Novel anionic photoacid generators (PAGs) and corresponding PAG bound polymers for sub-50 nm EUV lithography

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A new series of anionic photoacid generators (PAGs) and corresponding polymers were prepared. The thermostability of PAG bound polymers was superior to that of PAG blend polymers. PAG incorporated into the polymer main chain showed improved resolution when compared with the PAG blend polymers. This was demonstrated by extreme ultraviolet lithography (EUVL) results: the fluorine PAG bound polymer resist gave 45 nm (1 : 1), 35 nm (1 : 2), 30 nm (1 : 3) and 20 nm (1 : 4) Line/Space as well as the 50 nm (1 : 1) elbow pattern.

1. Introduction

Extreme ultraviolet lithography (EUVL) at 13.5 nm wavelength has emerged as a leading candidate to meet the resolution requirements of the microelectronic industry roadmap.¹ Although critical dimensions below 50 nm have been achieved, extensive research still needs to be conducted in the development of EUV technology to meet the 32 nm and the lower 22 nm technology nodes.² In addition to developing the exposure tools themselves, significant challenges remain in developing photoresist materials with all of the required imaging properties. An EUV resist system requires high sensitivity, low outgassing, sub-50 nm resolution and low line-edge roughness (LER). In addition to meeting these imaging requirements, the resist should also provide adequate etch resistance for process implementation. Currently, the major challenge for resist development is to cope with all requirements simultaneously. Indeed, a fundamental interplay exists among the above mentioned issues, there is no clear path to meet resolution, LER and sensitivity requirements simultaneously.³ Chemical amplification (CA) serves as a key technology to enhance the sensitivity of the photoresists. The acid formed by the photoacid generator (PAG) on exposure catalyzes reaction during post-exposure baking (PEB), leading to a polarity change in the pendant protecting group of the resist polymer.⁴⁻⁶ Acid diffusion control in the PEB process during which deprotection progress occurs is important. Through diffusion, acid can be uniformly distributed in the resin matrix. In this case, LER would be improved, but acid also diffuses into the non-exposed areas, and this contributes to LER.7 The outgassing of resists has also been identified as a problem in EUV lithographic processes, because of organic films that can be deposited on an exposure lens which can cause transmission loss and severe image distortion.⁸ Conventional CA photoresist formulations are complex mixtures of a protected polymer matrix and a small molecule

PAG. The inherent incompatibility can lead to PAG phase separation, non-uniform initial PAG and photoacid distribution, as well as acid migration during the PEB processes.⁹ To alleviate these problems, the potential use of a polymer bound PAG blended with a CA resist, for controlling acid diffusion and outgassing, has been reported.¹⁰ Several systems with ionic or non-ionic PAG incorporated in the main chain have been studied.¹¹⁻¹⁶ The incorporation of ionic PAG units into the main chain of the hydroxystyrene and adamantyl methacrylate based polymers showed improved EUV lithographic performance, such as faster photospeed and higher stability, lower outgassing, and lower LER than corresponding blend resists.^{14–16} In this paper, we report a series of novel anionic bound (vinyl functionalized PAG) and blend anionic PAGs as well as corresponding photoresists incorporating PAG in the main chain of the hydroxystyrene and adamantyl methacrylate based polymers (Fig. 1 and 2). An investigation of their thermostability, acid generating efficiency, outgassing and EUVL properties is also outlined.

2. Experimental

Materials

2,3,5,6-Tetrafluorophenol, 2,2'-azobisisobutyronitrile (AIBN), sodium 4-styrenesulfonate and triflic acid were purchased from Aldrich. Trifluoroacetic acid (TFA), trifluoroacetic anhydride (TFAA), and acetic acid 4-vinylphenyl ester were purchased from Tokyo Kasei Kogyo Co., Ltd. Japan. Methacrylic acid, isobutyric acid, sodium 4-phenylsulfonate and tetrabromophenol blue (TBPB) were purchased from ACROS ORGANICS. Triphenylsulfonium chloride 50% aqueous solution was purchased from City Chemical LLC. 2-Ethyl-2-adamantylmethacrylate (EAMA) and tetramethylammonium hydroxide (TMAH) were supplied by AZ Electronic Materials Ltd. All chemicals and solvents were used as received unless otherwise noted. AIBN was recrystallized from methanol before use, and tetrahydrofuran (THF) and acetonitrile were dried (over sodium, calcium hydride) before use. Hydroxystyrene (HOST) was prepared by the hydrolysis of acetic acid 4-vinylphenyl ester.

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Fig. 1 Photoacid generator (PAG) structures.



Fig. 2 Design of microstructures for EUV lithography.

Characterization

The NMR spectra were obtained on a JEOL500 spectrometer with DMSO- d_6 and TMS as the solvent and internal standard, respectively. Elemental analyses were performed at Atlantic Microlab Inc. UV-VIS absorption spectra were obtained on a Varian CARY 300 Bio UV-Visible spectrophotometer. Gel permeation chromatography (GPC, Waters Breeze software) was performed with THF or DMF as the eluent. The molecular weights of polymers were calculated with respect to polystyrene as narrow $M_{\rm w}$ standards. Thermogravimetric analyses (TGA) were performed on a TA instrument, Hi-Res TGA 2950 Thermogravimetric Analyzer 7, at a rate of 10 °C minheating to 800 $^\circ C$ with N_2 gas flow of 25 cm 3 min $^{-1}.$ Differential scanning calorimetry (DSC) measurements were performed on a TA instrument (DSC 2920) at a heating rate of 10 °C min⁻¹. For acid generating measurements, a 254 nm UV lamp (model R 52 G UVP lnc) was used. The outgassing experiments were performed at the Center of Nanotechnology, University of Wisconsin in Madison, and the data were analyzed by Intel Corporation. The EUV exposure was conducted at Lawrence Berkeley National Laboratory. The LER were measured at Georgia Institute of Technology. The thickness of the films was measured with a Woollam Variable Angle Spectroscope Ellipsometer. All scanning electron micrography (SEM) analyses were performed on a RAITH 150/SEM.

Synthesis of photoacid generators (PAGs)

These novel polymerizable PAGs and blend PAGs were synthesized as shown in Scheme 1. The detailed procedure

was reported previously.^{11,12} This scheme outlines a typical synthetic process for bound vinyl monomeric PAG (3), triphenylsulfonium salt 4-(methacryloxy)-2,3,5,6-tetrafluoro-benzenesulfonate (F4-MBS-TPS).

Synthesis of polymers

Terpolymers (**6a**, **6b**, **6c**) were prepared by free radical polymerization in sealed pressure vessels (Scheme 2). Hydroxystyrene (HOST), 2-ethyl-2-adamantylmethacrylate (EAMA), anionic PAG (**1**, **2**, **3**), and 2,2'-azobisisobuty-ronitrile (AIBN) as a free radical initiator (5 mol% to the monomers) were dissolved in freshly distilled anhydrous tetrahydrofuran (THF) and acetonitrile. Polymerization was performed at 65 °C for 24 h. The polymer solutions were precipitated into a large amount of diethyl ether or petroleum ether and dried under vacuum.

Copolymer HE (10) was prepared by a similar procedure (Scheme 3). Hydroxystyrene (HOST), 2-ethyl-2-adamantylmethacrylate (EAMA), and 2,2'-azobutyronitrile (AIBN) as a free radical initiator were dissolved in freshly distilled anhydrous tetrahydrofuran (THF) and maintained at 65 $^{\circ}$ C in sealed ampoules for 24 h, followed by precipitating into petroleum ether and dried under vacuum.

The PAG blend resists (10+4, 10+5) were prepared by blending PAG (4, 5) into copolymer (10) at 6.5 wt%, 7.1 wt%, 8.2 wt%, respectively.

The polymerization composition was calculated by ¹H NMR. The results are given in Table 1.



Scheme 1 Synthesis of photoacid generators (PAGs).



Scheme 3 Synthetic scheme of copolymer (10), and PAG blend resists (10+4, 10+5).

Acid generation efficiency

In order to investigate the acid generating rate for the bound PAGs and blend PAGs in photoresists, the following protocol was followed: resist films were spin-cast onto 4 inch Si wafers, whose weights were predetermined on an analytical balance, from 7.0 wt% resist solutions in cyclohexanone. After casting, the films were baked at 130 °C for 5 min to remove the solvent and were weighed again. The amount of resists on the film was calculated. The resist films were exposed to a 254 nm UV lamp equipped with a radiometer. Dose was calculated by exposure times multiplied by lamp intensity. Each film to be analyzed was stripped from the silicon wafer with DMF and added to 1 mL of a stock solution of 0.3 mM

tetrabromophenol blue (TBPB) in DMF. The total volume was then raised to 10 mL by addition of DMF. The resulting solution was characterized on a UV spectrometer. The amount of acid generated in the film by UV radiation was determined by monitoring the absorbance change of the TBPB indicator at 602 nm,¹⁷ against the calibration curves predetermined by using known amounts of triflic acid. Calibration curves showed a linear relationship between the amount of acid added to the indicator solution and the resulting absorbance intensity change at 602 nm. For comparison, the acid generating efficiency of each resist is expressed as mole of acid per mole of PAG units in the result. The number of moles of PAG units in each resist was determined by ¹H NMR and resist weight.

Table 1 Polymerization results

	Mole feed ratio			Polymer composition						
Polymer	HOST	EAMA	PAG	HOST	EAMA	PAG	Yield (%)	$M_{\rm w}^{\ a}/{ m PDI}$	$T_{\rm dec.}/^{\circ}{\rm C}$	$T_{\rm g}/^{\circ}{\rm C}$
HE (10)	40	60		45.8	54.2		58.5	4500/2.5	157	113
HE-VBS-TPS (6a)	30	65	5	41.7	48.6	9.7	44.3	3700/1.7	156	с
HE-MBS-TPS (6b)	25	73.5	1.5	37.7	55.8	6.5	35.4	3800/1.8	153	с
@HE-F4-MBS-TPS (6c $@$) ^d	25	72.5	2.5	35.0	57.9	7.1	37.3	3600/1.6	145	с
@@HE-F4-MBS-TPS (6c@@)e	25	72.5	2.5	40.2	51.6	8.2	36.8	3100/1.9	154	с
HE + IBBS-TPS (10+4)						6.5^{b}			138	
(a) HE + F4-IBBS-TPS $(10+5(a))^d$						7.1^{b}			131	
$@@HE + F4-IBBS-TPS (10+5@@)^{e}$						8.2^{b}			130	
									1	

^{*a*} The molecular weight was determined by GPC with THF or DMF as mobile phase and polystyrene as narrow standards. ^{*b*} wt%, in order to compare the thermostability and acid generating efficiency of PAG bound polymer with PAG blend polymer. ^{*c*} Could not be determined by DSC, probably due to rigidity of these polymers, resulting from the bulky adamantyl and triphenylsulfonium moiety of the PAG in the polymer. ^{*d*} The two samples marked @ were used for acid generation efficiency measurement. ^{*e*} The two samples marked @@ were used for outgassing and EUV exposure.

Outgassing and resist processing

The outgassing test was performed at the Center for Nanotechnology at the University of Wisconsin, at Madison. The outgassing chamber is built on the synchrotron beam line. A Si_3N_4 plate is located in the chamber and is analyzed by electron spectroscopy for chemical analysis (ESCA) for evidence of contamination build-up. Before the experiments start, the outgassing chamber is baked and pumped down overnight to ensure the chamber is clean. Each run first involves introducing a known amount of a toluene standard, typically 10 ng, in dry, clean nitrogen through the system and collecting the toluene and any contaminants in thermal desorption (TD) tubes. These data indicate the cleanliness of the chamber as well as providing an internal standard. The TD tubes are sent to Intel Corp. for gas chromatography/mass spectroscopy (GC/MS) analysis.

EUV exposures were conducted at Lawrence Berkeley National Laboratory, USA.¹⁸ The 0.3 NA MET based micro-exposure station is designed to deliver a diffraction limited resolution of approximately 30 nm under conventional illumination and smaller than 15 nm using dipole illumination. The synchrotron-based exposure station includes a custom coherence illuminator allowing arbitrary pupil fills with a maximum of approximately 0.83 in y and 1 in x to be generated. The coherence control being based on scanning rather than apertures in the condenser pupil plane, affords a low loss method of modifying the pupil fill.

For resist formulation, 3.3 g of polymer bound PAG resist was dissolved in 50 g of cyclohexanone. The same formulation condition was used for the polymer blend PAG resist. The resist solutions were filtered through 0.2 μ m filter, and spin-coated (3000 rpm, 60 s) onto silicon wafers primed with a 20% 1,1,1,3,3,3-hexamethyldisilazane (HMDS)–80% propylene glycol-1-monomethyl ether 2-acetate (PGMEA) solution. The post apply bake was carried out at 100 °C for 90 seconds. The thickness of the resists was determined to be in the range of 110–130 nm. The exposed wafers were baked at 100 °C for 90 s. The development was conducted in conventional 2.38 wt% TMAH for approximately 15 s and rinsed with de-ionized water.

The line-edge roughness $(3\sigma \text{ LER})$ were measured according to ITRS report and the guideline proposed by Yamaguchi and

co-workers.^{1,19} At least six 1 μ m long lines with 100 points (10 nm in pitch, high-spatial frequency) of each line were scanned. The threshold method was applied for determining the position of the line edge. The final LER was obtained by averaging the average value of each line.

3. Results and discussion

The anionic bound and blend PAGs were prepared in good yield, and characterized by ¹H, ¹⁹F and ¹³C NMR, as well as elemental analyses.

The terpolymers (6a, 6b, 6c(a), 6c(a)) and copolymer (10) were prepared by free radical polymerization and obtained in moderate yield from 35.4-58.5%, and the PAG contents were 9.7, 6.5, and 7.1, 8.2% (mole ratio) for HE-VBS-TPS (6a), HE-MBS-TPS (6b), and HE-F4-MBS-TPS (6c@, 6c@@), respectively. The molar compositions of each unit in the terpolymers were determined by ¹H NMR. The characteristic peaks were: 9.1 ppm from the hydroxyl group of HOST, 7.6-7.8 ppm from PAG's cation TPS, 6.6-6.9 ppm from HOST and PAG's anionic part, 0.7-2.6 ppm from the EAMA and main chain of the polymer. The molar composition was calculated based on the integral and proton numbers for the above corresponding peaks. The molecular weight was determined by GPC with THF or DMF as mobile phase. The results showed the copolymer (10) had a $M_{\rm w}$ of 4500 with PDI 2.5, and the other three terpolymers had similar $M_{\rm w}$ ranging from 3100-3800, and PDI from 1.6-1.9. As for the thermostability, the PAG bound polymers (T_{dec.} of **6a**, **6b**, **6c**@, **6c**@@ are 156, 153, 145 and 154 °C, respectively) are superior to the PAG blend polymers ($T_{dec.}$ of 10+4, 10+5(a), 10+5(a)(a) are 138, 131, 130 °C, respectively). The fluorine-free PAG polymers ($T_{dec.}$ of 6b, 10+4 are 153, 138 °C, respectively) showed better stability than fluorine-substituted PAG polymers ($T_{dec.}$ of 6c, 10+5@, 10+5@@ are 145, 131, 130 °C, respectively). The glass transition temperature of copolymer (10) was 113 °C. The other PAG bound polymers showed no obvious T_g , suggesting that these polymers are probably quite rigid, resulting from the restrictive motion of the bulky adamantly protecting group and the bulky triphenylsulfonium moiety of the PAG in the polymer chain. As reported previously for analogous rigid polymers,²⁰ no transitions were observed below the decomposition temperature for the polymers in this study also.



Fig. 3 Thermogravimetric analysis curves of a) 6c@@ (HE-F4-MBS-TPS) and b) 10+5@@ (HE + F4-IBBS-TPS). The weight loss (%) was measured under identical experimental conditions over a temperature range of 40 °C to 200 °C under N₂.

In order to test their thermal stability, thermogravimetric analysis was performed on the polymer bound PAG resist and the corresponding blend PAG resist. TGA curves of polymer bound PAG and polymer blend PAG resist are shown in Fig. 3. The weight loss (%) was measured under identical experimental conditions (*i.e.* temperature range between 40–200 °C). It was found that the polymer bound PAG resist showed less weight loss (2.9%) than the polymer blend PAG resist (6.5%) at 160 °C. These data demonstrate that the



Fig. 4 Acid generation efficiency vs. exposure doses.

polymer bound PAG resist is more thermally stable than the blend PAG resist.

In order to investigate the effect of the PAG bound or blended to the polymers on the photoresist performance, the acid generating efficiencies for the bound PAG and blend PAG in photoresists were measured (see Fig. 4). It indicates that the acid generation efficiencies for PAG blend polymers (24.5%, 25.0% for resists 10+4, 10+5, respectively) are higher than those of the PAG bound polymers (6.8%, 15.2%, 17.0% for 6a, 6b, 6c, respectively) at an exposure dose of 150 mJ cm⁻² at 254 nm. On the other hand, the PAG (MBS-TPS, F4-MBS-TPS) bound polymers (6b, 6c) showed higher efficiency than the VBS-TPS bound polymer (6a). It also shows no obvious difference between the fluorine substituted and non-fluorine PAGs.

In view of our previous research results on 193 nm photoresists,¹¹ which indicated the fluorine substituted PAG bound polymers or blend resists have a higher photospeed and better lithographic performance than fluorine-free PAG bound polymers or blend polymers, we therefore investigated the PAG F4-MBS-TPS bound polymer (6c@@) and F4-IBBS-TPS blend polymer (10+5@@) for outgassing and EUV lithography study.

The outgassing study is essential in order to perform exposures in vacuum, without the use of a purge gas to eliminate contaminants in the exposure chamber. Important design criteria for EUV systems and EUV resists are the chemical

Table 2 Outgassing results for the photoresists HE-F4-MBS-TPS(6c@@) and HE + F4-IBBS-TPS (10+5@@)

Resist HE-F4-MBS-TPS(6c@@): Total = 1.67×10^{13}									
R.T./min Peak area		Detected compd.	Ion (<i>m</i> / <i>z</i>)	Toluene/RF cts/molecule	Assume $F = 1$, outgassing conc. for single wafer/molecules cm ⁻²				
2.875 9.197 10.205 15.660 15.866	469854 2626 4648 367322 9833	Benzene Chlorobenzene Unknown ketone Unknown C11 ketone Unknown adamantyl compd.	78 112, 77 55, 98, 42 162, 91, 105 135, 164	$\begin{array}{rrrr} 7.87 \times 10^{-10} \\ 7.87 \times 10^{-10} \\ 7.87 \times 10^{-10} \\ 7.87 \times 10^{-10} \\ 6.44 \times 10^{-10} \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$				
Resist HE +	F4-IBBS-TPS (1	0+5@@): Total = 4.36 × 10 ¹²							
R.T./min	Peak area	Detected compd.	Ion (<i>m</i> / <i>z</i>)	Toluene/RF cts/molecule	Assume $F = 1$, outgassing conc. for single wafer/molecules cm ⁻²				
2.905 15.665 15.866	132890 88772 1307	Benzene Unknown C11 ketone Unknown adamantyl compd.	78 162, 91, 105 135, 164	$\begin{array}{rrr} 7.87 \ \times \ 10^{-10} \\ 7.87 \ \times \ 10^{-10} \\ 6.44 \ \times \ 10^{-10} \end{array}$	$\begin{array}{rrrr} 2.59 \ \times \ 10^{12} \\ 1.73 \ \times \ 10^{12} \\ 3.12 \ \times \ 10^{10} \end{array}$				

composition and quantity of outgassed material during and after exposure.^{21,22} The outgassing results of these resists are shown in Table 2. Ester type bulky protective groups such as the adamantyl group have high activation energy, so their deprotection reaction will take place mainly during the PEB step. The outgassing concentrations for F4-MBS-TPS bound resist and F4-IBBS-TPS blend resist are 1.67×10^{13} , 4.36×10^{12} , respectively, both are below 5×10^{13} , which is within the limits of the ITRS2005 specification for EUV lithography.¹

To explore and delineate the imaging properties such as photospeed and LER, the resists were exposed on the beam line at Lawrence Berkeley National Laboratory. The resist formulated with polymer bound F4-PAG sample showed better lithographic performance than the blend PAG sample. The top-down scanning electron micrographs of the polymer bound PAG resist are depicted in Fig. 5a and b: resolved 45 nm (1 : 1), 35 nm (1 : 2), 30 nm (1 : 3), 20 nm (1 : 4) patterns at a dose of 43.5 mJ cm⁻². The corresponding elbow patterns are depicted in Fig. 5c: resolved 50 nm (1 : 1) and 30 nm (1 : 2). The resist formulated with polymer blend F4-PAG resist (see Fig. 6a) showed resolved 50 nm (1 : 1), 45 nm (1 : 2), 35 nm (1 : 3), 30 nm (1 : 4) at a dose of 24.7 mJ cm⁻², the



Fig. 5 (a) Top-down SEM images of 20–120 nm (L/S) patterns (dose: 43.5 mJ cm⁻²) for polymer bound F4-PAG: HE-F4-MBS-TPS (**6c**@@). (b) Top-down SEM images (L/S) patterns (dose: 43.5 mJ cm⁻²) for polymer bound F4-PAG: HE-F4-MBS-TPS (**6c**@@). (c) Top-down SEM images of elbow patterns (dose: 43.5 mJ cm⁻²) for polymer bound F4-PAG: HE-F4-MBS-TPS (**6c**@@). L/S is the ratio of the line width to the spacing between the lines.



Fig. 6 (a) Top-down SEM images (L/S) patterns (dose: 24.7 mJ cm⁻²) for polymer blend F4-PAG: HE + F4-IBBS-TPS (**10**+5@@). (b) Top-down SEM images of elbow patterns (dose: 24.7 mJ cm⁻²) for polymer blend F4-PAG: HE + F4-IBBS-TPS (**10**+5@@).

corresponding elbow patterns showed resolved 60 nm (1 : 1) and 40 nm (1 : 2) patterns and unresolved 50 nm (1 : 1), 35 nm (1 : 2) patterns (Fig. 6b).

Among the issues of post-optical lithography, line edge roughness (LER) or line width roughness (LWR) in the CA resists is the most critical problem. The cause of LER is a complex combination of the exposure beam image, process factors, and resist material.⁴ The LERs (3σ) measured on the 45 nm EUV pattern features for polymer bound F4-PAG and polymer blend F4-PAG were 11.0 nm and 12.1 nm, respectively.²³ These LER should show significant improvement on the addition of base in the resist formulations. The PAG blend polymer HE + F4-IBBS-TPS showed faster photospeed than the corresponding PAG bound polymer (HE-F4-MBS-TPS). Although the bound PAG (F4-MBS-TPS) and blend PAG (F4-IBBS-TPS) have very similar structures, the lower efficiency for the PAG bound polymer appears to be due to a decrease in acid generating efficiency of the PAG. These results indicate that the PAG bound resist improved the resolution.

4. Conclusions

A new series of anionic PAGs bound or blend polymers were prepared and characterized. The thermostability of PAG

bound polymers was superior to PAG blend polymers. Although the acid generating efficiency of PAG blend polymers was higher than that of the PAG bound polymers, higher resolution was observed in the PAG bound polymer. This was indicated by the fluorine PAG bound polymer resist HE-F4-MBS-TPS (6c) giving 45 nm (1 : 1), 35 nm (1 : 2), 30 nm (1 : 3), 20 nm (1 : 4) L/S, and 50 nm (1 : 1), 35 nm (1 : 2) elbow patterns as well as the LER which is comparable with conventional EUV resist LERs of 6–14 nm^{3,24–26} Additional studies to optimize photospeed, to investigate the correlation of reactivity ratios and composition heterogeneity of the polymer resist are under way. The synthesis of anionic PAGs with faster photospeed is being conducted, which will be reported subsequently, along with acid diffusion studies.

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