

Design, Synthesis, and Evaluation of a Novel Amphiphilic Alicyclic Polymer Having γ -Hydroxy Acid Structure

Takashi Hattori,* Yuko Tsuchiya, Ryoko Yamanaka, and Hiroshi Shiraishi

Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo 185-8601, Japan

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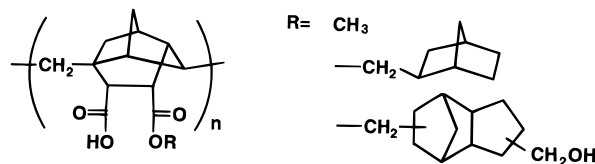
An amphiphilic alicyclic polymer having γ -hydroxy acid structure has been developed by reduction of poly(5-methylenebicyclo[2,2,1]-2-heptene)-*co*-(maleic anhydride). This polymer exhibits moderate transparency at 193 nm and good alkali solubility. A two-component negative resist system, consisting of the polymer and an onium salt, produces sub-micrometer patterns without swelling distortion by using an ArF excimer laser stepper. Infrared spectroscopy shows that the insolubilization reaction is mainly intramolecular esterification of γ -hydroxy acid to γ -lactone. The swelling distortion of sub-micrometer patterns can thus be avoided by drastically decreasing the number of carboxyl groups in the exposed area.

Introduction

ArF excimer laser lithography is expected to be the major fabrication technology for 1-Gbit DRAMs. However, the critical dimension will likely become smaller than 0.2 μm for 1-Gbit DRAMs, a size comparable to the wavelength of ArF excimer laser light (193 nm). Therefore, ArF excimer laser lithography will need to be used in conjunction with a resolution enhancement technique such as a phase-shifting mask,^{1,2} and phase-shifting lithography requires a negative resist system.

Methacrylate polymers containing alicyclic hydrocarbons^{3–6} and copolymers of norbornene derivatives^{7–11} have been proposed as the base polymer for ArF single-

Scheme 1. Alicyclic Polymers Having Half-Acid Ester Structure



layer resists due to their high transparency and good dry-etching resistance. We have developed alicyclic polymers having half-acid ester structure that exhibit moderate transparency, good dry-etching resistance, and good alkali solubility (Scheme 1).¹² These developed polymers have carboxyl groups as their alkali-soluble groups because other alkali-soluble structures, like the phenolic group, shows strong absorption at 193 nm.

We applied a chemical amplification mechanism¹³ to design high-performance ArF resists. We have examined the use of acid-catalyzed insolubilization reactions between the alicyclic polymer having half-acid ester structure and aliphatic carbinols as a potential negative ArF single-layer resist (Scheme 2).¹⁴ Although an aliphatic carbinol, 1,4-dioxane-2,3-diol, exhibited high insolubilization reactivity, the obtained patterns showed swelling distortion in the sub-micrometer range. This is apparently due to the penetration of the aqueous base developer into the remaining carboxyl groups in the exposed area. It is thus necessary to reduce the number of carboxyl groups drastically in the exposed region in order to get fine patterns with negative ArF resist systems.

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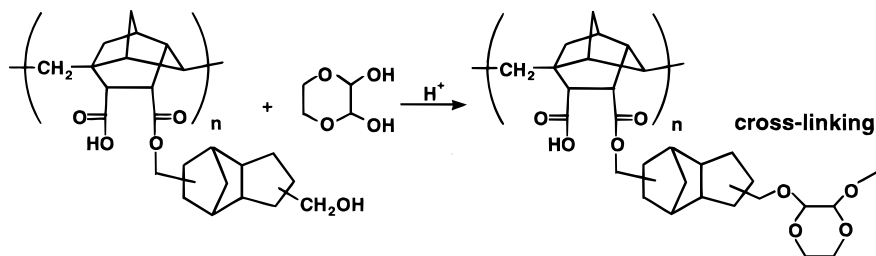
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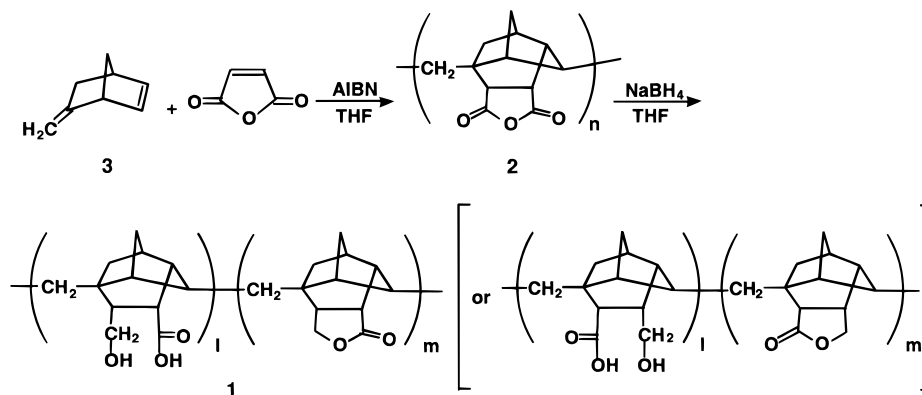
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Scheme 2. Acid-Catalyzed Reaction of Alicyclic Polymers Having Half-Acid Ester Structure and 1,4-Dioxane-2,3-diol



Scheme 3. Synthesis of Alicyclic Polymer Having γ -Hydroxy Acid Structure (Polymer 1)



Scheme 4. Acid-Catalyzed Reaction of Alicyclic Polymers Having γ -Hydroxy Acid Structure (Polymer 1)

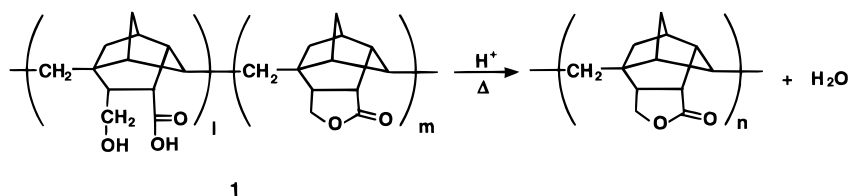


Table 1. Results of Copolymerization and Reduction

polymer	yield (%)	M_w	M_n	M_w/M_n		polymer	yield (%)	M_w	M_n	M_w/M_n
2a	92	5800	2500	2.28	→	1a	72	4400	2300	1.92
2b	94	5600	2700	2.09	→	1b	76	5000	2300	2.14

It is well-known that γ -hydroxy acid and δ -hydroxy acid easily become cyclic esters, γ -lactone and δ -lactone, respectively, by intramolecular esterification in the presence of acid. In this paper we describe an amphiphilic alicyclic polymer **1** having γ -hydroxy acid structure, which is derived from a copolymer of a nonconjugated cyclic diene and maleic anhydride (copolymer **2**) (Scheme 3). Polymer **1** has the potential to be a negative ArF single-layer resist that does not show swelling distortion because the number of carboxyl groups is drastically decreased in the exposed area (Scheme 4). We also describe the basic properties and lithographic performance of polymer **1**.

Experimental Section

Materials. 5-Methylenebicyclo[2.2.1]-2-heptene (**3**) and maleic anhydride were obtained commercially and used without any purification. Triphenylsulfonium triflate (TPS) (Midoru Kagaku Co.) was used as the photoacid generator. The developer was dilute NMD-3 (2.38% tetramethylammonium hydroxide (TMAH) solution) obtained from the Tokyo Ohka Kogyo Company.

Polymer Preparation. Polymer **1** was synthesized as shown in Scheme 3. Copolymerization of **3** and maleic anhy-

dride was done in tetrahydrofuran (THF) for 7 h using 2,2'-azobis(isobutyronitrile) (3.9 mol %) as the initiator according to the literature.^{15,16} The initial molar ratio of **3** to maleic anhydride was 1:1.

To convert the cyclic anhydride in copolymer **2** to γ -hydroxy acid, it was first reduced to γ -lactone by NaBH₄ according to the literature.^{17,18} After the reduction, the reaction mixture was poured into water, which became clear and slightly viscous. Next, dilute aqueous hydrochloric acid was added until weak acidity was shown, and then the mixture was extracted with ethyl acetate. The extract was washed with water and dried over anhydrous sodium sulfate. After removal of the sodium sulfate, the solution was concentrated and poured into *n*-hexane to precipitate alicyclic polymer **1** having γ -hydroxy acid structure. The yields, molecular weights, and molecular weight distributions of the obtained polymers are summarized in Table 1.

Characterization. The structure of the polymer was determined using infrared spectroscopy (Perkin-Elmer FT-IR 1720X) and ¹H NMR spectroscopy (JEOL LA-400) in acetone-

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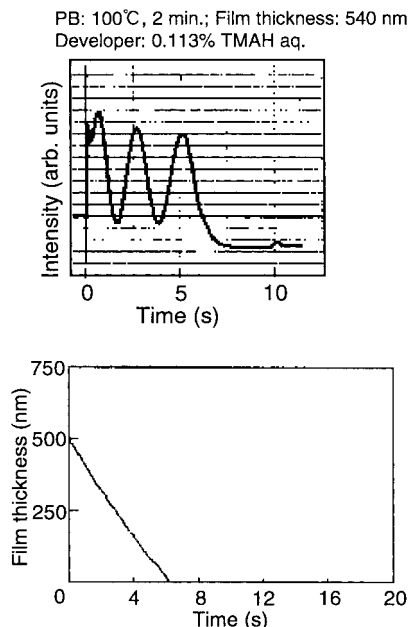


Figure 1. Dissolution behavior of polymer **1** measured by DRM.

*d*₆. The acid-catalyzed reaction of the resist was also investigated using infrared spectroscopy. The molecular weight of the polymer was measured using gel-permeation chromatography (GPC) with a Hitachi L-6000 liquid chromatography system calibrated with polystyrene standards in THF. The system was equipped with Gelpack A150, 140, and 120 GPC columns (Hitachi Chemical Co.).

Resist films were obtained by spin-coating from a solution in cyclohexanone onto silicon substrates. The resist films were baked on a hot plate at 70–130 °C. The thickness of the films was measured with an Alphastep 200 (Tencor Instruments) profilometer. The absorbance of the polymer films at 193 nm was measured with a Hitachi U-3410 UV spectrophotometer. The dissolution rate of the resist films was measured on a homemade interferometric dissolution rate monitor (DRM). The developer was an aqueous solution of tetramethylammonium hydroxide with a concentration of 0.113% or 2.38%.

Deep-UV exposures were made with a Xe–Hg lamp using an interference filter with a maximum transmittance at 250 nm. Lithographic evaluations were made with a Nikon ArF excimer laser stepper (0.55 NA).

Results and Discussion

Results of Polymer Synthesis and Structure Analysis. The molecular weight of the polymer before (copolymer **2**) and after reduction (polymer **1**) are shown in Table 1. The molecular weight (M_w) of copolymer **2** was about 6000; it became slightly smaller after reduction.

According to the literature,^{15,16} copolymerization between **3** and maleic anhydride involves an addition cyclization process yielding a 1:1 alternating copolymer. As a result, these copolymers had an alicyclic main chain and anhydride moiety, as shown in Scheme 3.

In the infrared spectrum of copolymer **2**, the carbonyl group of the acid anhydride appeared at 1860 and 1780 cm^{-1} , the ether linkage of the acid anhydride appeared at 1079 and 922 cm^{-1} , and the alkyl group appeared at 2945 and 2880 cm^{-1} .¹⁶ No remarkable olefin proton due to unreacted double bond of the diene was observed in the ¹H NMR spectrum.¹² In the infrared spectrum of polymer **1**, new peaks of the carbonyl group and the

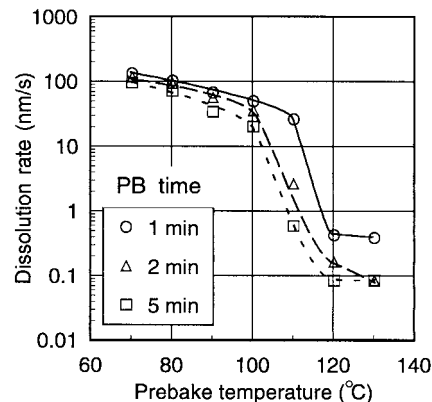


Figure 2. Dissolution rate of the film of polymer **1** as a function of PB temperature.

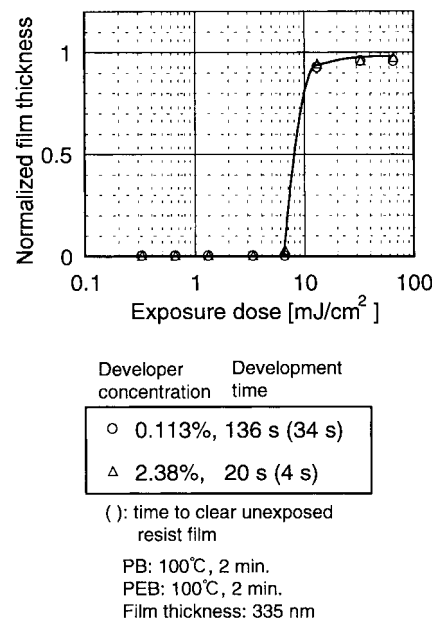


Figure 3. Exposure characteristic curves for polymer **1**/TPS resist. Polymer **1**/TPS = 100/5 (wt ratio).

ether linkage of γ -lactone appeared at 1766 and 1180 cm^{-1} , and the peaks of the acid anhydride almost disappeared. A broad peak due to the carboxylic acid and the hydroxyl group of γ -hydroxy acid appeared at 2400–3600 cm^{-1} . The carbonyl group of γ -hydroxy acid appeared at 1704 cm^{-1} . Therefore, polymer **1** was found to contain both γ -lactone and γ -hydroxy acid structures.

Properties of Alicyclic Polymer Having γ -Hydroxy Acid Structure. Polymer **1** showed a relatively small absorption of 0.81 μm^{-1} at 193 nm. Compared to copolymer **2** ($A = 1.1 \mu\text{m}^{-1}$), which has a cyclic acid anhydride structure, the absorption became smaller by reduction. Therefore, an alicyclic polymer having γ -hydroxy acid structure seems to be suitable as the polymer for ArF excimer laser resists.

The dissolution behavior of polymer **1** in aqueous TMAH (0.113%) as measured by DRM is shown in Figure 1. The amplitude of the reflective intensity of the monitor light barely changed during the development, and an induction time was not observed. The dissolution rate was 80 nm/s. This means that the film of polymer **1** dissolves gradually in the developer without swelling or roughing. Polymer **1** has am-

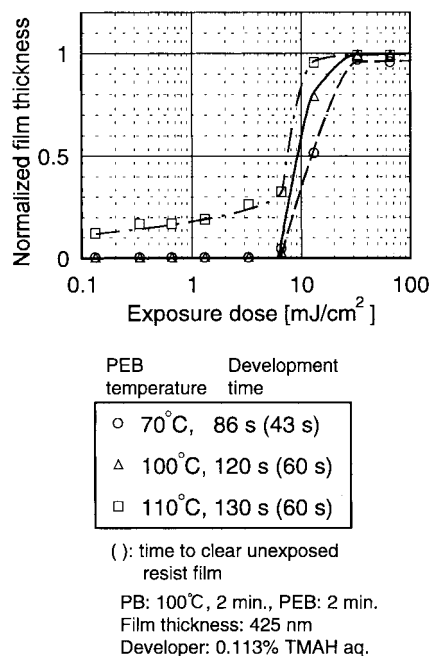


Figure 4. Effect of PEB temperature on exposure characteristic curves. Polymer 1/TPS = 100/5 (wt ratio).

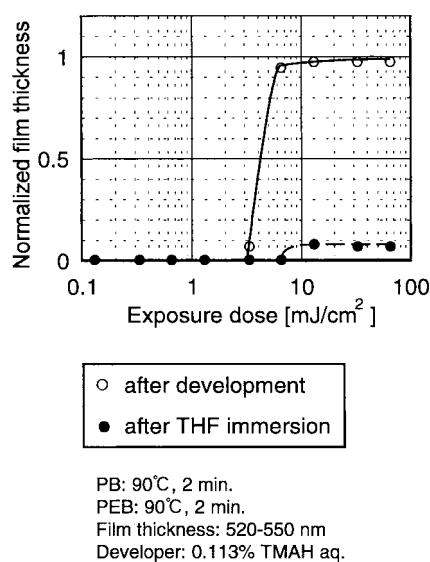
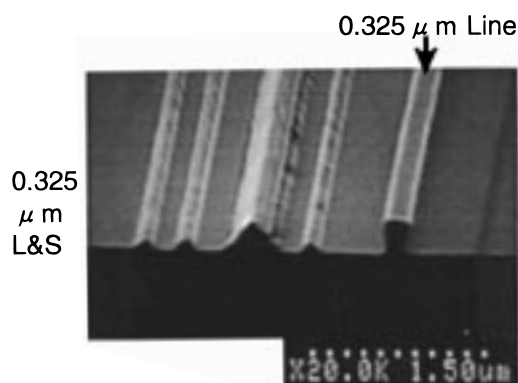
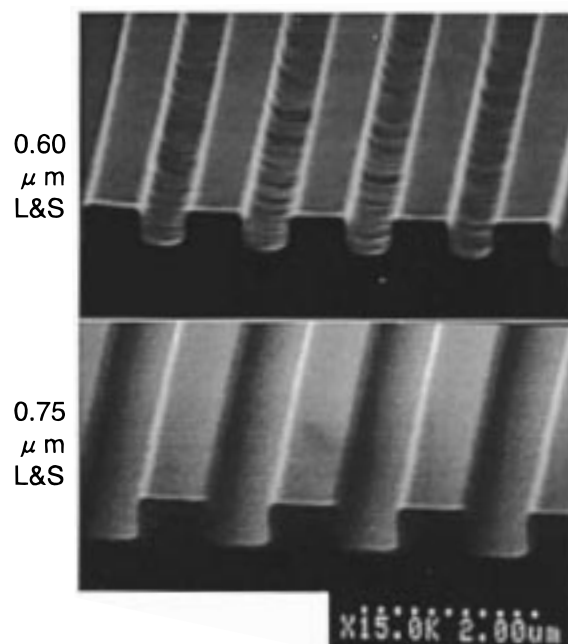


Figure 5. Change in film thickness of polymer 1/TPS resist (100/5 wt ratio) after THF immersion (60 s).

phiphilic structure, a hydrophobic alicyclic main chain with hydrophilic γ -hydroxy acid groups, like that of novolak resin. Therefore, the dissolution characteristics are as good as those of phenolic resins.

The dissolution rate of the film of polymer 1 is plotted as a function of the prebake (PB) temperature in Figure 2 for three PB times. The dissolution rate varied with the PB temperature; it was 0.1–100 nm/s in 0.113% aqueous TMAH developer. The dissolution rate decreased gradually with an increasing PB temperature below 100 °C. It dropped drastically when the PB temperature was more than 100 °C. This is considered to be due to intramolecular esterification of the γ -hydroxy acid to γ -lactone. Houlihan et al. reported that poly(norborne-*alt-cis*-4-hydroxy-2-butenic acid), which has γ -hydroxy acid structure, is thermally stable up to 150 °C.¹⁹ The different thermal stabilities of the two



Resist: Polymer 1/TPS=100/3 (wt. ratio)
 Film thickness: 560 nm

Figure 6. SEM photographs of patterns produced by ArF excimer stepper (0.55 NA) with polymer 1/TPS resist.

polymers indicates that the thermal stability of γ -hydroxy acid depends on the polymer structure.

Two-Component Resist Systems Using Polymer 1. Using polymer 1 and TPS (5 wt %), we prepared a two-component resist system. The exposure characteristic curves of the resist are shown in Figure 3. The resist was exposed by 250-nm deep-UV light and developed in 0.113% or 2.38% aqueous TMAH developer. This two-component resist functioned well as a negative resist with high sensitivity ($10 \text{ mJ}/\text{cm}^2$) and high contrast. The sensitivity was independent of the developer concentration.

The exposure characteristic curves of the resist with different postexposure baking (PEB) temperatures are shown in Figure 4. The unexposed part of the resist became insoluble when the PEB temperature exceeded 100 °C, due to the intramolecular esterification of the γ -hydroxy acid to γ -lactone, as shown in the previous

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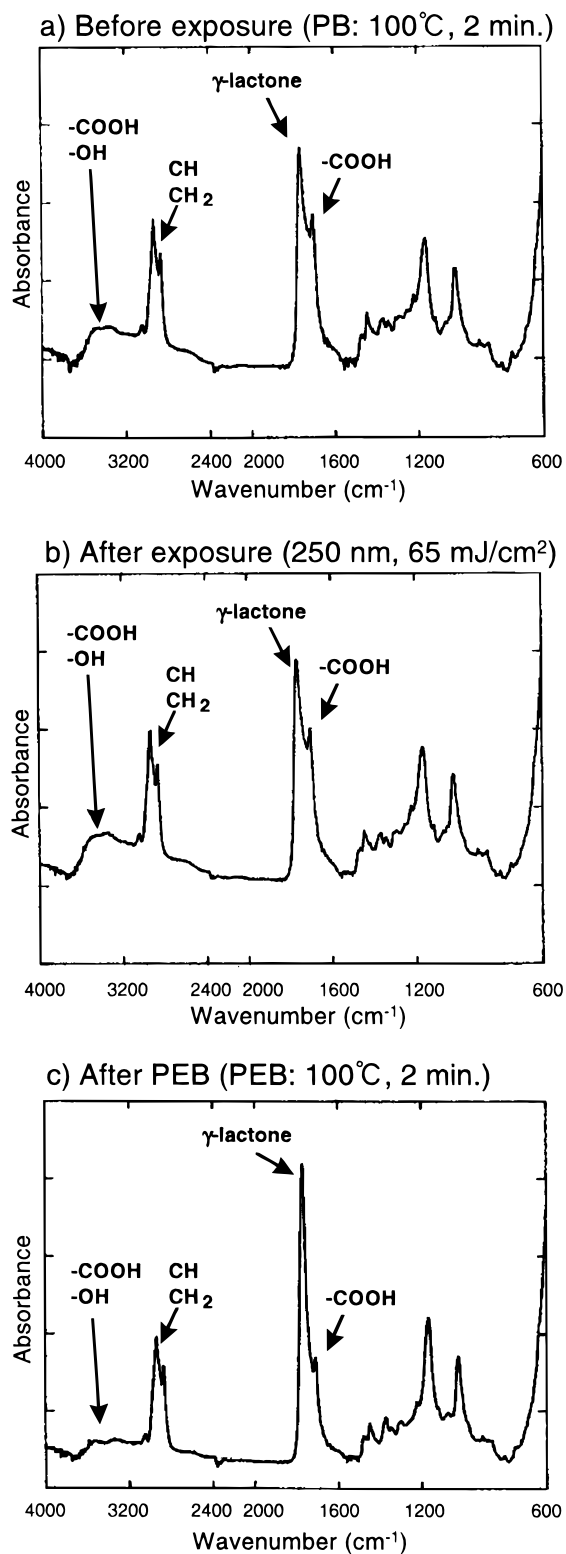


Figure 7. Infrared spectra of resist composed of polymer 1/TPS (100/5 wt ratio) (a) before exposure, (b) after exposure, and (c) after PEB.

section. When the PEB temperature was below 100 °C, the sensitivity was not much affected. As we examined the effect of TPS concentrations, sensitivity was found to vary from 30 to 3 mJ/cm² depending on the TPS concentration (2–10 wt %).

Figure 5 shows the gel formation characteristics obtained by immersing the resist films in tetrahydro-

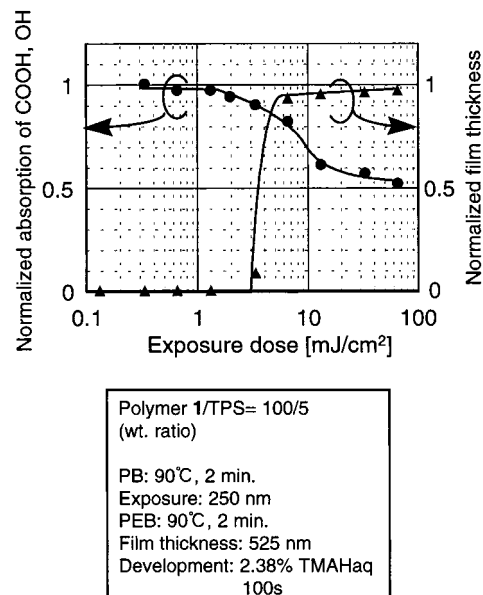


Figure 8. Normalized amount of COOH and OH as a function of exposure dose.

furan (THF) after aqueous base development. The normalized film thickness drastically decreased after THF immersion for 60 s. Because THF is a good solvent for all components of the resists, these results show that gel formation barely occurred in this resist system. Therefore, the insolubilization of the resist system is mainly due to intramolecular esterification of the γ -hydroxy acid to γ -lactone. Furthermore, intermolecular esterification, which causes cross-linking, hardly occurs.

The polymer 1/TPS = 100/3 (wt ratio) resist was patterned using an ArF excimer laser stepper. (Process conditions: prebake at 90 °C for 2 min, PEB at 90 °C for 2 min, and development in TMAH (2.38%) for 40 s.) As shown in Figure 6, 0.75- μ m line-and-space patterns were achieved by using a resist film thickness of 0.56 μ m with a dose of 19.5 mJ/cm². We could not obtain smaller line-and-space patterns because of the incomplete dissolution of the unexposed area in fine patterns or the collapse of the patterns. However, a 0.325- μ m isolated line pattern was obtained without swelling distortion. Therefore, using γ -hydroxy acid structure makes it possible to obtain negative ArF resists that can produce fine patterns without swelling distortion.

Acid-Catalyzed Reaction of Polymer 1. The acid-catalyzed reaction of polymer 1 was measured using infrared spectroscopy. Figure 7 shows the infrared spectra of the resist film (polymer 1/TPS = 100/5 (wt ratio)) coated on sodium chloride substrates. No remarkable changes were observed with deep-UV exposure at a dose of 65 mJ/cm² (Figure 7b). After postexposure baking, the absorption at 2400–3600 cm⁻¹, which was due to carboxylic acid and hydroxyl groups, drastically decreased. Furthermore, the absorption of the carbonyl group of γ -hydroxy acid at 1704 cm⁻¹ also became smaller. In contrast, the absorption at 1769 cm⁻¹ due to the ester structure, especially γ -lactone, distinctly increased.

This kind of drastic change in the amount of COOH and OH was not observed in the resist previously reported,¹⁴ which was composed of alicyclic polymers

having half-acid ester structure, an aliphatic carbinol, and a photoacid generator and showed swelling distortion. Considering that gel formation hardly occurs in this resist system, as shown in the previous section, the acid-catalyzed reaction of polymer **1** is considered to be mainly intramolecular esterification of the γ -hydroxy acid to γ -lactone, as expected.

We measured the area of the absorption at 2400–3600 cm^{-1} due to carboxylic acid and hydroxyl groups by using infrared spectroscopy and plotted the normalized amount of COOH and OH as a function of the exposure dose (Figure 8). We found that the amount of COOH and OH drastically decreased at about 5 mJ/cm^2 of the exposure dose. This dose corresponds to the dose of residual film thickness become about 1.0 after development. The amount of γ -hydroxy acid in the insoluble part after development was found to be 50–60% of the amount in the unexposed region.

In the resist using polymer **1**, our alicyclic polymer with γ -hydroxy acid structure, the number of carboxyl groups is reduced drastically in the exposed area. As a result, the swelling distortion of sub-micrometer patterns can be avoided. Although the resolution capability of this resist is poor at present, this approach is a key to obtaining aqueous alkali developable negative ArF single-layer resists that do not cause swelling distortion.

Conclusion

We have developed alicyclic polymer **1** having γ -hydroxy acid structure by reduction of a nonconjugated cyclic diene and maleic anhydride copolymer. This polymer has an amphiphilic structure: a hydrophobic alicyclic main chain with hydrophilic γ -hydroxy acid groups. Polymer **1** exhibited moderate transparency ($0.8 \mu\text{m}^{-1}$) at 193 nm and good alkali solubility (0.1–100 nm/s in 0.113% aqueous TMAH). A two-component negative resist system, consisting of polymer **1** and onium salt, produced sub-micrometer patterns without swelling distortion by using an ArF excimer laser stepper. Infrared spectroscopy indicated that insolubilization occurred due to intramolecular esterification of γ -hydroxy acid to γ -lactone. As a result, the number of carboxyl groups decreased drastically in the exposed area, so that swelling distortion of sub-micrometer patterns could be avoided. Therefore, the number of carboxyl groups in the exposed region needs to be drastically reduced to obtain aqueous alkali developable negative ArF single-layer resists.

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