New Photoresist Based on Amorphous Low Molecular Weight Polyphenols

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We have investigated the possibility of amorphous low molecular weight polyphenols as a chemically amplified positive-tone electron-beam (EB) resist. Two low molecular weight polyphenols, 4,4'-methylenebis[2-[di(2-methyl-4-hydroxy-5-cyclohexylphenyl)]methyl]phenol (3M6C-MBSA), and 4,4'-methylenebis[2-[di(4-hydroxy-2,5-dimethylphenyl)]methyl]phenol (25X-MBSA) as a base matrix, and poly(*p*-hydroxystyrene) (PHS) with a weight average molecular weight of 8400 as a reference were selected. Those phenol groups were protected by 1-ethoxyethyl groups to control the dissolution rate of these materials in 0.26 N tetramethylammonium hydroxide (TMAH) aq. developer. Etching rates under CF₄/CHF₃/He mixed gas process, dissolution rates with the developer, sensitivities with EB exposure, resolution and surface roughness were evaluated. The resist based on 3M6C-MBSA showed the excellent pattern profile and 60 nm lines and spaces (lines/spaces=1/1) resolution. And, even 50 nm lines and spaces pattern was partially resolved. In addition, as compared with PHS, smaller surface roughness of 3M6C-MBSA films was observed by AFM measurement.

Keywords: chemical amplification positive-tone resist, amorphous polyphenols, low molecular weight

1. Introduction

As shrinking gate length for 65nm technology node and below, line edge roughness (LER) of fabricated resist patterns becomes one of the most significant issues [1-3]. For this issue, many studies such as processing parameters that may affect the LER and development models to explain the generation process of the LER were reported [4-9]. On the point of material structure as candidates for resist base materials, the application of compounds with low molecular weight and/or narrow polydispersity may be one of the key concepts to dissolve this issue due to its reduced molecular size compared with linear polymers against the feature size to be printed [10-14]. In addition, for common photo-resists used in commercial production of semiconductor devices, high etching durability and high sensitivity, as well as high resolution, are generally desired.

Thus, novel low molecular weight polyphenols with high dry-etching durability due to their phenolic structure were applied for developing a chemically amplified positive-tone EB resist system with high sensitivity. Surface roughness of the resist films, which might be related to pattern roughness, was also investigated by using an atomic force microscope (AFM) [15,16].

2. Experimental

2.1. Materials

Two low molecular weight polyphenols, 4,4'-methylenebis[2-[di(2-methyl-4-hydroxy-5-cyclohexylphenyl)]methyl]phenol (3M6C-MBSA) and 4,4'-methylenebis[2-[di(4-hydroxy-2,5-dimethylphenyl)]methyl]phenol (25X-MBSA) were donated by Honsyu Chemical Industry Co. and poly(*p*-hydroxystyrene) (PHS) was obtained from DuPont company. These polyphenols and PHS

were used as received. The structures of polyphenols and PHS, protected with 1-ethoxyethyl (EE) groups, are shown in Figure 1. EE-protected polyphenols and PHS were prepared by the acid catalyzed addition reaction of ethyl vinyl ether with polyphenols or PHS using *p*-toluenesulfonic acid in THF at 25 °C for 12 h. Various degrees of protection were obtained by selecting the appropriate feed ratio of the starting materials. Purity of unprotected 3M6C-MBSA and 25X-MBSA was determined with a HPLC with TOSOH HLC-8220 GPC. Differential scanning calorimetry (DSC) was performed with SII EXSTR6000 series DSC-6200.

Figure 1. Structures of EE protected 3M6C-MBSA, 25X-MBSA and PHS.

Table 1. Characteristics of non-protected low molecular weight polyphenols and PHS

Polyphenols	M_w	PD	T_g (°C)
3M6C-MBSA (Purity:~100%)	777	1.03	138
25X-MBSA (Purity:99.5%)	481	1.01	N/A
PHS	8400	2.65	170

Table 2. Protection ratio of low molecular weight polyphenols and PHS

Protected Polyphenols	EE Protection ratio (mol%)
3M6C-MBSA-1	8.2
3M6C-MBSA-2	13.3
3M6C-MBSA-3	19.9
3M6C-MBSA-4	26.2
25X-MBSA-1	10.1
25X-MBSA-2	21.2
25X-MBSA-3	33.1
25X-MBSA-4	39.9
25X-MBSA-5	50.1
PHS-1	30.7

The protection ratios of hydroxyl groups with EE groups were determined by $^1\text{H-NMR}$ at 30 °C in deuterated DMSO for low molecular weight polyphenols and deuterated acetone for PHS with a JEOL JNM-GX400 FT-NMR spectrometer. Weight average molecular weights (M_w) and polydispersity ratios (PD) of polyphenols and PHS were determined in tetrahydrofuran by a GPC with a TOSOH Shodex GPC SYSTEM calibrated with polystyrene standards. Characteristics and EE protection ratio of polyphenols and PHS are summarized in Table 1 and 2, respectively.

2.2. Etching Rate Measurements

The etching rates of unprotected polyphenols, PHS, and polymethacrylate derivatives used as a common ArF resist polymers, were measured under $\text{CF}_4/\text{CHF}_3/\text{He}$ mixed gas process with a parallel-plate-type system (TCE-7811X, Tokyo Ohka Kogyo Co.). In etching conditions, a gas pressure was 300 mTorr. Flow rates of CF_4 , CHF_3 and He was 75 sccm, 45 sccm, and 200 sccm, respectively, and an acceleration power was 1000 W. After blanket etching of sample films for 120 s, surface roughness was observed with a Hitachi S-4700 scanning electron microscopy (SEM).

2.3. Measurements for Dissolution Rate

To determine the appropriate protection ratio for dissolution in alkaline developer, the samples were formulated with polyphenols with various degrees of protection and casting solvent. The sample viscosity was adjusted to make films of 500 nm thickness with casting solvent that contained 60 wt% propylene glycol monomethyl ether 2-acetate (PGMEA) and 40 wt% ethyl lactate (EL). The films were spin-coated onto silicon wafers pretreated with 1,1,1,3,3,3-hexamethyl disilazane (HMDS). The coated wafers were baked at 110 °C for 90 s and

then developed with a dissolution rate monitor MODEL RDA-808 RB (Litho Tech Japan Co.). The developer used was NMD-3 2.38% (Tokyo Ohka Kogyo Co.) of 0.26 N TMAH at 23 °C. Dissolution rates were determined by measuring film thickness before and after development, and by monitoring dissolution time during development.

2.4. Lithographic Characterization

To investigate lithographic performance of polyphenols and PHS, resist samples consisting of polyphenols, a photo acid generator (PAG), a quencher and a casting solvent were formulated. Triphenylsulfonium perfluoro-1-butanefluoroborate (TPS-PFBS) and tri-octylamine (TOA) were used as PAG and quencher, respectively. Casting solvent consisted of 60 wt% PGMEA and 40 wt% EL. The resist formulations were described in Table 3. The EB exposure characteristics such as a dissolution contrast curve and de-protection behavior of acetal residue were measured, and EB lithographic evaluation was conducted by using Hitachi HL-800D EB lithography tool (70 kV) connected to coater/developer in-lined system. The sample films were spin-coated onto silicon wafers and baked on a hot plate at 110 °C for 90 s as post-applied bake (PAB). The film thickness was determined by using multi-wavelength interference thickness measurement tool, Nanospec model 6100A produced by NANOMETRICS Co. Following EB exposure, the resist films were baked at 110 °C for 90 s as post-exposure bake (PEB) and developed in NMD-3 2.38% of 0.26 N TMAH at 23 °C for 60 s. E_{size} was determined to be an optimum dose when the feature size of 100 nm (lines/spaces=1/1) was given. Cross-sectional fabricated patterns were observed with the SEM.

Table 3. Resist sample formulations

Sample	Polyphenols	PAG cont.	Quencher cont.
Resist A	3M6C-MBSA-3		
Resist B	25X-MBSA-5	TPS-PFBS 10 wt%	TOA 1.0 wt%
Resist C	PHS-1		

2.5. Measurement for Surface Roughness

An AFM was used to measure the surface roughness of the resist films based on low molecular weight polyphenol, which were post exposure baked and developed in NMD-3 following EB ex-

posure, for comparison with that of PHS films. AFM scans were taken with Digital Instruments Nanoscope IV for incident various doses.

3. Results and Discussions

3.1. DSC Analysis

Unprotected and protected polyphenols were found to form amorphous glasses readily when the melt samples were cooled. Figure 2 shows DSC curves of 3M6C-MBSA and 3M6C-MBSA-3. The sample was heated to the melting point as annealing. After cooling the resulting isotropic liquid, the sample that was again heated showed the glass transition at 138 °C and 109 °C for 3M6C-MBSA and 3M6C-MBSA-3, respectively. No crystallization behavior was observed on further heating above the T_g s of them. A similar DSC curve was obtained for 25X-MBSA-5 at the T_g of 77 °C. We confirmed that all samples formed uniform amorphous thin films by using a spin-coat method.

Figure 2. DSC curves as heating scan of 3M6C-MBSA and 3M6C-MBSA-3. Heating rate 10 °Cmin⁻¹. The amorphous glass sample was obtained by the melt one at a cooling rate of 50 °Cmin⁻¹.

3.2. Dry Etching Durability

The dry-etching durability of low molecular weight polyphenols was examined and compared with those of PHS and ArF methacrylic ter-polymer. Dry-etching durability is correlated with the mass fraction of resist base materials existing as cyclic carbon [17,18]. Consequently, the dry-etching durability of 3M6C-MBSA and 25X-MBSA may be similar to that of PHS. Figure 3 shows the etching rates relative to PHS. Although MBSA series have lower molecular weights than PHS, it seemed that

these polyphenols have adequate dry-etching durability. Figure 4 depicts SEM images of sample films after etching for 120 s. In PHS and 3M6C-MBSA, these surfaces revealed almost the same roughness, but ArF polymer showed significant rough surface. The surface of the 25X-MBSA film was the most smooth.

Figure 3. Normalized etching rates of 3M6C-MBSA, 25X-MBSA, PHS and ArF methacrylic polymer.

Figure 4. Cross sectional SEM images of (a) 3M6C-MBSA, (b) 25X-MBSA, (c) PHS and (d) ArF methacrylic polymer films after etching for 120 s.

3.3 Dissolution Rate

The dissolution rates of 3M6C-MBSA and 25X-MBSA with various EE-protection ratios in an aqueous alkaline developer were measured and plotted in Figure 5. For 3M6C-MBSA, the protection of 19.9 mol% indicates a good inhibition effect for alkaline solubility, on the other hand for 25X-MBSA, even the protection of 50.1 mol% can't control the dissolution rate below 0.1 nm/s.

This difference of the dissolution-inhibition effect between 3M6C-MBSA and 25X-MBSA is attributed to the steric hindrance of *ortho*-substituents to the hydroxyl groups that affects the dissolution rate of PHS for an aqueous alkaline developer [19]. The cyclohexyl group in 3M6C-MBSA causes the large steric hindrance to the hydroxyl groups. In fact, the unprotected 3M6C-MBSA shows the small dissolution rate of 52.3 nm/s. On the other hand, unprotected 25X-MBSA shows the large dissolution rate of 700 nm/s, which is thirteen times as large as that of 3M6C-MBSA due to the lower steric hindrance to the hydroxyl groups. Therefore, 50.1 mol% protected 25X-MBSA is difficult to control the dissolution rate below 0.1 nm/s that is commonly desired for chemically amplified resist base polymer.

Figure 5. Dissolution rates of 3M6C-MBSA and 25X-MBSA protected by EE with various protection ratios.

3.4 Lithographic Performance

The FT-IR spectra of resist films unexposed and exposed with the EB lithography tool was measured. The results are shown in Figure 6. A cleavage reaction of acetal bonds occurs by EB irradiation and PEB treatment as the characteristic signals for acetal bonds at around 1080 cm^{-2} and 950 cm^{-2} become weak. [20,21].

The sensitivity curves for resist-A and B exposed with 50 kV EB lithography tool indicate a good sensitivity as shown in Figure 7. From the FT-IR spectra and sensitivity curves, these protected polyphenols were found to work as a chemically amplified positive-tone resist.

Figure 6. FT-IR spectra of (A) resist-A and (B) resist-B films that were (a) unexposed and applied PEB, (b) applied PEB after exposure at $30 \mu\text{Ccm}^{-2}$ and (c) indicated the differential spectrum between (a) and (b).

Figure 7. Sensitivity curves for resist-A and B film exposed by 50 kV EB tool.

Next, EB imaging evaluation of resists A, B and C with 150 nm film thickness was performed. The results are shown in Figure 8. Resists-A and C achieved 60 nm and 70 nm lines and spaces resolution, respectively. And, even 50nm lines and spaces pattern was partially remained with the resist-A. Regardless of their low molecular weights without any cross-linking system, the resist-A could fabricate the nano-structure, but resist-B couldn't. The

model process condition was PAB of 110 °C and PEB of 110 °C. The T_g of 25X-MBSA-5 (50.1 mol% protection ratio) was 77 °C due to the high protection ratio that decreased free phenolic hydroxyl groups in 25X-MBSA and inhibited the intermolecular hydrogen bonding. This low T_g of 25X-MBSA-5 prevented the formation of the patterns in this model process condition. It might be necessary for 25X-MBSA-5 to apply lower PAB and PEB temperature for the process condition to fabricate the patterns. The E_{size} of resist-A and C were found to be $32 \mu\text{Ccm}^{-2}$ and $25 \mu\text{Ccm}^{-2}$, respectively. This E_{size} of resist-A seems promising for application of manufacturing due to higher sensitivity with chemically amplified system.

Figure 8. The cross section profiles of the resist-A (3M6C-MBSA-3), B (25X-MBSA-5) and C (PHS-1) with 150 nm film thickness on silicon wafers. PAB 110 °C-90 s, PEB 110 °C-90 s, development time 60 s.

3.5 Surface Roughness Study

Figure 9 shows the measured Root Mean Square (Rms) roughness of resist-A film surface for a $1 \mu\text{m} \times 1 \mu\text{m}$ region as compared with that of resist-C. A drastic increase in roughness is apparent as the dose increases to $20 \mu\text{Ccm}^{-2}$ and $15 \mu\text{Ccm}^{-2}$ in resist-A and C, which then decreases rapidly. Although the shape of the curves is similar to each other, the resist-C shows a larger maximum roughness than the resist-A. As reported in a previous paper [22], the shape of these curve might be related to the dissolution rate distribution of resists at a dose nearby the transition point from the low dissolution rate to the

high dissolution rate as shown in Figure 7. On the other hand, as comparing the maximum surface roughness of resist-A and C, surface roughness can be suppressed by low molecular weight with a narrow polydispersity [15].

Figure 9. The surface roughness at various doses for the 1 μm by 1 μm region AFM scans. Development time 15 s.

4. Conclusions

The resists based on the low molecular weight polyphenol, 3M6C-MBSA protected by the 1-ethoxyethyl group as an acid labile protecting group can work as a common chemically amplified positive-tone resist and achieve 60 nm lines and spaces resolution by using EB lithography tool. Furthermore, the surface roughness of resist films exposed at various doses and then developed for 15 s confirmed that the resist based on 3M6C-MBSA showed smaller surface roughness than PHS based with higher *M_w* and broad polydispersity due to its small distribution changes of dissolution rate during exposure.

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