Novel Polymeric Anionic Photoacid Generators (PAGs) and Photoresists for sub-100 nm Patterning by 193 nm Lithography

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ABSTRACT

A series of new anionic PAGs, as well as PAG bound polymers designed for use in 193 nm photoresist materials have been synthesized and characterized. These novel materials provide optical transparency at 193 nm and also etch resistance. The fluorine substituted PAG bound polymer and PAG blend resist provided 110 nm (220 nm pitch) line/space at 11.5, 13.0 mJ/cm^2, and 80 nm isolated features at 3, 1 mJ/cm^2, respectively. The LER (3σ) results showed the fluorinated PAG bound polymer have LER values 6.7 nm and 6.8 nm for isolated 80 nm and dense 110 nm lines respectively, which were lower than the PAG Blend polymers

Key Words: 193-nm lithography, photoacid generator (PAG), anionic PAG, polymer resist, LER.

1. INTRODUCTION

There is a rapidly approaching roadblock of critical importance in semiconductor processing technology. It is anticipated that lithography at 193 nm or EUV (13.5 nm) wavelength will provide a solution to this critical patterning challenge[1]. In liquid immersion lithography, a fluid is introduced between the last optical element and the photoresist allowing increased NA and therefore a higher resolution[2]. In fact, significant progress has been made in developing exposure tools. On the other hand, development of new photoresist materials that can be used with these new short wavelength exposure tools is essential. In general, chemical amplification (CA) serves as a key technology to enhance the sensitivity of the photoresists. CA resists consisting of a polymer matrix with plasma etch resistance capability, are mixed with a small molecular photoacid generator (PAG) that provides the ability to produce a relief pattern in the CA resist thin film via radiation exposure. The inherent incompatibility between polymer matrix and the photoacid generator leads to problems including PAG phase separation, non-uniform initial PAG and photoacid distribution, as well as acid migration during the post-exposure baking (PEB) processes[3]. To alleviate these problems, several systems with ionic or non-ionic PAG incorporated in the main chain have been studied[4-10], and recently published molecular photoresists, which were composed of three components: monomer, cross-linker and photoacid generator[11]. 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 line edge roughness (LER) than corresponding blend resists[10]. Here we report novel anionic PAG bound or blend photoresists The design of microstructure was based on a methacrylate polymer backbone due to minimal 193 nm absorbance: γ-butyrolactone methacrylate (GBLMA) was included in the microstructure to improve adhesion, 2-ethyl-2-adamantyl-methacrylate (EAMA) was incorporated as the acid-cleavable bulky alicyclic substituent groups to improve resolution, sensitivity, and dry etch resistance.

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Polymeric and monomeric PAGs with or without fluorine, namely, VBS-TPS (**1**), MBS-TPS (**2**), F4-MBS-TPS (**3**), IBBS-TPS (**4**), and F4-IBBS-TPS (**5**). Corresponding, PAG bound polymers GBLMA-EAMA-VBS-TPS (**6a**), GBLMA-EAMA-MBS-TPS (**6b**), GBLMA-EAMA-F4-MBS-TPS (**6c**) and PAG blend resists: GBLMA-EAMA blend IBBS-TPS (**7+4**), GBLMA-EAMA blend F4-IBBS-TPS (**7+5**) were prepared, characterized, and exposed at 193 nm for imaging evaluations. These PAGs and corresponding resists are depicted in figures 1 and 2.

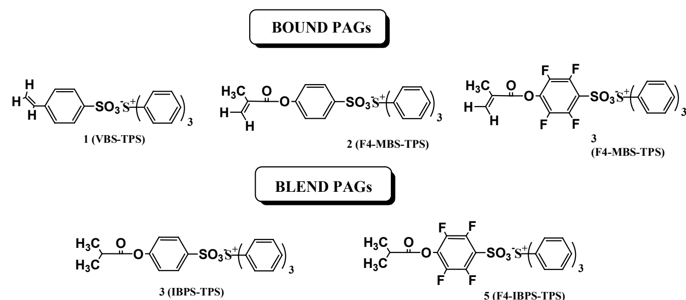

Figure 1. PAG Structures

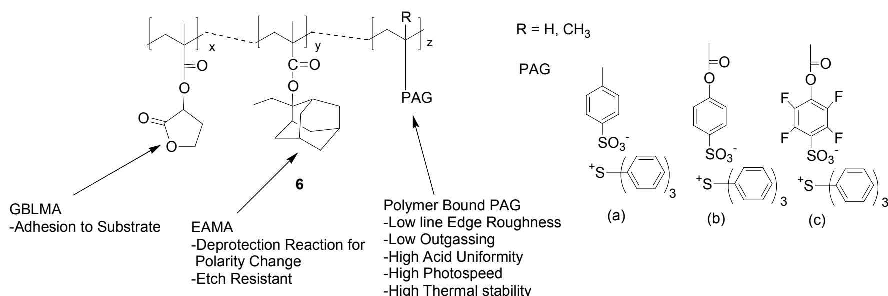

Figure 2. Design of microstructure for PAG incorporated resists

2. EXPERIMENTAL SECTION

Materials and measurements

Acetic acid 4-vinylphenyl ester was purchased from Tokyo Kasei Kogyo Co., Ltd. Japan. 2-Ethyl-2-adamantyl-methacrylate (EAMA) and γ-Butyrolactone methacrylate (GBLMA) was supplied by AZ Electronic Materials Ltd. All chemicals and solvents were used as received unless otherwise noted. AIBN was recrystallized from methanol, and tetrahydrofuran (THF) and acetonitrile were dried (over sodium, calcium hydride) before use. These novel polymerizable PAGs and blend PAGs were synthesized as previously reported[12].

The NMR was performed on a JEOL500 spectrometer with DMSO-d_6 and TMS as the solvent and internal standard, respectively. Gel permeation chromatography (GPC, Waters Breeze software) was performed with THF as the eluent. The molecular weights of polymers were calculated with respect to polystyrene as narrow M_w standards. Thermogravimetric analyses (TGA) were performed on a TA instrument, Hi-Res TGA 2950 Thermogravimetric Analyzer 7, at a rate of 10 ^oC/min, heating to 800 ^oC with N_2 gas flow of 25 cm^3/min. Differential scanning calorimetry (DSC) measurements were performed on a TA instrument (DSC 2920) at a heating rate of 10 ^oC/min. The resists were exposed using the 193 nm ASML 5500/950B optical lithography system, with 0.63 NA at the NSF National Nanotechnology Center, Raleigh, NC. The exposed wafers were evaluated on a Raith 150 SEM. The thickness of the films was measured with a Woollam Variable Angle Spectroscope Ellipsometer. The line-edge roughness (3σ LER) of the isolated and dense lines of both PAG bound polymer and blend resist samples were measured according to ITRS

report and the guideline proposed by Yamaguchi and co-workers[1,13]. At least six 1-μm-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. The AFM was performed at Universidad Autonoma Metropolitana– Iztapalapa, Mexico.

Synthesis of Polymers

Polymers were prepared by free radical polymerization in sealed pressure vessels. γ-Butyrolactone methacrylate (GBLMA), 2-ethyl-2-adamantyl-methacrylate (EAMA), anionic PAG(1,2,3), and 2, 2'-azobutyronitrile (AIBN, 2 mol %) as a free radical initiator were dissolved in freshly distilled anhydrous tetrahydrofuran (THF) and acetonitrile (2:1), the solution was purged with nitrogen and further deoxygenated with two freeze-thaw cycles. Polymerization was performed at 65˚ C for 24 hrs, and then precipitated into a large amount of diethyl ether or petroleum ether and dried at reduced pressure. The copolymer (GE) was prepared by a similar procedure for terpolymers, γ-butyrolactone methacrylate (GBLMA), 2-ethyl-2-adamantyl-methacrylate (EAMA), and 2, 2'-azobutyronitrile (AIBN) as a free radical initiator were dissolved in freshly distilled anhydrous tetrahydrofuran (THF) at 65˚ C for 24 hrs, and followed by precipitating into petroleum ether, dried at reduced pressure. The polymerization composition was calculated by ^{1}H NMR. Different feed ratios were used to prepare PAG bound polymers, and exposed under a UV 254 nm lamp to do initial imaging evaluation. The sample with about 5 or 6 % PAG loading in the polymer backbone gave better lithographic performance. Therefore, around 6% PAG loading samples were exposed at 193 nm. Molecular weight, thermogravimetric analyses (TGA), and differential scanning calorimetry results are given in Table 1.

Table 1. Polymerization results for PAG bound polymers and PAG blend resists

Polymer / resist	Mole Feed Ratio			Polymer Composition			Yield / %	Mw (PDI)	Stability / ºC	Tg / ºC
	GBLMA	EAMA	PAG	GBLMA	EAMA	PAG				
GBLMA-EAMA(**7**)	40	60		59.6	40.4		68.7	5700 (3.0)	144	109
GBLMA-EAMA-VBS.TPS(**6a**)	30.7	66.5	2.8	52.5	41.1	6.4	17.4	3700 (2.3)	163	100
GBLMA-EAMA-MBS.TPS(**6b**)	25	72.5	2.5	50.2	43.5	6.3	20.4	4100 (1.9)	166	148
GBLMA-EAMA-F4-MBS.TPS (**6c**)	25	72.5	2.5	55.3	39.2	5.5	31.5	2100 (3.3)	151	142
GBLMA-EAMA + IBBS.TPS (**7+4**)						6.4*			173	
GBLMA-EAMA + F4-IBBS.TPS (**7+5**)						5.5*			168	

* wt.%, in order to compare the thermostability and lithographic properties of PAG bound polymer with PAG blend resist.

Resist processing

For resist formulation, 0.2g of polymer bound PAG resists were dissolved in 3.4 g of cyclohexanone. The resist solutions were filtered through 0.2 μm filter, and spin-coated (2500 rpm, 60s) onto silicon wafers primed with a 20% 1,1,3,3,3-hexamethyl-disilazane (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 120 -150 nm. The exposed wafers were baked at 100˚ C for 90 s. The development was conducted in conventional 2.38-wt % tetramethyammonium hydroxide (TMAH) for approximately 10-20s and rinsed with de-ionized water. In order to compare the lithographic feature, blended PAG resists were similarly prepared by blending 5.5wt % of F4-IBBS-TPS, and 6.4 wt % IBBS-TPS to coplymer (GBLMA-EAMA) and exposed.

3. RESULTS AND DISCUSSION

The polymerization results showed that these polymers were obtained in low to moderate yield, and the PAG contents were 6.4, 6.3 and 5.5 % (mole ratio) for GBLMA-EAMA-VBS.TPS (**6a**), GBLMA-EAMA-MBS.TPS (**6b**), and GBLMA-EAMA-F4-MBS-TPS (**6c**), respectively. The molecular weight of these polymers ranged from 2100-5700. As for their thermostability, the fluorine-free PAG resists (**6a, 6b, 7+4**) were superior to fluorine-substituted PAG resists (**6c, 7+5**), and the PAG blend resists (**7+4, 7+5**) showed better stability than PAG bound resists (**6a, 6b, 6c**). The glass transition temperature (***T***g) of copolymer (**7**), polymer GBLMA-EAMA-VBS.TPS (**6a**), GBLMA-EAMA-MBS-TPS (**6b**), and GBLMA-EAMA-F4-MBS-TPS (**6c**) were 109, 100, 148, 142 ^{o}C, respectively.

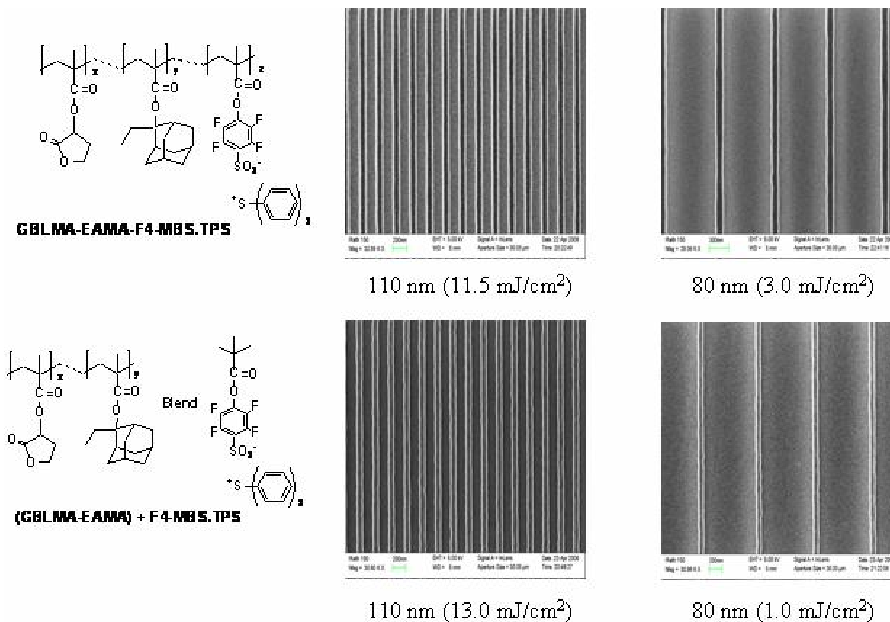

Figure 3. SEM images of polymers 6c(GBLMA-EAMA -F4-MBS-TPS) and PAG blend resist 7+5 (GBLMA-EAMA + F4-IBBS.TPS)

Exposed wafers were evaluated on a Raith 150 SEM. Top down SEM images are shown in figures 3. The fluorinated PAG bound polymer **6c** (GBLMA-EAMA-F4-MBS.TPS) provided 110 nm line/space at 11.5 mJ/cm^2, 80 nm isolated features at 3.0 mJ/cm^2, and fluorinated PAG blend resist **7+5** (GBLMA-EAMA + F4-IBBS.TPS) provided 110 nm line/space at 13 mJ/cm^2, and 80 nm isolated features at 1.0 mJ/cm^2, which is within roadmap standards.[1] The LER (3σ) results showed that the fluorinated PAG bound polymer **6c** (GBLMA-EAMA-F4-MBS.TPS)have LER values 6.7 nm and 6.8 nm for isolated 80 nm and dense 110 nm lines respectively, while the fluorinated PAG blend resist **7+5** (GBLMA-EAMA + F4-IBBS.TPS)have LER values 8.6 nm and 8.9 nm. The improvement may be due to the covalent bonding of PAG into polymer main-chain which provides more uniform distribution by controlling acid diffusion and higher loading of PAG than the blend sample. These facts may lead to more uniform deprotection during post-exposure baking and less roughness at the developed line edge.

The fluorine-free PAG bound polymer **6a** (GBLMA-EAMA-VBS.TPS) provided 120 nm line/space at 65 mJ/cm^2, 80 nm isolated features at 35 mJ/cm^2, and the fluorine-free PAG blend resist **7+4** (GBLMA-EAMA + IBBS-TPS) provided 130 nm line/space at 22 mJ/cm^2, 110 nm isolated features at 12 mJ/cm^2, which showed lower photospeed compared with the photoresists based on fluorine substituted PAGs.

The results indicate that fluorine substituted PAG bound polymers or blend resists have a higher photospeed and good lithographic performance. This probably results from the higher electronegativity of the fluorine atom that can improve transparency at 193 nm and especially increase the acidity of PAG[14,15]. This is also evident from a comparison of fluorinated PAG blend resist **7+5** (GBLMA-EAMA + F4-IBBS.TPS) and fluorine-free PAG blend resist **7+4** (GBLMA-EAMA + IBBS.TPS). Both the PAG blend resist **7+5** (GBLMA-EAMA + F4-IBBS.TPS) and bound polymer **6c** (GBLMA-EAMA-F4-MBS.TPS) have similar photospeed as observed for 110 nm line/space. For the 80 nm isolated

lines, the fluorinated blend PAG resist exhibited a higher photosensitivity. However, the LER data indicates that the PAG bound resist improved the resolution and thereby control of acid diffusion as discussed above. The latter is critical for next generation resists. Since 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 as reported by us previously[12]. Incorporation of the PAG into the polymer main-chain may result in the creation of pathways which non-productively dissipate absorbed energy or which decrease the efficiency of energy transfer to the PAG molecule[16,17]. Further investigations are required to better understand the causes for the observed behavior**.** On the other hand, the PAG (F4-MBS-TPS) bound polymer **6c** (GBLMA-EAMA-F4-MBS.TPS) showed higher photospeed than the VBS-TPS bound polymer **6a** (GBLMA-EAMA–VBS.TPS).

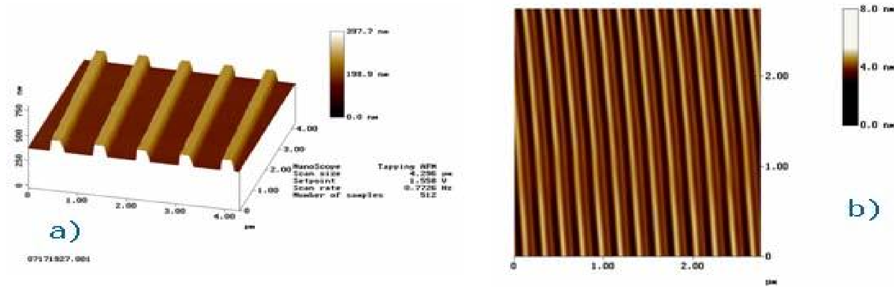

Figure 4: a) AFM image showing a 3D rendering of **6c** (GBLMA-EAMA-F4-MBS.TPS): a) 80 nm isolated line, b) 110 nm line space features

Atomic force microscopy (Digital Instruments Dimension 3100 AFM) provided 3-D topographic images of the lithographic patterns. In order to minimize the effect of the tip on the images, a high aspect ratio (HAR) tip was used in tapping mode for all the experiments. The HAR tip consists of a sharp 2 µm spike mounted on a 125 µm long cantilever which has a resonant frequency of 320 kHz, and a spring constant in the range 20-80 N/m. The aspect ratio of the spike is 5:1, and thus, the end of the tip has a cone half angle of 5.7˚. Scans were taken at a speed of 1 Hz, with the fast scan axis perpendicular to the lines of the lithographic patterns. AFM was measured for both photoresists: F4-PAG bound and blend polymers: the results indicated that F4-PAG bound polymer has improved surface and sidewall roughness then the blend samples. Figure 4 gave the images of 80 nm isolated lines and 110 nm line space of F4-PAG bound polymer **6c**.

4. CONCLUSION

A new series of PAG bound or blend polymers were prepared and characterized. The thermostability of nonfluorine PAG bound or blend resists were superior to that of the fluorine-substituted PAG bound or blend resists. Both the fluorine substituted PAG bound polymer and blend resist showed faster photospeed and good lithographic performance. Sub-100 nm patterns were obtained for these systems. The fluorinated PAG bound polymer showed lower LER values than the PAG blend resist. The improvement may be due to the covalent bonding of PAG into polymer main-chain which provides more uniform distribution by controlling acid diffusion and higher loading of PAG than the blend sample. Further investigations on outgassing and acid diffusion studies will be reported subsequently.

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