Affinity Analysis of Photoacid Generator in the Thin Film of Chemical Amplification Resist by Contact Angle Measurement

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In extreme ultraviolet (EUV) lithography development, the reduction of line width roughness (LWR) is a one of the significant issues. It has been reported that the LWR of photoacid generator (PAG) bounded resist is lower than that of PAG blended resist. It is considered that the chemical composition distribution of PAG bounded resist is more uniform than PAG blended resist. However, it has not been evaluated systematically and experimentally. In this study, we introduced the contact angle measurement method for the evaluation of the chemical composition distribution between PAG blended resist and PAG bounded resist. It is clarified that the resist thin film has a different chemical composition distribution from the center to the outside of wafer regardless of the type of resists. In particular, the chemical composition distribution of the bounded resist showed the opposite behavior to that the blended one.

Keywords: Contact angle measurement, PAG bounded resist, PAG blended resist, Chemical amplification resist

1. Introduction

Extreme ultraviolet (EUV) lithography has been used for the production of 7-nm node semiconductor devices in 2019 and for high volume mass production of 5-nm-logic devices in 2020. However, the semiconductor industry continuously requires more advanced device nodes. The next generation EUV photoresist is needed to satisfy with half pitch of smaller than 10 nm, sensitivity of higher than 15 mJ/cm², and low line width roughness (LWR) of lower than 1 nm [1].

The origins of LWR have been considered such as photon shot noise, acid diffusion for photoacid generator (PAG) in the chemical amplification resist (CAR), and the chemical composition distribution in the resist thin film. Especially, several methods of the chemical composition distribution analysis for the resist thin film have been reported applying TOF-SIMS analysis [2-6], MC-SIMS [7], and the resonant soft X-ray scattering (RSoXS) [8, 9]. In these reports, it has been considered that the chemical composition distribution of the resist thin film is not uniform in the nano-scale. However, the

consideration of the photoresist design satisfied with low-LWR has not been achieved yet.

Generally, it is known that there are two types of the CARs, such as PAG-blended resist (blend resist) and PAG-bounded resist (bound resist). The blend resist is a mixture of the base-resin (polymer or molecule), PAG, and amine additive in the solvent. On the other hands, the bound resist is not a mixture, because the PAG unit is contained in the base polymer. The difference of the blend and bound resists has been reported by many researchers [10-18], and especially, Watanabe et al. have reported that the bound resist is more less line edge roughness (LER) than blend resist [11]. The reason of low LER for bound resist is expected that the uniformity of bound resist is better than blend one, however, the chemical composition distribution analysis has not been evaluated.

Thus, this paper is proposed that a method of the contact angle measurement for the composition distribution of the bound resist and the blend resist thin films on the silicon wafer. The base polymer used in positive-tone CARs mainly has hydroxy

groups and hydrophobic protecting groups, and PAG is hydrophobic because that does not have hydroxy groups. Therefore it was expected that the chemical composition distribution could be evaluated from the difference affinity (between hydrophobicity and hydrophilicity) by measuring the water-contact angle on the resist thin film surface. This paper focus on the evaluation of the chemical composition distribution by the contact angle measurement on the resist thin film such as blend resists and a bound resist.

2. Experimental

The contact angle measurement was examined with different the degree of introduction of PAG, PAG structure, and the types of resist.

2.1. Materials

dimethylsulfoxide (DMSO), DMSO- d_6 , diethyl ether (Et₂O), tetrahydrofuran (THF), γ -butyl lactone, propylene glycol monomethyl ether acetate (PGMEA), dimethyl amino pyridine (DMAP), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), and dehydrated dimethyl formamide (DMF) were used as purchased. hexamethyldisilazane (HMDS), poly(hydroxystyrene-*co-tert*-butylacrylate) (PHS-TBA), triphenylsulfonium-nonaflate (PAG-1) and triphenylsulfonium-triflate (PAG-2) were purchased from Tokyo Ohka Kogyo Ltd. PAG-3, 4, 5 were provided by San-Apro Ltd. Table 1 shows the structure of PAGs which were employed in this study.

2.2. Measurements

NMR (^1H and $^{19}\text{F}\{^1\text{H}\}$) spectra were recorded on JEOL JNM-ECZ600R (600 MHz) spectrometer. The peaks were referenced to DMSO ($\delta 2.50$) in the DMSO- d_6 solvent for ^1H NMR. Gel permeation chromatography (GPC) was performed at 60 °C on Waters Alliance e2695 HPLC system equipped with a differential refractometer detector e2998 and a variable-wavelength UV-vis detector e2410, using DMF (10 mmol/l phosphoric acid and KBr) as eluent at a flow rate of 0.6 mL min $^{-1}$ with Shodex AsahiPak GF-7HMQ columns. The molecular weights were calibrated based on polystyrene standards. The image of the droplet profile and calculate contact angle were recorded on Excimer SImage Entry 6.

2.3. PAG-5 introducing to the side chain of base polymer (synthesis of bound resist)

It can be introduced into phenolic acid group under mild conditions due to PAG-5 has carboxylic group. Thus, the condensation reaction of PAG-5 and PHS-TBA was examined (Scheme 1).

Table 1. Summary of PAG structures.

PAG	Structure	
	Cation	Anion
PAG-1		$\text{C}_4\text{F}_9\text{SO}_3^-$
PAG-2		CF_3SO_3^-
PAG-3		$\text{C}_4\text{F}_9\text{SO}_3^-$
PAG-4		CF_3SO_3^-
PAG-5		CF_3SO_3^-

Scheme 1. The condensation reaction of PHS-TBA with PAG-5.

PHS-TBA (1239 mg, 5.0 mmol), EDC·HCl (105 mg, 0.55mmol), DMAP(10 mg, 0.082 mmol) and PAG-5 (311 mg, 0.50 mmol) were charged to 50 ml two-necked flask and purged N₂ gas. Dehydrated DMF (10 ml) was added to mixture then stirred at r.t. for 22 h. After the reaction, the reaction mixture was poured into water (150 ml). The resulted solid was obtained by suction filtration and dried under vacuum for 6 h at 60 °C. The obtained crude product was dissolved a small amount of THF, and the mixture solution was poured into a large amount of Et₂O. The resulted solid (79% yield) was obtained by suction filtration and dried under vacuum for 6 h at 60 °C.

The ration of the microstructure of the PHS unit

and the degree of introduction of PAG group in the polymer was calculated from the ^1H NMR peak area ratio using the following eq (1), and (2).

$$[\text{PHS unit}] / ([\text{PHS unit}] + [\text{TBA unit}]) = (\text{phenyl} / 4) / [(\text{phenyl} / 4) + \{\text{alkyl} - (\text{phenyl} / 4) \times 3\} / 12] \quad (1)$$

$$[\text{PAG unit}] = \text{PAG} / 18 \times [\text{PHS unit}] \quad (2)$$

The signals and their positions are as follows: ^1H NMR: δ 8.19-7.39 (PAG), 7.20-6.06 (phenyl) and 2.05-0.0 (alkyl); ^{19}F $\{^1\text{H}\}$ NMR: δ -77.7 (CF_3).

2.4. Photo resist thin layer coating on the silicon wafer

The resist solutions were filtered through a 0.22 μm PTFE syringe filter prior to spin-coating on silicon wafers which were treated by the adhesion process by HMDS. Spin-coating was performed at 3000 rpm for 30 s to form HMDS thin films on silicon wafers. Then these spin-coated films were prebaked at 130 $^\circ\text{C}$ for 90 s. Then, the solutions of sample #1-6 in PGMEA and sample #7 in γ -butyl lactone were spin-coated on the silicon wafer to prepare corresponding thin films. Spin-coating was performed at 2500 rpm for 45 s to form thin films on silicon wafers. Then these spin-coated films were prebaked at 110 $^\circ\text{C}$ for 60 s. The resist thickness was measured by the optical-interference-type film thickness measurement tool (NanoSpec6100, NANO metrics Inc.).

The average film thickness and the degree of introduction (DI) of PAG (mol%) in each of the prepared samples show in Table 2.

Table 2. Summary of prepared resist samples.

Sample	Thickness (nm)	PAG structure	DI of PAG (mol%)	Resist type
1	41	-	0	Polymer
2	45	PAG-1	2.2	Blended
3	45	PAG-1	4.3	Blended
4	43	PAG-2	2.2	Blended
5	43	PAG-3	2.2	Blended
6	43	PAG-4	2.2	Blended
7	22	PAG-5	5.2	Bounded

2.5. Contact angle measurement on the resist thin layer surface

The contact angle was measured by the sessile

drop method. The measurement points on a 4 inch silicon wafer show in Fig. 1 (blue dot). Ultrapure water (18.2 M Ω) was used as a measurement solvent, and the liquid volume was 2.0 μl (the liquid diameter was calculated 1.6 mm when contact angle = 90 $^\circ$). The $\theta/2$ method was used to calculate the contact angle. The droplet images were captured 10 s after dripping. The average value and standard deviation of the measured values at each distance (0, 20, 40 mm) from a wafer center were calculated and plotted.

Fig. 1. Measurement points (blue dots) of the contact angle on a silicon wafer.

3. Results and discussion

3.1. Introduction of PAG-5 into base polymer (synthesis of bound resist)

The reaction of PHS-TBA with PAG-5 was carried out using EDC $\cdot$ HCl as a condensation reagent under DMAP as a base catalyst at r.t. for 22 h, obtaining the polymer with $M_n = 4,500$ ($M_w/M_n = 1.88$) at 79% yield. The DI of PAG-5 as calculated by ^1H NMR spectroscopy was found to be 5.2 mol%. Obtained polymer having PAG was poorly dissolved in PGMEA, acetonitrile, and diethyl ether, however, dissolved in γ -butyrolactone, THF, and DMSO. Thus, γ -butyrolactone was chosen as solvent for the preparation of resist thin film.

3.2. Contact angle measurement of samples with different DI of PAG.

Figure 2-a) summarizes the results of contact angle measurement of samples #1-3 with different DI of PAG. The horizontal axis and the vertical axis show the distance from the center of silicon wafer and the contact angle of droplet, respectively. The contact angle on polymer sample #1 (black triangle) is $79.8 \pm 1.5^\circ$ in the vicinity of the center. However, the case of the blend resists sample #2 (red circle), and #3 (brown circle) are $81.3 \pm 1.4^\circ$ and $83.3 \pm 1.6^\circ$, respectively. As the results, it indicates that blend resists are more hydrophobic than polymer without PAG. PHS-TBA as a base polymer has hydroxy groups derived from hydroxystyrene unit.

Fig. 2. Contact angle results of sample resists of a) sample #1-3, b) sample #2, and #4-6, and c) sample #6 and #7. Polymer (▲), blend resist (●), and bound resist(■).

However, PAG is without hydroxy groups. Therefore, it is considered that the reason of the increasing of hydrophobicity on the blend resist thin film is derived from PAG.

Interestingly, comparison of the contact angle between the center and the outside of the wafer, the contact angle tended to be smaller in polymer without PAG and larger in blend resist. Kawai *et al.* measured the refractive index and contact angle of resist thin films composed of novolak resin and naphthoquinone diazide after the spin coating, and it is reported that the refractive index and contact angle increased as the amount of residual solvent in the thin film decreased [19, 20]. Furthermore, the refractive index and the contact angle increase from the center to the outside of the silicon wafer. Therefore, it was considered that the difference in the amount of residual solvent was caused by the difference in the drying speed of the solvent between the center and the outside of the wafer.

Actually, the contact angle of the blend resist increased from the center of the wafer to the outside in our results too. However, the result of polymer without PAG showed opposite behavior as shown Fig. 2-a). As the results, it means that the contact angle behavior changes between presence and absence of PAG. It is suggested that the differences in hydrophobicity between PAG and polymer caused by the differences in the distribution of contact angles on the resist thin film surface.

3.3. Contact angle measurement of samples with different PAG structure.

Next, the effect of the difference of PAG structures was evaluated. The contact angle measurement results of blend resists with different PAG structures are summarized as shown in Fig. 2-b). The contact angle of each samples increased from the center of the wafer to the outside. Focusing on the structure of the cations, samples #2 and 4 (blue circle) using PAG having three phenyl groups had an approximate curve slope of 0.02 °/mm or larger. On the other hand, the slopes of the approximate curves of samples #5 (purple circle) and 6 (pink circle) using PAG having four phenyl groups were relatively small to be 0.013 °/mm to 0.016 °/mm, respectively. Furthermore, when focusing on the structure of the anion, it was shown that the slope of the approximate curve of $C_4F_9SO_3^-$ (samples #2, 5) tends to be smaller than that of $CF_3SO_3^-$ (samples #4, 6). As the results, it means that the chemical composition of the surface also changes depending on the structure of cations and anions of PAG, and it is considered that it is affected by the difference in molecular size or hydrophobicity of PAG. In other words, the chemical composition of the thin film surface can be adjusted by the structure of PAG. Since the chemical composition of the thin film surface is more uniform as the slope of the approximate curve is smaller, it is predicted that sample #5 has the most uniform chemical composition in samples #2, 4, 5, and 6.

3.4. The comparison of the contact angle between a blend resist and a bound resist.

In the above, the blend resist was mainly described however, the comparison with the bound resist will be explained below. Fig. 2-c) shows the comparison results of the blend resist sample #6 and the bound resist sample #7 (green square), which have the same cation and anion of PAG structure. Surprisingly, the contact angle of sample #7 did not increase from the center of the wafer to outside, which is different behavior of sample #6. This difference indicates the resist type introducing PAG

into the base polymer affects the chemical composition on the resist thin film surface. This is significant result suggesting that the chemical composition distribution of the blend resist and the bound resist are different.

4. Conclusion

In this paper, we evaluated the effects of differences in PAG structure, the types of resist on the thin film surface on the chemical composition distribution using the contact angle measurement method. The contact angle behavior of the blend resists increased from the center of the wafer to the outside. The chemical composition of the surface changes depending on the structure of cations and anions of PAG. The contact angle behavior of the base polymer and the bound resist decreased from the center of the wafer toward the outside. It is clarified that the resist thin film has different chemical composition distributions from the center to the outside of wafer regardless of the type of resists. Especially, the difference behavior of the contact angles between blend resists and bound resist are significant to understand the differences in LWR performance. In the future, we will measure the LWR of blend resists and bound resists after EB or EUV exposure to examine the correlation with the uniformity.

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