Investigation of Acid-Catalyzed Insolubilization Reactions for Alicyclic Polymers with Carboxyl Groups

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Acid-catalyzed insolubilization reactions between novel amphiphilic alicyclic polymers (named ALPHA) and aliphatic carbinols have been investigated for aqueous base-developable ArF single-layer negative resist. The combination of an ALPHA polymer (PMBH-BHMTCD) and an aliphatic carbinol (1,4-dioxane-2,3-diol (DD)) exhibited the highest insolubilization reactivity. It was found that the resist composed of PMBH-BHMTCD, DD, and N-trifluoromethanesulfonyloxynaphthalimide showed high dissolution rate contrast. However, the obtained patterns showed swelling distortion in the sub- μm range. FT-IR spectrometry indicated that the dominant insolubilization reaction was the crosslinking induced by acid-catalyzed etherification. It is concluded that the swelling distortion in the sub- μm range was due to remaining carboxyl groups in the exposed area.

Keywords: amphiphilic alicyclic polymers, ArF single-layer negative resist, aliphatic carbinol, etherification

1. Introduction

ArF excimer laser lithography is expected to be the major fabrication technology for 1-Gbit DRAM fabrication. However, the critical dimension will become smaller than 0.2 μm for 1-Gbit DRAM. This size is comparable to the wavelength of ArF excimer laser light (193 nm). Therefore, ArF excimer laser lithography is likely to be used practically in conjunction with a resolution enhancement technique such as a phase-shifting mask [1,2]. Negative resist systems are required for the phase-shift lithography.

This paper deals with acid-catalyzed insolubilization reactions of alicyclic polymers with carboxyl groups for aqueous base-developable ArF single-layer negative resist. Alicyclic groups, such as adamantyl [3], norbornyl [4], isobornyl [5], and tricyclodecanyl [6], have been introduced to the methacrylate polymer-based positive ArF resist system because of their high transparency and good dry etching resistance. Recently, polymers with alicyclic groups in their main chain have been applied to ArF positive resist systems [7, 8]. In this study, we used novel alicyclic polymers having half-acid ester structure (ALPHA) [9] that exhibited moderate transparency at 193 nm, good dry etching

resistance, and good aqueous-base solubility characteristics.

We examined various acid-catalyzed insolubilization reactions which have been applied to novolak or phenolic resin-based negative resists. A typical acid-catalyzed cross-linker for phenolic resin-based negative resist, hexamethoxymethylmelamine (HMMA) [10] is an effective cross-linker for aliphatic polymers with carboxyl groups. However, HMMA shows too much absorbance at 193 nm because of its aromatic structure.

Aromatic carbinol compounds were another candidates for the acid-catalyzed insolubilization reagents. They have various acid-catalyzed reactivities such as pinacol rearrangement [11], etherification [12], and intramolecular dehydration [13,14]. These reactions are caused by the OH groups in carbinol, which do not depend on the aryl structures. Therefore we selected several aliphatic carbinols as transparent insolubilization reagents for ArF negative resist systems.

2. Experimental

2.1. Materials

ALPHA polymers [9] used in this study are a series of various alcohol-hydrolyzed products of 5-

methylene-bicyclo(2.2.1)-2-heptene and maleic anhydride copolymer (PMBH). ALPHA has an amphiphilic structure in the monomer unit that is similar to phenolic resins widely used as the base resin for various high performance resists. By using various alcohols for the alcoholysis, dissolution characteristics and reactivities of ALPHA can be changed. Structures and abbreviations of ALPHA polymers investigated in this work are listed in Table 1.

Table 1. Molecular structures of ALPHA polymers used in this work.

ALPHA polymers
PMBH-Me	R = -CH ₃
PMBH-Pr	-CH(CH ₃) ₂
PMBH-CE	-CH ₂ CH ₂ -
PMBH-Ad
PMBH-NM	-CH ₂ -
PMBH-BHMTCD	HOCH ₂ - -CH ₂ -

Aliphatic carbinols used here were 1,4-dioxane-2,3-diol (DD) purchased from Tokyo Kasei Kogyo Co. and 2-methyl-2-adamantanol (2-Me-2-AdOH) obtained from Aldrich Co. N-trifluoromethanesulfonyloxynaphthalimide (NIOTF) synthesized in this laboratory was used as a photo acid generator (PAG) in this work. Chemical structures of these compounds are shown in Figure 1.

Fig. 1. Molecular structures of compounds used in this work.

The developer was an aqueous solution of tetramethylammonium hydroxide (TMAH) with an appropriate concentration. Tetrahydrofuran (THF) was used to confirm the gel-formation characteristics of a sample resist system.

2.2. Resist composition and processing

Resist formulations were prepared by dissolving the ALPHA polymer, PAG, and aliphatic carbinols described above in cyclohexanone. Resist films were spin-coated from the formulations onto silicon substrates, prebaked (PB) on a hot-plate at 100 °C for 5 min, and then exposed to deep-UV radiation from a Xe-Hg lamp through (or without) an interference filter (250 nm). After post-exposure baking (PEB) on a hot-plate at 100 °C for 5 min, the resist films were developed in an aqueous TMAH solution developer. After the development, the resist films were rinsed with de-ionized water. Lithographic evaluations were made by using a Canon KrF excimer laser stepper (NA = 0.45).

2.3. Characterization

The film thickness was determined with an Alpha Step 200 (Tencor) profilometer. The infrared difference spectrum was measured with a Perkin-Elmer FT-IR 1720X spectrometer. Sample films were spin-coated onto a sodium chloride substrate.

3. Results and Discussion

3.1. Insolubilization reagents

In the course of the study of negative resists utilizing acid-catalyzed carbinol reactions [11-13], it was found that several aliphatic carbinols act as effective reagents for novolak resin based negative resists. As aliphatic structures have the advantage of transparency at 193 nm, we examined these aliphatic carbinols as the insolubilization reagent for aliphatic polymers with carboxyl groups. It was found that 1,4-dioxane-2,3-diol (DD) and 2-methyl-2-adamantanol (2-Me-2-AdOH) have relatively high reactivity among aliphatic carbinols. Therefore, the insolubilization reaction induced by aliphatic carbinols can be applied to the ArF single-layer negative resist system. In the following section, we examine DD and 2-Me-2-AdOH as the insolubilization reagents for ALPHA polymers.

Reactivity of ALPHA polymers with DD and 2-Me-2-AdOH was evaluated by using model resist compositions (ALPHA/DD or 2-Me-2-AdOH/NIOTF=100/20/5 weight ratio). Each resist composition film was fully exposed to radiation from a Xe-Hg lamp without an interference filter. Table 2 lists relative remaining film thickness obtained after PEB and development. In Table 2, it can be seen that ALPHA polymers with large ester structures, such as PMBH-CE, -Ad, and -BHMTCD, have high reactivity with carbinols. In particular, the combination of PMBH-BHMTCD

Table 2. Film Thickness ratio of unexposed to exposed region for a Xe-Hg lamp exposure.

PMBH polymer/aliphatic carbinol/NIOTF=100/20/5 (wt. ratio)

ALPHA polymers	aliphatic carbinols	
	2-Me-2-AdOH	DD
PMBH-Me	0	0
PMBH-Pr	0	0
PMBH-CE	0.74	0.38
PMBH-Ad	0.5	0
PMBH-NM	0	0
PMBH-BHMTCD	0.47	1

and DD shows the highest remaining thickness. This suggests high sensitivity for deep-UV exposure.

Figure 2 shows the deep-UV exposure characteristic of the resist composition: PMBH-BHMTCD/DD/NIOTF = 100/20/5. As shown in Figure 2, the resist system shows high sensitivity and contrast. However, the resist using the other ALPHA polymers, such as PMBH-CE and -Ad, have no sensitivity for deep-UV exposure. PMBH-BHMTCD has a hydroxymethyl group ($-\text{CH}_2\text{OH}$) in its ester structure. This structure is different from the other ALPHA polymers evaluated in this experiment. It was reported that etherification of secondary alcohol compounds was responsible for the insolubilization of the novolak resin based resist system [12]. Therefore, it is considered that the dehydration reaction occurs between the hydroxy group in DD and the hydroxymethyl group in the PMBH-BHMTCD, which causes the insolubilization of the PMBH-BHMTCD resist system.

In Figure 3, the dissolution rate change of the resist (PMBH-BHMTCD/DD/NIOTF = 100/20/5) film is plotted as a function of exposure dose. The dissolution rate in the fully exposed region, dose range of 70 - 400 mJ/cm^2 , is about 7×10^{-2} nm/s . On the other hand, the dissolution rate in the unexposed region is about 45 nm/s . As the dissolution rate ratio of unexposed to exposed area is about three orders of magnitude, a high resolution capability for this resist can be expected.

3.2. Lithographic performance

Patterning of the resist (PMBH-BHMTCD/DD/

Fig. 2. Sensitivity curve of the resist system with PMBH-BHMTCD polymer.

PMBH-BHMTCD/DD/NIOTF=100/20/5 (wt. ratio)

PEB: 100 °C 5 min

Development: 0.12 %TMAH solution

Fig. 3. Dissolution rate of the PMBH-BHMTCD resist as a function of exposure dose.

PMBH-BHMTCD/DD/NIOTF=100/20/5 (wt. ratio)

PEB: 100 °C 5 min

Development: 0.12 %TMAH solution

NIOTF = 100/20/5) was carried out with a KrF excimer laser stepper. Process conditions were as follows: prebake at 100 °C for 2 min, PEB at 100 °C for 2 min, and development in TMAH solution (0.12%) for 40 sec. As shown in Figure 4(a), 1- μm line-and-space patterns were achieved by using a resist film thickness of 0.6 μm with a dose of 47 mJ/cm^2 . However, we could not obtain sub- μm patterns because of the swelling distortion of line patterns (shown in Figure 4(b)). As shown in Figure 3, the resist exhibited large enough dissolution rate ratio of unexposed to exposed area. Therefore we investigated the insolubilization mechanism of the resist system in the following section.

Fig. 4. SEM photographs of patterns produced by a KrF excimer laser stepper (NA=0.45) with the resist composed of PMBH-BHMTCD/DD/NIOTF (100/20/5 wt. ratio)

- (a) 1- μm line-and-space patterns with a dose of 47 mJ/cm^2
 (b) Isolated line patterns with a dose of 67 mJ/cm^2

3.3. Insolubilization mechanism

Figure 5 shows gel-formation characteristics of the resist PMBH-BHMTCD/DD/NIOTF= 100/20/5 obtained by immersing it into THF solvent after aqueous base development. In Figure 5, the film thickness does not change after THF immersing for 60 sec. As THF is a good solvent for all the components of the resist, the obtained result shows that the gel-formation occurred in the resist system. Therefore, it is suggested that the insolubilization of the resist system is due to the cross-linking to yield gelation.

Fig. 5. Film thickness change of the PMBH-BHMTCD resist before and after THF immersing. PMBH-BHMTCD/DD/NIOTF=100/20/5 (wt. ratio)

PEB: 100 $^{\circ}\text{C}$ 5 min
 Development: 0.12 %TMAH solution

Figure 6 is the IR difference spectrum between before and after deep-UV exposure at a dose of 200 mJ/cm^2 with PEB. The IR difference spectrum shows decreases in the C-O stretching band of alcohol (1017 cm^{-1}) and the C=O stretching band of carboxylic acid (1721 cm^{-1}). On the other hand, the C-O-C stretching band of ether (1068 cm^{-1}) and the C=O stretching band of the carboxylic acid ester (1750 cm^{-1}) appear in the IR difference spectrum. These IR absorption band changes indicate that the acid-catalyzed etherification and esterification occur in the exposed region of the resist. However, the intensity of the increasing ester C=O stretching band is weak compared with that of the increasing ether C-O-C stretching band. Therefore it is found that the etherification is more dominant than the esterification in the resist matrix. The insolubilization of the resist system is concluded to be caused by the cross-linking due to the etherification occurring between DD and the hydroxymethyl group ($-\text{CH}_2\text{OH}$) belonging to the ester structure.

The spectrum also shows that almost all carboxylic acid groups remain in the exposed region of the resist film. The exposed region is insoluble for the aqueous base solution because of the acid-catalyzed cross-linking; however, the number of carboxylic acid groups is nearly the same in each exposed/unexposed region. Therefore, it is suggested that the swelling of fine exposed patterns induced by the penetration of the aqueous alkali

Fig. 6 Infrared difference spectrum before and after post exposure baking
(deep-UV exposure dose is 200 mJ/cm²)
PMBH-BHMTCD/DD/NIOTF=100/20/5 (wt. ratio)
PEB: 100 °C 5 min, Development: 0.12 %TMAH solution

developer is due to the remaining carboxylic acid groups in the exposed area.

It is noted that the remaining carboxylic groups in the exposed region play an important role in the negative-tone reaction of alicyclic polymers with carboxyl groups. In order to avoid the swelling, it is necessary to reduce the number of carboxyl groups drastically in the exposed region or find effective dissolution inhibitors for alicyclic polymers with carboxyl groups. The swelling due to the remaining carboxylic groups in the exposed region is a critical issue for the application of carboxylate polymers as the base resin of negative resist systems.

4. Conclusion

Aliphatic carbinols were investigated as the transparent insolubilization reagents for the aqueous base-developable ArF single-layer negative resist. A novel amphiphilic alicyclic polymer, ALPHA, was used as the base polymer for the resist. The resist, composed of PMBH-BHMTCD/DD/NIOTF, exhibited the highest insolubilization reactivity. It was found that the resist showed high dissolution rate contrast and it was expected to show good lithographic performance. However, obtained patterns by using a KrF excimer laser stepper showed swelling distortion in the sub- μ m range. FT-IR spectrometry indicated that the insolubilization due to the acid-catalyzed etherification

occurred in the PMBH-BHMTCD matrix. As a result, the number of carboxyl groups was nearly the same in each exposed / unexposed region and this caused the swelling of fine exposed patterns due to the penetration of the aqueous base developer into the exposed area. Therefore it is necessary to reduce the number of carboxyl groups drastically in the exposed region or to find effective dissolution inhibitors for alicyclic polymers with carboxyl groups.

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References

1. M. D. Levenson, N. S. Viswanathan, and R. A. Simpson, *IEEE Trans. Electron Devices*, **ED-29** (1982) 1828; M. D. Levenson, D. S. Goodman, S. Lindsey, P. W. Bayer, and H. A. E. Santini, *IEEE Trans. Electron Devices*, **ED-31** (1984) 753.
2. T. Terasawa, N. Hasegawa, T. Kurosaki, and T. Tanaka, *Proc. SPIE*, **1088** (1989) 25.
3. Y. Kaimoto, K. Nozaki, S. Takechi, and N. Abe, *Proc. SPIE*, **1672** (1992) 66; S. Takechi, M. Takahashi, A. Kotachi, K. Nozaki, E. Yano, and I. Hanyu, *J. Photopolym. Sci. Technol.*, **9** (1996) 475.
4. M. Endo, K. Hashimoto, K. Yamashita, A.

- Katsuyama, T. Matsuo, Y. Tani, M. Sasago, and N. Nomura, *IEDM Tech. Digest 1992*, (1992) 45.
5. G. M. Wallraff, R. D. Allen, W. D. Hinsberg, C. F. Larson, R. D. Johnson, R. DiPietro, G. Breyta, N. Hacker, and R. R. Kunz, *J. Vac. Sci. Technol.*, **B11** (1993) 2783; R. D. Allen, I. Y. Wan, G. M. Wallraff, R. A. DiPietro, D. C. Hofer, and R. R. Kunz, *J. Photopolym. Sci. Technol.*, **8** (1995) 623.
 6. K. Nakano, K. Maeda, S. Iwasa, J. Yano, Y. Ogura, and E. Hasegawa, *Proc. SPIE*, **2195** (1994) 194; K. Maeda, K. Nakano, T. Ohfuji, and E. Hasegawa, *Proc. SPIE*, **2724** (1996) 377.
 7. R. D. Allen, R. Sooriyakumaran, J. Opitz, G. M. Wallraff, R.A. DiPietro, G. Breyta, D. C. Hofer, R. R. Kunz, S. Jayaraman, R. Shick, B. Goodall, U. Okoroanyanwu, and C. G. Willson, *Proc. SPIE*, **2724** (1996) 334; R. D. Allen, R. Sooriyakumaran, J. Opitz, G. M. Wallraff, G. Breyta, R. A. DiPietro, D. C. Hofer, R. R. Kunz, U. Okoroanyanwu, and C. G. Willson, *J. Photopolym. Sci. Technol.*, **9** (1996) 465.
 8. T. I. Wallow, F. M. Houlihan, O. Nalamasu, E. A. Chandross, T. X. Neenan, and E. Reichmanis, *Proc. SPIE*, **2724** (1996) 355.
 9. T. Hattori, Y. Tsuchiya, R. Yamanaka, K. T. Hattori, and H. Shiraishi, *J. Photopolym. Sci. Technol.*, submitted.
 10. J. W. Thackeray, G. W. Orsula, M. M. Rajaratnam, R. Sinta, D. Herr, and E. Pavelchek, *Proc. SPIE*, **1466** (1991) 39.
 11. S. Uchino, T. Iwayanagi, T. Ueno, and N. Hayashi, *Proc. SPIE*, **1466** (1991) 429.
 12. S. Uchino, M. Katoh, T. Sakamizu, and M. Hashimoto, *Microelectronic Eng.*, **18** (1992) 341.
 13. T. Ueno, S. Uchino, K. T. Hattori, T. Onozuka, S. Shirai, N. Moriuchi, M. Hashimoto, and S. Koibuchi, *Proc. SPIE*, **2195** (1994) 173.
 14. S. Migitaka, S. Uchino, T. Ueno, J. Yamamoto, K. Kojima, M. Hashimoto, and H. Shiraishi, *Proc. SPIE*, **2724** (1996) 613.