ALKYLATED POLY(4-HYDROXYSTYRENE) DERIVATIVES FOR DEEP ULTRAVIOLET LITHOGRAPHY

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Alkylated Poly(4-hydroxystyrene) copolymers have been prepared and evaluated for use in deep-uv lithography. These materials have been modified to lower the dissolution rates of poly(4-hydroxystyrene) while maintaining the other desirable properties such as optical absorbance, glass transition temperature, and etch resistance. Lower dissolution rates make these polymers more attractive for application in dissolution inhibition resist schemes. The application of these materials to resists employing diazo compound inhibitors and three component resists using acid photogenerators and acid-sensitive dissolution inhibitors is described.

1. Introduction

Although current resist materials in combination with advanced exposure tools and processing techniques are adequate for the current generation microelectronic device fabrication, new materials will probably be required for the 0.35 micron geometries necessary for 64 MB DRAM devices. This is due to practical resolution limitations imposed by 365 nm optical lithography. For higher resolution, shorter wavelength deep-uv irradiation is necessary. A recent survey of Japanese electronics companies indicated that 50% of these memory device manufacturers were planning to use deep-uv lithography for 64 MB DRAM.¹ The other half will use 365 nm lithography in conjunction with phase shifted masks.

The standard diazonaphthoquinone/novolac resists used at 365 nm are positive working resists which function on the basis of dissolution inhibition. The novolac polymers which are used for these applications have many desirable physical properties including moderate dissolution rates in aqueous base solution, high optical transmission at 365 nm, glass transition temperatures higher than 100 ° C, and reasonable reactive ion etch resistance.² However the application of novolac polymers in optical lithography is limited to wavelengths greater than 300 nm due to the high, unbleachable absorption at shorter wavelength. The effect of high residual absorption has been predicted based on resist modeling to give rise to images with highly sloping side walls³ and this effect has been observed experimentally.⁴ The deep-uv optical properties of

novolac polymers were improved by using p-cresol monomer⁵ but the lithographic performance of this polymer was limited because of a high dose requirement resulting from the need for nearly complete conversion of the dissolution inhibitor in order to develop the exposed film.

Poly(4-hydroxystyrene) (PHS) has considerably better optical properties at 248 nm than novolac as well as superior thermal properties and similar etch resistance. However the aqueous base dissolution rates of PHS films are faster than novolac by a factor of about ten. Higher dissolution rates, in general, lower the performance of dissolution inhibition type photoresists. Resist films comprised of diazonaphthoquinone in PHS show poor dissolution rate discrimination between exposed and unexposed film.⁶ However sulfonium salt dissolution inhibitors containing acid-labile sidegroups function very well lithographically in PHS.⁷

The aqueous base dissolution rates of PHS can be lowered by the incorporation of alkyl groups in the aromatic rings of PHS. Polymeric derivatives containing alkyl groups at the 3 and/or 5 positions have dissolution rates in aqueous base very similar to novolac. This modification makes the use of PHS more widely applicable for photoresist applications which use dissolution inhibition. Furthermore this structural change does not adversely affect the optical, thermal, and etch resistance properties of PHS.

2. Experimental

Materials:

Triphenylsulfonium hexafluoroantimonate (1) was prepared by a literature procedure.⁸ Dicarbonate (2) was prepared by reaction of bisphenol A with di-*t*-butyldicarbonate.⁹ 3,5-dimethyl-4-*t*-butoxycarbonyloxystyrene (3) was prepared in two steps from commercially available 3,5-dimethyl-4-hydroxybenzaldehyde (4). 4-*t*-Butoxycarbonyloxystyrene (5) was prepared as described previously.¹⁰ The *t*-butoxycarbonyloxy (t-BOC) protected precursor copolymer (6) was prepared by radical polymerization of 3 and 5 in toluene solution with benzoylperoxide initiator. Phenolic copolymer (7) was formed by heating a chloroform solution of 6 with trifluoroacetic acid.

Scheme 1. Preparation of 3,5-dimethyl PIIS derivatives

Measurements:

^1H and ^{13}C NMR analyses were performed on an IBM instruments AF250 spectrometer. Ultraviolet spectra were recorded on a Hewlett-Packard Model 8450A UV/Visible Spectrometer. Thermal analyses were done on a DuPont DSC 1090 instrument. Molecular weights were determined on a Waters Model 150C Liquid/Gel Permeation Chromatograph with refractive index detector (polystyrene standards). Dissolution kinetics were determined from rate data generated on a Perkin Elmer Developmental Rate Monitor Model 5900.

Lithographic Evaluation:

Films were prepared by spin coating of filtered solutions. A postapply bake was performed at 90°C for 5 minutes on a hot plate. Exposure was performed followed by postexposure bake on a hot plate. Contact optical exposures were performed on an Optical Associates 30/5 Exposure Tool through 254 nm band pass filters. Projection printing was done with a Perkin Elmer 500 Micralign Exposure System with a 300 nm band pass filter or with an Ultratech X248E deep-uv stepper. Post exposure bake was done at 70-90°C for 90 seconds. Development was performed by immersion in a rapidly stirred developer solution.

3. Results and Discussion

Preparation of alkylated PHS derivatives

The effect of alkyl substituents was evaluated by a modeling program which was used to compute aqueous hydration energy. The results of these calculations showed that alkyl substituents at the 3 and 5 positions of poly(4-hydroxystyrene) significantly affect the hydration energy and would be expected to lower the dissolution rates of the resin with aqueous base.

The 3,5-dimethyl PHS copolymers **7** were synthesized as shown in Scheme 1. The dimethyl monomer (**3**) was prepared by reaction of benzaldehyde derivative **4** with di-*t*-butyldicarbonate followed by reaction with the methylene Wittig reagent. Radical copolymerization of **3** and **5** gave a random copolymer whose composition varied only slightly from the feed ratio. The removal of *t*-BOC functionality was performed by heating with trifluoroacetic acid.

Polymer properties

The copolymers were analyzed by ^1H NMR to determine the composition. For a series of varying compositions of copolymer **7**, the mole fraction of dimethyl component in the copolymer (**X**) was nearly equal to the mole fraction in the feed.

The glass transition temperatures for copolymers **6** and **7** were measured by DSC analysis. For the *t*-BOC protected copolymer **6** an increase in the mole fraction of the methylated component lead to a slight increase in the glass transition temperature. For the phenolic copolymer **7**, however, increases in the methylated component resulted in a decreased T_g (Table 1).

X	T _g (DEG C)	
	COPOLYMER 6	COPOLYMER 7
0	129	188
.25		182
.40	127	179
.60	133	175
.75	135	172
1.0		159

Table 1. Glass transition temperatures for copolymers 6 and 7

As expected from model studies, the dissolution rates of these copolymers is strongly dependent on copolymer composition. The dissolution rate in 0.27 N potassium hydroxide solution was measured using a dissolution rate monitor and is shown in Figure 1 plotted versus the mole fraction of the dialkyl substituted component (X). Increasing X dramatically decreases the dissolution rate. Copolymer with X = 0.4 has a dissolution rate which is an order of magnitude less than PHS and thus in the same range as novolac. Material with X in the range 0.4-0.5 was most useful for lithographic applications.

Figure 1. Effect of copolymer composition on the dissolution rates with 0.27N KOH solution.

The ultraviolet absorbance was measured for the copolymers 7. As expected, incorporation of the methyl substituents had little effect on the PHS deep-uv optical properties. Novolac film is also shown for comparison (Table 2). The absorbance of the copolymer at 248 and 254 nm is significantly improved relative to novolac and is low enough to make this material applicable for deep-uv photoresists.

POLYMER	ABSORBANCE (MICRON) ⁻¹	
	248 NM	254 NM
COPOLYMER 7 (X = .4)	.21	.25
NOVOLAC (VARCUM 6000-7)	.71	.49

Table 2. Absorbance value for 7 and novolac at deep-uv wavelengths.

The etch resistance of these materials was evaluated and compared with novolac resin. The films were etched using a reactive ion etcher with an oxygen plasma. The etch rates of the copolymer 7 was found to be similar to that of novolac.

Lithographic properties

When formulated with a diazonaphthoquinone derivative (4-cumylphenyl ester of 2-diazo-1-naphthoquinone-4-sulfonic acid) and exposed with near-uv radiation, alkylated PHS derivatives function in a fashion similar to DNQ/novolac resists. Film dissolution studies were carried out by quartz crystal microbalance (qcm) analysis.¹¹ The resist films show typical positive photoresist behavior, i. e. increases in dissolution rate with increasing exposure. No induction period (delay before the onset of development) was observed. Images were obtained by projection printing with a 300 nm filter on a Perkin-Elmer 500 exposure tool. The images (Figure 2) show nearly vertical wall profiles for 1.25 micrometer (μm) dimension features.

DNQ sensitizers are not well suited for application at deep-uv wavelengths because the photoproducts are not transparent in this region. However other classes of diazo compounds do photobleach in the deep-uv region and have been applied as deep-uv photoresist sensitizers. One such class is the diazopiperidinedione sensitizers which have been successfully imaged when combined with novolac resin.¹² The contrast of this binary resist system is quite poor ($\gamma = 1.3$) due to a combination of resin absorbance and poor selectivity of the photoproduct toward reaction with phenolic resin.

Figure 2. SEM micrographs of 1.25 micron features obtained from exposure of DNQ/7 films.

Binary resists prepared from diazopiperidinediones and alkylated PIIS derivatives were evaluated as deep-uv resists. The resist films showed positive resist characteristics with contrast ($\gamma = 1.6$) slightly improved relative to the novolac version of the same resist. Projection printed images show highly rounded image profiles. Low contrast for this resist system is most likely due to an undesirable side reaction between the diazopiperidinedione photoproduct and the resin.

The use of acid sensitive dissolution inhibitors was also explored. These are three component resist systems containing phenolic resin, acid photogenerator 1, and acid-sensitive dissolution inhibitor 2. This resist system (BPABOC) was investigated previously using novolac as the phenolic polymer¹³ and found to be a highly sensitive positive deep-uv photoresist. However the contrast ($\gamma = 1.8$) was low due to novolac absorption and as a result the image wall profiles were sloping and resolution was limited.

BPABOC was reinvestigated using alkylated PHS derivatives and found to be significantly improved relative to the novolac version. The sensitivity of BPABOC was less than 5 mJ/cm² and the contrast was greater than 3.0. Film dissolution rates were analyzed by qcm and significant induction effects were observed for unexposed and lightly exposed films. The significantly higher contrast for BPABOC in alkylated PHS is likely due to a combination of inductive effects and superior transmittance for the resin. Projection printed images of BPABOC in alkylated PHS have improved sidewall profiles as expected for higher contrast materials. Submicron resolution has been achieved using an Ultratech deep-uv stepper (Ultrastep X-248E) and 0.7 micron features are shown in Figure 3.

A comparison of dissolution rates was carried out for BPABOC resists formulated in four different resins systems. In all cases the composition of the resist was maintained at 12.5% 2, 4% 1, and 83.5% phenolic resin. The phenolic polymers which were investigated include copolymers of 3-ethyl-4-hydroxy-styrene and 4-hydroxystyrene, a copolymer of styrene and 4-hydroxystyrene, and novolac. The results show (Table 3) that the best dissolution rate

discrimination was obtained for the ethylhydroxystyrene copolymer containing 40% of the ethyl monomer unit.

Figure 3. SEM micrographs of 0.7 micron features obtained from exposure of BPABOC in alkylated PHS polymer on an Ultratech X-248E deep-uv stepper.

POLYMER	R (MICRON/M)	R _o (MICRON/M)	R/R _o
ST/HS	.88	.27	3.2
EtHS/HS (X = 0.6)	1.5	.020	73
EtHS/HS (X = 0.4)	1.3	<.01	>200
NOVOLAC	.91	.021	43

Table 3. Comparison of dissolution rates for BPABOC resist formulated in various phenolic resins.

4. Conclusions

Alkylated poly(4-hydroxystyrene) derivatives have been prepared and evaluated for deep-uv lithography applications. The copolymers showed a wide range of dissolution rates in aqueous base and, by proper choice of copolymer composition, dissolution rates identical with novolac resins can be obtained. The combination of lower dissolution rates and superior optical properties makes these materials attractive for use in dissolution inhibition resist schemes. Both binary resists using diazonaphthoquinone and three component acid-catalyzed resist perform well lithographically in these resins.

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