–$HCMA_{0.4}$–$IBMA_{0.2}$-$MAA_{0.1}$), features with dimensions below 0.5 μm were lifted off during development. This was due to poor adhesions of these polymers to silicon substrates. Our current efforts are concerned with making improvements in adhesion for these resists.

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